POLYMER ALLOYS AND COMPOSITES BASED ON POLY(3-HYDROXYBUTYRATE)

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POLYMER ALLOYS AND COMPOSITES BASED ON POLY(3-HYDROXYBUTYRATE)

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LIST OF ABBREVIATIONS

ata-PHB	atactic PHB
DBTDL	dibutyltin dilaurate
D-PHB	low-molecular weight PHB
DSC	differential scanning calorimetry
EPR	ethylene-propylene rubber
FTIR	fourier transform infrared
GPC	gel permeation chromatography
HAP	calcium hydroxyapatite
HIPS	high-impact polystyrene
K_2SO_4	potassium sulphate
MSS	molten salt synthesis
NMR	nuclear magnetic resonance
PB	polybutadiene
PBA	poly(1,4-butylene adipate)
PBSA	poly(butylene succinate-*co*-butylene adipate)
PBSC	poly(butylene succinate-*co*-ε-caprolactone)
PBT	poly(butylene terephthalate)
PC	bisphenol-A polycarbonate
PCL	poly(ε-caprolactone)
PCL-*b*-PEG	block copolymer of poly(ε-caprolactone) and poly(ethylene glycol)
PE	polyethylene
PEA	poly(ethylene adipate)
PECH	poly(epichlorohydrin)
PEEK	poly(etheretherketone)
PEG	poly(ethylene glycol)

PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PHA	poly(3-hydroxyalkanoate)
PHB	poly(3-hydroxybutyrate)
PHBV	poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
P(HB-co-12% HV)	PHBV with 12 mol% of hydroxyvalerate content
P(HB-*co*-76% HV)	PHBV with 76 mol% of hydroxyvalerate content
phenoxy	poly(hydroxyl ether of bisphenol A)
PLA	poly(lactic acid)
PLLA	poly(L-lactide)
PMO	poly(methylene oxide)
PP	polypropylene
PPL	poly(β-propiolactone)
PS	polystyrene
PTMO	poly(tetramethylene oxide)
PTMS	poly(tetramethylene succinate)
PVAc	poly(vinyl acetate)
PVPh	poly(*p*-vinylphenol)
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
XRD	X-ray diffractometry

LIST OF SYMBOLS

ΔH_c	crystallization enthalpy	$\mathrm{J \cdot g^{-1}}$
$\Delta H_{\mathrm{m}(i)}$	melting enthalpy of component *i*	$\mathrm{J \cdot g^{-1}}$
$\Delta H_{\mathrm{norm}(i)}$	normalized melting enthalpy of component *i*	$\mathrm{J \cdot g^{-1}}$
ΔH_ref	melting enthalpy of 100 % crystalline polymer	$\mathrm{J \cdot g^{-1}}$
ΔT	undercooling	K
ε_b	elongation at maximum strength	mm
ε_r	elongation at break	mm
C	carbon	-
Ca	calcium	-
E_b	flexural modulus	MPa
G	radial growth rate	$\mathrm{\mu m \cdot s^{-1}}$
H	hydrogen	-
K	generalized crystallization rate constant	$\mathrm{min^{-n}}$
K_A	overall rate constant of crystallization	$\mathrm{min^{-n_A}}$
M_w	weight-average molecular weight	$\mathrm{kg \cdot mol^{-1}}$
n	generalized Avrami exponent	-
n_A	Avrami exponent	-
N	nitrogen	-
O	oxygen	-
P	phosphorus	-
r	correlation coefficient	-
s	cooling rate	$\mathrm{K \cdot min^{-1}}$
S_b	flexural strength	MPa
Sn	tin	-
S_r	flexural stress at break	MPa

