

CHAPTER III

LITERATURE REVIEW

In this chapter, the literature reviews are summarized into 2 parts as follows:

1. Miscibility and mechanical properties study of PHB by polymer/additives blending.
2. Brittleness mechanism of PHB and related topics.

1. Miscibility and mechanical properties study of PHB by polymer/additives blending.

Bibers *et al.* [2001] studied the mechanical properties and degradability of the systems of PHB, PHB biomass and plasticizers including Polyethylene glycol (PEG) and oxypropylated glycerine or Laprol (LAP). The aim of this work is to study the possibility to use PHB biomass instead of pure PHB for some products which lower purity of PHB was requested such as agrochemicals containing matrices and seed immobilization film for agriculture. The PHB biomass contains 70-90% by weight of PHB and the rest consists of cell wall, lipids and proteins. The systems of PHB biomass/plasticizer and PHB/plasticizer were prepared by mixing in chloroform and casted into film shape. The thin films with the thickness 0.03-0.04 mm were cut into dumbbell shape specimens. The crosshead speed was set at 2 mm/min. The results on the tensile testing showed that the %elongation at break of PHB biomass/LAP system is better than PHB biomass/PEG system over the entire range of the composition. The %elongation at break of PHB biomass/LAP was changed from 4 to 25% when the LAP content was increased from 5 to 50%. The presence of cell residue causes structural defects. Maximum tensile strength of PHB biomass/plasticizer that is practically constant around 3 MPa over the entire range confirms this conclusion. From the results of mechanical properties, they suggested that PHB biomass/plasticizer system with 30% plasticizer content was suitable for some applications, i.e., biodegradable matrices for agrochemical and seeds incrustation. From the biodegradability study, pure PHB biomass and PHB containing

10% by weight of PEG exhibit the fastest rate of degradability. The degradation completes in 22 days. They explained that the hydrophilicity of PEG and high biodegradability of biomass made the microvoids formed in the polymer matrix. These microvoids increase the specific surface area for degradation activity of enzyme excreted by microorganisms. The system of PHB with 33% by weight of LAP showed the slowest of degradability. The calculated average lifetime of this system is around 6-8 months.

Galego *et al.* [2000] studied the mechanical properties of the composites of copolymer poly(β -hydroxybutyrate-co-hydroxyvalerate) (PHBV) and hydroxyapatite (HA). The aim of this work is to develop the biocompatible polymer to use in bone fracture fixation. PHBV which contains four different contents of valerate monomer was used in this experiment including 0, 8, 12 and 24%. The composites of PHBV and HA are prepared by melt pressing. The quantity of HA used in this work is 70% by weight. From the mechanical study, the composites containing 8 % of HV monomer had highest modulus of elasticity at about 2.75 GPa. Mechanical properties of the composites were strongly effected by HV monomer content. The %elongation at break of the composites varied around 5% over the range of HV monomer content studied. Maximum tensile strength of the composites was decreased when HV monomer content was increased. From the data of maximum tensile strength of dense bone (about 137.8 MPa) and sponge bone (41.4 MPa), they suggested that the composite containing 8% by weight of HV monomer can be used as implant bone for fracture fixation.

Ikejima and Inoue [2000] studied the crystallization behavior and biodegradability of the PHB/chitin and chitosan blend. The decrease of the degree of crystallization of PHB in the blends was observed. The suppression of the PHB/chitosan blends was observed in a wider range of compositions than that in PHB/chitin blends. The suppression of PHB crystallization might be caused by two factors. One is the formation of the intermolecular hydrogen bond between the PHB carbonyl groups and the chitin/chitosan hydroxyl and/or amine groups. Another is the rigid environment that arises from inflexible polysaccharide molecules. The biodegradability of PHB/chitin and

PHB/chitosan was improved with an increasing of PHB content. The PHB/chitin blends which contains 25% of PHB showed faster rate of biodegradability than that of pure PHB and pure chitosan. They concluded that the acceleration of the biodegradation is attributed to the suppression of crystallinity of PHB. The biodegradability of the PHB/chitosan system was found to be significantly improved, inspite of the low biodegradability of the pure chitosan.