t_0	time where 1 % of crystallinity has been measured	min
$t_{0.5}$	half time of crystallization	min
$t_{0.5}^{-1}$	reciprocal half time of crystallization	min^{-1}
$t_{0.5}^{-1}$ (calc)	calculated reciprocal half time of crystallization	min^{-1}
$\overline{t_{0.5}^{-1}}$	average of reciprocal half time of crystallization	min^{-1}
t_a	annealing time	min
T	temperature	^{0}C
T_a	annealing temperature	^{0}C
T_c	crystallization temperature	^{0}C
$T_{c,1}$	crystallization temperature range of PHB	^{0}C
$T_{c,2}$	crystallization temperature range of PCL	^{0}C
T_c^{-1}	reciprocal crystallization temperature	K^{-1}
T_d	decomposition temperature	^{0}C
$T_{d(ons)}$	onset temperature of decomposition	^{0}C
T_g	glass transition temperature	^{0}C
T_m	melting temperature	^{0}C
T_m^0	equilibrium melting temperature	^{0}C
T_{ons}	onset temperature of crystallization	^{0}C
v	volume	ml
w	weight	g
$w_{f(i)}$	weight fraction of component *i*	-
w_i	weight of component *i*	g
X	normalized crystallinity	-
X_T	normalized crystallinity at a temperature *T*	-

ALOI DAN KOMPOSIT POLIMER BERASASKAN POLI(3-HIDROKSIBUTIRAT)

ABSTRAK

Aloi-aloi polimer poli(3-hidroksibutirat) (PHB) dengan poli(ε-kaprolakton) (PCL) dan juga dengan kalsium hidroksiapatit (HAP) kumis bioseramik telah dikaji. Sifat-sifat terma dan kinetik penghabluran komponen polimer dalam sistem-sistem aloi telah diselidik secara meluas di bawah keadaan isoterma dan bukan-isoterma dengan menggunakan kalorimeter pengimbasan pembezaan. Bagi adunan PHB/PCL, kestabilan terma polimer turut disiasat melalui analisis thermagravimetrik. Kumis dan komposit yang disediakan telah dicirikan dengan mikroskopi pengimbasan elektron (SEM), mikroskopi optik dan juga teknik pembelauan X-ray. Sifat-sifat mekanik komposit tersedia diperiksa pada mod lenturan dengan ujian pembengokokan tiga-titik. PHB dan PCL merupakan polimer separa-berhablur yang tidak serasi dalam kedua-dua keadaan amorfus dan berhablur. Dalam adunan PHB/PCL, penghabluran bermula dengan penghabluran PHB semasa PCL dalam keadaan leburan dan diikuti oleh penghabluran PCL dalam habluran PHB. Semasa penambahan komponen adunan yang kedua, tiada kesan amorfus PCL yang jelas terhadap kehabluran PHB dapat dikenalpastikan. Bagi PCL, sisihan negatif daripada perlakuan sempurna berlaku dalam adunan yang mengandungi 50 %berat PHB dan lebih. Kinetik penghabluran keseluruhan telah dicirkan dengan salingan setengah-masa penghabluran. Keputusan menunjukkan bahawa ciri-ciri penghabluran keseluruhan tidak diubahkan dengan ketara oleh kehadiran komponen yang kedua. Takat lebur keseimbangan kedua-dua PHB dan PCL berada malar pada satu anggaran yang baik dengan komposisi adunan. Untuk mengaruh keserasian adunan PHB dengan PCL, penyerasian melalui pentransesteran telah disiasat di bawah pengaruh dibutiltin dilaurat (DBTDL) sebagai fungsi masa (t_a) dan suhu penyepuhlindapan. Hasil kajian tidak menampilkan bukti pentransesteran yang nyata. Penambahan mangkin dan rawatan terma tidak

menyebabkan perubahan kelakuan peleburan PCL, manakala suhu peleburan PHB menyusut sedikit dengan peningkatan t_a bagi semua adunan. Di bawah keadaan kajian, degradasi terma komponen PHB dipercayai mengatasi tindakbalas-trans antara PHB dan PCL dalam leburan di bawah pengaruh DBTDL dengan ketara.

Kumis HAP takorganik yang semulajadi telah dirangkumkan ke dalam matriks PHB sebagai pengisi bagi polimer. Kumis HAP telah disediakan daripada serbuk tulang dengan prosedur sintesis garam lebur. Teknik-teknik penuangan larutan dan peleleran-skru tunggal digunakan untuk menyediakan komposit-komposit PHB/HAP. Cerapan mikroskopi memperlihatkan bahawa partikel-partikel HAP membentuk sebaran yang tidak homogen dalam matriks PHB dan lekatan antaramuka di antara polimer/pengisi adalah lemah. Pengumpulan pengisi dapat diperhatikan di kawasan-kawasan tertentu matriks polimer. Semasa penghabluran, sferulit PHB yang membesar merangkumi partikel-partikel PHB yang bersaiz mikrometer dan menyebabkan rangkuman kumis secara intrasferulitik dalam fasa polimer pukal. Penelitian optik menunjukkan bahawa penambahan pengisi dalam julat komposisi yang dikaji tidak mempengaruhi penghabluran PHB. Pemeriksaan SEM pada permukaan retak spesimen leleran mempamerkan kebanyakan kumis diorientasikan dalam susunan membujur. Berbanding dengan homopolimer PHB, suhu peleburan dan kehabluran PHB dalam komposit dan juga sifat-sifat lenturan komposit tidak dipengaruhi oleh kandungan HAP. Kesan keadaan pemprosesan terhadap kelakuan-kelakuan peleburan dan penghabluran komposit tidak jelas. Ia mungkin mempengaruhi ciri-ciri komposit terutamanya berkaitan dengan taburan pengisi. Penghabluran secara bukan-isoterma yang dijalankan dengan kadar-kadar pendinginan malar telah dibincangkan dengan pendekatan Avrami kuasi-isoterma. Kinetik penghabluran komposit PHB/HAP daripada leburan juga telah ditaksirkan secara isoterma dengan mikroskopi pengutuban optik. Kadar penghabluran bukan-isoterma PHB meningkat sedikit dengan kehadiran kumis, manakala kadar pertumbuhan jejari tidak bergantung pada pecahan berat pengisi di bawah keadaan isoterma.

POLYMER ALLOYS AND COMPOSITES BASED ON POLY(3-HYDROXYBUTYRATE)

ABSTRACT

Polymer alloys of poly(3-hydroxybutyrate) (PHB) with poly(ε-caprolactone) (PCL) as well as with bioceramic calcium hydroxyapatite (HAP) whiskers were studied. Thermal properties and crystallization kinetics for the polymeric constituents of the alloy systems were assessed extensively under isothermal and non-isothermal conditions using differential scanning calorimetry. For PHB/PCL blends, thermal stability of the polymers was also investigated by thermogravimetric analysis. Synthesized whiskers and prepared composites were characterized by means of scanning electron microscopy (SEM), optical microscopy as well as X-ray diffraction technique. Mechanical properties of the resulting composites were examined in flexural mode via three-point bending testing method. PHB and PCL are semicrystalline polymers that are immiscible both in the amorphous and crystalline states. In PHB/PCL blends, crystallization sets in with crystallization of PHB while PCL is in the molten state and subsequent crystallization of PCL in crystalline PHB. Upon addition of the second component, no distinct influence of amorphous PCL on crystallinity of PHB is recognized. For PCL, negative deviations from perfect behaviour occur in blends containing 50 wt% of PHB and more. Overall kinetics of crystallization was characterized by reciprocal half time of crystallization. Results show that the overall crystallization features of both blend components are not prominently altered by the presence of second component. Equilibrium melting temperatures of both PHB and PCL stay constant with respect to blend composition to a good approximation. To induce improved compatibility of blends of PHB and PCL, compatibilization via transesterification was investigated under the influence of dibutyltin dilaurate (DBTDL) as a function of annealing time (t_a) and temperature. Results do not show clear evidence of transesterification. Addition of catalyst and subsequent thermal treatments do not lead to change in melting behaviour of PCL whereas the melting temperature of PHB component decreases slightly with ascending t_a in all blends. For the conditions studied, it is believed that thermal degradation of PHB component prevails considerably over the transreaction between PHB and PCL in melt under influence of DBTDL.