Zhang *et al.* [2000] studied the miscibility, melting and crystallization behavior of the blends of PHB/poly(epichlorohydrin-co-ethyleneoxide) (PECH-EO) and PHBV/PECH-EO. From the DSC measurement, single glass transition temperature (T_g) was observed for each blend. T_g s of the blends are composition dependent and intermediate between those of the component polymers, indicating that PHB/PECH-EO and PHBV/PECH-EO are miscible. The apparent melting temperature of PHB decreases slightly with an increasing of PECH-EO content. Crystallization of PHB and PHBV was affected by PECH-EO content. The phase crystallinity of PHB remains unchanged in the cast blend. The radial growth rate of PHB and PHBV spherulites are delayed by PECH-EO at higher crystallization temperature.

Hay and Sharma [2000] studied the effects of polyvinyl acetate (PVAc) on crystallization behavior and morphology of PHB. The single glass transition, which was varied between those of two polymers, was observed in the blends. They found that two polymers were miscible over the entire range of compositions. They found a conflict of evidence in that the presence of PVAc both inhibits the crystallization rate of the blends at low temperature and accelerates it at temperature close to the melting point of PHB. The crystallization rate acceleration was attributed to an increase in the nucleation density that was produced in blending with PVAc. They claimed that impurities in PHB homopolymer which was low in quantity act as nuclei crystallization, such that few spherulites are observed. They concluded that blending PHB with PVAc was considered to add impurities with a resulting increase in nucleation density of the blends. The texture and shape of the spherulites was markedly affected by blend composition, since on increasing PVAc content the surface of the spherulites become rougher, i.e., granular

in appearance with a distortion from the spherical shape and the development of less well-defined spherulite boundaries.

Yoshie *et al.* [2000] studied the degradability of the plasticized system of PHB and low molecular weight additives such as dodecanol, lauric acid, tributyrin and trilaurin. The degradability of polymer was measured by weight loss of specimens immersed in the enzyme extracted from bacteria. The mixtures of PHB and additives were prepared by solution casting method. They concluded that for a small amount of additives, the degradation of PHB was accelerated while the large amount of plasticizer retarded the degradability of polymer. SEM technique was used to describe the acceleration and retardation of biodegradability of PHB/additive system. The retardation of degradability was occurred in the sample containing high content of plasticizer because there is a segregation of additives on the surface of specimens of the blend. The segregation decreases activity of the enzyme of the microorganisms.

Withey and Hay [1999] studied the effect of seeding agents, i.e, saccharine and phthalimide on crystallization on PHB and copolymer of poly(β -hydroxybutyrate-co-hydroxyvalerate). The effect of these additives as nucleating agents was compared with PHB conventional nucleating agent, boron nitride. They claimed that crystallization of PHB at relatively low temperature is attributed to the formation of secondary crystallization. This leads to the embrittlement of PHB. If PHB can be crystallized at higher temperature, more perfect crystallization would be produced. The embrittlement of PHB will be inhibited. They found that the effectiveness as nucleating agent of saccharine and phthalimide is less than boron nitride.

Bibers *et al.* [1999] studied the effects of plasticizers, i.e., dioctyl sebacate, dibutyl sebacate, polyethylene glycol, Laprol 503, Laprol 5003 on the mechanical properties of PHB. The blend films were prepared by solution casting. The films of PHB/additives system were cut into dumbbell shape. The crosshead speed was set at 2 mm/min. The results showed that the maximum tensile strength values of all PHB/plasticizers systems were linearly reduced with an increasing in plasticizer content.

For all PHB/plasticizer systems, the %elongation at break was increased gradually with an increasing in the plasticizer content up to 10% by weight. The %elongation at break was sharply increased when the plasticizer content was around 15-30%. They suggested that the maximum acceptable content of plasticizer is 20-30%. This value was based on the minimum value of maximum tensile strength which used in major field of applications (about 10 MPa). From DSC measurement, the results showed that the ratio of amorphous to crystalline content is practically constant. The changes of mechanical properties in PHB/plasticizer systems were due to the considerably weakened intermolecular interactions in the amorphous regions of PHB.

Maekawa *et al.* [1999] studied the miscibility and mechanical properties of the polymer blends of PHB and cellulose propionate (CP). The blends were prepared by solution casting and melt-quenched method. The tensile properties were measured by cutting the polymer films into strip-shaped specimens. The dimension of specimens is 25 x 3 mm. The initial gauge length and testing speed were set at 15 mm and 0.15 mm/s, respectively. They concluded that the polymer blends are miscible over the entire range of composition. For the samples prepared by solution casting method, the %elongation at break of the samples containing 100% PHB was around 1%. The %elongation at break of the samples containing 50% by weight of CP was changed to 3%. The %elongation at break was improved significantly in the samples prepared by melt-quenched method. The %elongation at break of the samples containing 50% CP which prepared by melt-quenched method was around 90%. They concluded that the increase of ductility of these blends is attributed to the decrease of crystallinity of the blends. They claimed that the brittleness of PHB is related to cracking of the PHB spherulites. This conclusion is first discovered by Barham *et al.*, [1986]. Since the crystallinity of melt-quenched sample is suppressed rapidly, the tensile behavior of the blend is influenced by amorphous phase of polymer only.