Natural inorganic HAP whiskers were incorporated into PHB matrix as fillers for the polymer. HAP whiskers were prepared from biological bone powder using molten salt synthesis procedure. Solution casting and single screw-extrusion techniques carried out preparation of PHB/HAP composites. Microscopy observations demonstrate that HAP particles form an inhomogeneous dispersion in PHB matrix and interfacial adhesion between polymer/filler is weak. Aggregation of fillers can be seen in certain regions of the polymer matrix. Upon crystallization, growing PHB spherulites incorporate the micrometer-sized HAP particles leading to an intraspherulitic inclusion of whiskers in the bulk polymer phase. Optical examination shows that addition of fillers in the composition range studied does not affect crystallization of PHB. SEM examination on fracture surfaces of extruded specimens reveals that majority of whiskers is oriented in a longitudinal alignment. As compared to the pure component, melting temperature and crystallinity of PHB in composites as well as composite flexural properties are unaffected by HAP content. Influence of processing conditions on the melting and crystallization behaviours of composites is not obvious. Non-isothermal crystallization performed with constant cooling rates was discussed in terms of a quasi-isothermal Avrami approach. Kinetics of crystallization for PHB/HAP composites from melt was also assessed isothermally by optical polarizing microscopy. The non-isothermal crystallization rate of PHB increases slightly by presence of micrometer-sized whiskers while under isothermal conditions the radial growth rate is independent of the weight fraction of fillers.

CHAPTER 1
INTRODUCTION

1.1 General

Since the introduction of the first truly synthetic polymer, Bakelite in 1910, polymeric materials made a great contribution to enhance globally the standard of living and lifestyle [1]. The explosive commercial success of plastics in the decades after the Second World War fuelled a renaissance in polymer research with the commercialization of a series of polymers ranging from polyolefins to polyesters. The success of polymeric materials lies greatly in their strength, low cost, durability and stability to chemical and biological attack [2]. These attractive properties have led to widespread applications of polymers replacing conventional structural materials such as glass, metal and wood; on the other hand, leading to long-term environmental and waste management issues.

As a consequence, biodegradable polymers are gaining increasing attention from material researchers and industry since 1970s. Biodegradable polymers can be efficiently degraded into non-toxic water-soluble oligomers that can subsequently be reutilized into energy and products of carbon dioxide and water through several metabolic procedures of microorganisms [3, 4]. Currently, the commercial biodegradable polymers are predominantly restricted to aliphatic polyesters, polyether and poly(vinyl alcohol) [5]. Biodegradable polymeric materials can be divided into two categories based on whether they are polymerized biologically or synthetically [6]. The first type consists of naturally occurring processable polymers that is represented prominently by poly(3-hydroxyalkanoate)s (PHAs). Polymers belonging to the latter category are synthetic polymers with vulnerable groups susceptible to enzymatic attack. Among them, the very important biodegradable synthetic polymers are aliphatic polyesters, like poly(ε-caprolactone) (PCL), poly(lactic acid) (PLA), poly(glycolic acid) and poly(tetramethylene succinate) (PTMS).