Yoon *et al.* [1998] studied the miscibility of PHB with ethylene-vinyl acetate (EVA) copolymer containing 70% (EVA70) or 85% (EVA85) of vinyl acetate. They found that the blend of PHB/EVA70 was immiscible because the glass transition temperature

(T_g), melting temperature (T_m), and the spherulite growth rate under the isothermal crystallization were independent of the blend composition. They found that T_m , the spherulite growth rate and the equilibrium melting temperature of the PHB/EVA85 system decreased with an increasing of the EVA85 content. They concluded that PHB is miscible with EVA85.

Lee *et al.* [1997] studied the miscibility of polymer blend of PHB and poly(vinylidene chloride-co-acrylonitrile) [P(VDC-AN)]. Each blend showed a single glass transition temperature and large melting point depression of PHB. All the blends containing more than 40% of PHB contents showed linear spherulitic growth behavior and the growth rate decreased with P(VDC-AN) content. They concluded that PHB/P(VDC-AN) blends are completely miscible in all proportions.

Xing *et al.* [1997] studied the miscibility and crystallization behavior of polymer blend of PHB and polyvinylphenol (PVPh). PVPh is an amorphous polymer which has the glass transition temperature around 144°C. The single composition-dependent glass transition temperature of the blend was observed. They concluded that the blend system is miscible. The presence of amorphous PVPh component resulted in a reduction in the rate of spherulite growth of PHB. The equilibrium melting point of PHB in the blends decreased with an increase in PVPh content. The melting enthalpy of PHB in the blend was substantially lowered and approached zero at about 40% of PVPh content.

Avella *et al.* [1997] studied the miscibility and mechanical properties of the blends of PHB and polymethylene oxide (POM). The blends were melt-mixed in a brabender and then cooled in liquid nitrogen. By using DSC, optical microscopy, SEM and dynamic mechanical thermal analysis (DMTA), it was reported that the polymer blends are immiscible over the entire range of composition. Sheets of polymer blend were prepared by hot-compression-moulding method. The specimens used in tensile testing were cut into dumbbell shape. The crosshead speed was set to 1 mm/min. The results showed that blending PHB with POM did not improve the mechanical properties

of PHB. %Elongation at break was decreased from 2.6% for pure PHB, to 1.1% for the blend containing 60% by weight of POM. The %elongation at break of the blend containing 80% by weight of POM and pure POM is 4.4% and 10.7%, respectively.

Pizzoli *et al.* [1994] studied the isothermal crystallization behavior and morphology of PHB/cellulose ester (CE) blend. Two different CEs were used to blend with PHB. At low PHB content, a strong dependence of the glass transition temperature (T_g) on the blend composition was observed. The T_g seemed to change slightly in the blends containing high content of PHB. The PHB crystallization rate was decreased by the appearance of CE. Three main factors can be taken into accounts to explain the depression of PHB crystallization rate:

1. A dilution effect which diminished the number of crystallizable elements at the growing lamellar front.
2. A decrease of segmental mobility due to the changes in the glass transition temperature associated with the presence of intimately mixed high- T_g component
3. A reduction of the driving force for crystallization due to melting point depression

From optical microscopy, the crystallization of the PHB/CE system was observed. At the same content of CE, there is no apparent morphology difference in the system containing different type of CE. Type of CE does not play the fundamental role in the determining of PHB morphology. On the other hand, the crystallization temperature and blend composition are the main factor which affects the PHB morphology.