Polymers, which are biodegradable, offer an alternative viable way to the environmental waste management by replacing the conventional petroleum-based non-biodegradable plastic materials particularly when recovery for recycling or incineration is difficult or not cost-effective [2]. Furthermore, originally limited to the bioabsorbable surgical sutures application and drug delivery system, biodegradable polymers are also slowly, but progressively extending their use to different areas of biomedical applications, including dental repair, temporary internal fixation and ligament construction [7-8]. Particularly for use in orthopaedic implant devices, many biodegradable polymers are biocompatible and bioabsorbable, and can be designed to exhibit more bone-like properties. Their mechanical properties can be strong enough to withstand weight-bearing applications, yet they still retain a degree of elasticity not available with metal alloys. Most important, the degradation rate of these materials can be engineered to be consistent with the rate of new bone growth and slowly be absorbed by the body. Nevertheless, the biodegradable polymers developed so far are expensive. Besides, their physical properties and processability such as low melting temperature (T_m) and high crystallinity, as well as their poor mechanical properties are often inferior to non-biodegradable polymers [9].

Therefore, endeavour to enhance the performance of the existing ecologically useful polymeric materials has acquired significant importance in these few decades. Polymer blending and incorporation of fillers into polymer matrix are promising ways to obtain new materials with desirable characteristics in a synergistic way, via physical combination of entities with divergent properties [10-11]. These techniques not only offer opportunity to retain the attractive features of the original components such as biodegradability, but also the ability to tailor properties with two or more known entities.

Compared with the development of new polymers, they are effective and convenient routes to create new and useful materials with greater versatility and flexibility at considerably reduced time and cost. To develop polymer mixtures with desirable properties, an in-depth understanding of various key aspects of the systems primarily in terms of their phase behaviour and morphology, is essential. For multicomponent systems, polymer alloy is a generalizing term embracing both heterogeneous polymer blends and polymer composites. It refers to a heterogeneous system consisting of chemically different constituents and comprising at least one polymer component.

Poly(3-hydroxybutyrate) (PHB) which is a bacterial biosynthesis polyester has long been the subject of both industrial and academic interest, due to its technological properties as well as its outstanding biodegradability and biocompatibility. However, the high price, narrow processing window and poor mechanical performance have greatly excluded this biopolymer from many practical and large scale industrial applications. In this present work, we have undertaken research with the aim of finding partners suitable to be mixed with PHB to obtain new PHB-based materials with improved properties and processability. Here, attempts to modify the physical properties and improve the mechanical performance of PHB by means of blending and reinforcement with inorganic filler were investigated. PHB was alloyed with a synthetic biodegradable polyester, PCL as well as bioceramic calcium hydroxyapatite (HAP) whiskers, respectively. The first system comprises both aliphatic polyesters that are semicrystalline. While, the latter are composite materials consisting of biological origin ceramic as fillers and a crystallizable polymeric substance as the matrix. Combinations of PHB with PCL and HAP are realistic pathways that may offer opportunities to enhance performance, improve the processability and lower the cost of material without sacrificing the interesting features of the microbial thermoplastic.

1.2 Polymer Blends

Comparison with chemical modification, blending is a more cost-effective way to modify properties of two or more polymers simultaneously, which offers high degree of synergism. It is also an alternative route for recycling industrial and municipal scrap [12]. Polymer blends are physical mixtures of structurally different homopolymers or copolymers resulting from common processing steps, which do not lead to chemical bonding between the components [1, 13]. From the morphology viewpoint of the parent polymers, three types of polymer blends can be distinguished: amorphous/amorphous, amorphous/semicrystalline and semicrystalline/semicrystalline. Polymer mixtures may be single phase or multiphase systems. For thermodynamic reasons, most polymer blends are not miscible on molecular level. Miscible blends are molecularly dispersed systems, while pure phases of the constituents coexist in immiscible systems. For immiscible blends, physical properties of the materials are strongly dependent on both the morphology of the dispersion and the interfacial adhesion.

For miscible system, miscibility may result in new properties and produce a range of materials with properties completely different from those of the neat blend constituents [14]. Whereas, combined properties are obtained if each component forms its own phase. To achieve a synergistic property enhancement from all components via polymer blending, immiscibility is therefore usually desired in many cases where each phase can contribute its own characteristics to the product [15]. One good example is illustrated by high-impact polystyrene (HIPS) that combines the properties of a rigid polystyrene (PS) and an elastomer polybutadiene (PB). HIPS is an useful immiscible polymer blend exhibiting the strength of PS along with the toughness supplied by PB [1]. For most immiscible blends, however, the theoretically expected properties are often not achieved because of poor adhesion of the phases created. To realize such blend in which the components are able to interact in complementary manner and yield enhanced properties, it is essential to improve the interphase adhesion of the blend.