Gassner and Owen [1994] studied the miscibility and mechanical properties of the blends of PHB and poly(ϵ -caprolactone) (PCL). The blends were mixed and compression-moulded. The polymer blends showed immiscibility. From DSC and dynamic mechanical thermal analysis (DMTA) study, they concluded that PCL formed a continuous matrix and PHB spherulites were encapsulated as islands in the PCL matrix. For the blends containing PCL content less than 60% by weight, PHB become the continuous matrix. The inclusion of PCL has a little effect on reducing the brittleness of

the blends. The tensile testing speed was set at 10% of the specimen length per minute. The results showed that the modulus of elasticity was decreased systematically from 2.10 GPa, for samples containing pure PHB, to 0.36 GPa, for samples containing pure PCL. The %elongation at maximum stress showed an improvement in ductility. The %elongation at maximum stress can be divided into two groups, for the blends containing PCL content more than 60% and less than 60%. For the blends containing more than 60% of PCL, the %elongation at maximum stress was varied from 4.4% to 7.4% when the PCL content was increased from 60% to 100%. For the blends containing PCL content less than 60%, the %elongation at maximum strain was varied in the narrow range from 1.0% to 1.8% when the PCL content was increased from 0% to 60%.

Dubini Paglia *et al.* [1993] studied the crystallization and thermal behavior of polymer blend of PHB and poly(epichlorohydrin) (PECH). All blends showed a single composition-dependent glass transition temperature. The influence of blend composition on the overall crystallization rate and on the spherulite growth rate suggested that the two polymers formed a miscible blend in the amorphous phase. They concluded that after crystallization the PECH molecules are rejected in the interlamellar or interfibrillar regions of PHB spherulites, where they formed a homogeneous mixture with uncrystallized PHB molecules.

Ceccorulli *et al.* [1993] studied the miscibility of the polymer blends of PHB and cellulose acetate butyrate (CAB) and the effect of low molecular weight plasticizer such as di-*n*-butyl phthalate (DBP) on the glass transition temperature of pure PHB, pure CAB and the blend of PHB and CAB. PHB/CAB blends were prepared by melt mixing and then injection-moulding. The ternary blends of PHB/CAB and DBP were prepared by dry blending and then melting in the DSC pan. For the polymer/DBP blends, the results show that both PHB/DBP and CAB/DBP systems are miscible over the whole range of composition. DBP is an effective plasticizer for PHB and CAB by lowering the glass transition temperature of PHB and CAB. Two separated glass transition temperatures were observed in the intermediate range of DBP content in the blend of CAB/DBP.

They concluded that this phenomenon is previously observed in several systems which glass transition temperature of polymer and diluent are considerably different. For PHB/CAB, the glass transition temperature shifts to lower temperature when the PHB content in the blend is increased. For the ternary blend of PHB/CAB and DBP, increasing of DBP content further decreased the glass transition temperature of PHB/CAB. For the fixed amount of DBP content in the ternary blend, the glass transition of the ternary blend decreases significantly when the PHB content is increased. The depression is larger for the higher content of DBP in the ternary blend.

Ceccorulli *et al.* [1992] studied the effects of biodegradable plasticizer, di-*n*-butyl phthalate (DBP), on the glass transition temperature of PHB. From the literatures they observed, they believe that PHB kept in the granules in the cytoplasm of microorganisms is plasticized because its mobility and the absence of crystallinity are observed. The glass transition of PHB kept in the granule is estimated around -40°C . PHB/DBP blends were prepared by melt-mixing in the DSC pan. They concluded that DBP Exhibits the plasticizing effect toward PHB. The amount of added DBP to lower the glass transition of PHB from -5°C to -40°C is 30% by weight. They concluded that there are no relation between plasticizing PHB with adding DBP and phenomenon occurred with PHB kept in the granule because plasticization does not imply an inability of macromolecules to crystallize. PHB still crystallize in the PHB/DBP blend. The absence on crystallinity of PHB kept in the granules is not effected by PHB plasticization. The different mechanisms are needed to explain the prevention of crystallization of PHB kept in the granule.

Scandola *et al.* [1992] studied the miscibility of the blend of PHB with cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP). CAB and CAP are cellulose ester of which the glass transition temperatures are around 103°C and 145°C , respectively. The blends of PHB/CAB and PHB/CAP were prepared by melt mixing method. They concluded that PHB was miscible with either CAB or CAP. The blends were completely amorphous in the PHB/CAB system with containing 50-95% of CAB and in the PHB/CAP system which containing 40-95% of CAP, while blends containing

lower CAB and CAP content were partially crystalline. Glass transition temperature, which was decreased with an increasing of PHB content, was observed in the blends that were amorphous.

Azuma *et al.* [1992] studied the thermal behavior and miscibility of PHB/poly(vinyl alcohol) (PVA) blend system. Glycerine was added to the blend system as a plasticizer for PVA. The DSC thermogram of each blend shows three endothermic peaks. The peaks which represent the fusion of PHB crystalline phase, the fusion of PVA crystalline phase and the decomposition of PHB are positioned at about 170°C, 220°C and 250°C, respectively. Melting temperature (T_m) of PHB crystalline phase decreased with an increasing of PVA content. The T_m of PVA crystalline phase remains almost unchanged. Glycerine did not have a significant effect on the T_m of PHB. They found that these blends are partially miscible in amorphous phase. The degree of miscibility for PHB/PVA blends is found to be composition dependent. The miscibility of PHB and PVA was enhanced with an increasing of PVA content.

Avella and Martuscelli [1988] studied the miscibility of polymer blend of PHB and poly(ethylene oxide) (PEO). The blends exhibited a single glass transition temperature and a depression of the equilibrium melting temperature. The presence of PEO caused a depression in the growth rate of PHB spherulites. They concluded that the blend of PHB and PEO was miscible in the melt and in the amorphous state.

2. Study of brittleness mechanisms of PHB and related topics.

de Koning and Lemstra [1993] studied the mechanism of PHB brittleness and the effect of brittleness on mechanical properties of PHB. From the tensile testing, the result showed that the %elongation at break of suddenly prepared PHB is around 40%. When the samples were stored for more than 2 weeks, the %elongation at break decreased to less than 10%. They summarized that the cause of the brittleness are the cracks generated in large spherulites, the physical ageing and the progressive

crystallization. This contradicted the theory about the crack in spherulite. They noted that the brittleness is occurred in PHB in which small spherulites were generated too. Commercial PHB which boron nitride is added as nucleating agent showed very fine spherulites and the samples prepared from commercial PHB showed the brittleness too. The physical ageing is a phenomenon happened in all glassy materials. The physical ageing can be completely reversed by heating the material above the glass transition temperature (T_g) or by mechanical strain. Their results showed that PHB that stored for 150 days was brittle. The %elongation at break of PHB stored for 150 days is around 7%. When heating at 70°C for 5 minutes was applied to PHB, the %elongation at break improved to 13%. This sample showed brittleness characteristic again when the sample was stored for another 5 days. The brittleness can not be removed permanently. This result showed that the process is not physical ageing because the physical ageing can be removed permanently. They suggested that the brittleness of PHB is attributed to the progressive crystallization. It was also shown that the density increased significantly upon the storage day. From the conversion of density to crystallinity, the crystallinity of as- moulded PHB is 56% and can be increased to 63% when the sample was stored upon 200 hours at 25°C. They concluded that crystallization of PHB is not completed during moulding process, so the progressive crystallization occurred on the subsequent storage. Progressive crystallization constrains the amorphous chains between the crystals and the embrittlement occurs. They suggested that the simple annealing treatment could be toughen PHB and prevent the brittleness to the larger magnitude.

de Koning *et al.* [1992] studied the ageing process that embrittles PHB and the effect of additives and external stress on ageing process. Ageing process happened within several weeks when PHB sample was stored at room temperature. This ageing process can be partially reversed by the employment of heat or mechanical strain. The toughness of PHB could be improved only small and temporary. They believed that the ageing process was influenced by the adding of additives and mechanical orientation, that affected the segmental mobility in the amorphous phase of PHB. There are two types of PHB used in this experiment. The first type of PHB is commercial PHB which 1% by weight of boron nitride was added as nucleating agent and the second type is

virgin PHB powder which used to be the reference. From the experiment, they concluded that the ageing phenomenon is the intrinsic property of PHB and is not affected by the extraneous compounds or mechanical orientation.

Barham and Keller [1986] studied the cracking mechanism in PHB spherulites. They found that the crack usually forms in PHB spherulites a few hours after PHB sample was cooled to room temperature. There are two types of crack in PHB spherulites. The crack runs either radially or circumferentially within spherulites. They found that only circumferential crack was found in the PHB sample crystallized above 120°C . Both circumferential and radial crack were found in the PHB sample crystallized at 60°C . When PHB sample was strained, the preexisting cracks grow and join up. This phenomenon embrittles PHB. They suggested that the circumferential crack is attributed to the difference in radial and circumferential thermal expansion coefficients. This difference generates large internal stress that caused cracking. They found a relationship between the radial crack and growth mechanism of PHB spherulites but further work was required to conclude this relationship.



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