For improving miscibility of a heterogeneous system, compatibilization represents a promising path that is mainly achieved by inducing chemical or physical interactions *in situ* between constituents in molten state or by addition of a compatibilizing agent, primarily a block or graft copolymer [5, 8, 16].

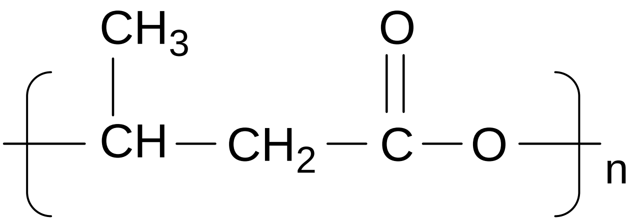
1.3 Polymer Composites

In addition to the conventional techniques of blending and copolymerization [3, 9, 17-24], reinforcement with inorganic fillers for enhancing the properties of a polymer has gained increasing attention in recent years. In industry, polymer composites have been widely used in areas of electronics, transportation, construction and consumer products. Compared to pure polymers, incorporation of fillers contributes often to a more competitive price for the thermoplastics and a general improvement in their mechanical behaviour and dimensional stability, as well as exhibits significant changes in material properties such as thermal and biodegradation properties [23, 25-30]. For biomaterial engineering, bioceramics are added to reinforce polymeric materials as well as to increase the bioactivity and osteoconductive nature of the scaffold [27, 31-33]. On the other hand, the polymers can be employed as binders for the particulate ceramics to produce composites with improved handling and retention characteristics [23].

The characteristics of reinforcement particles (including content, shape and size), dispersion degree of fillers, and interfacial adhesion level of polymer/filler, are key factors in determining the ultimate properties of the resulting composite materials [25, 27, 29, 34-36]. Frequently, physical mixtures of organic polymers and inorganic particles may lead to unfavourable separation into discrete phases and particle agglomeration [37]. This will subsequently weaken the performance of the materials, particularly their mechanical properties. For the design of organic-inorganic systems, a critical challenge therefore lays in the control of interfacial adhesion between the two dissimilar phases and the achievement of a uniform dispersion of inorganic material in the organic medium. These two factors linked closely to the processing techniques and conditions [25, 27, 29, 38]. In consequence, a variety of preparation methods have been usually attempted in preparing similar polymer composites. For example, techniques that have been carried out to prepare polymer matrix composites containing bioceramic HAP take account of extrusion [27], compression moulding [23, 32, 38], injection moulding [25, 38-39], solvent casting [28, 30, 40-41], forging process [26] and hot pressing [42].

Among the fillers, natural fibres such as straw, starch, flax, and hemp, have emerged as renewable and cheap reinforcement for composite materials [36, 43-45]. The earliest natural fibre-polymer composites were prepared by reinforcing thermosetting matrices such as epoxy, phenol-formaldehyde and polyester resins [46-47]. To date, various polymer composite systems based on different thermoplastics, such as polypropylene (PP), polyamide-6, PS, polyurethane, have been studied [37, 48-49]. Lately, special attention has been paid to the development of novel composites, so-called biodegradable polymer composites for both macromolecular and biomedical lines of research. In these particular research areas, much works have been focused on the applications of ceramic and natural fillers in combination with biodegradable polymers [25-28, 30, 35-36, 43-45]. Some examples are polymer-ceramic composites comprising PCL, PHB and PLA because of their attractive biodegradable and biocompatible properties.

1.4 Poly(3-hydroxybutyrate) (PHB)



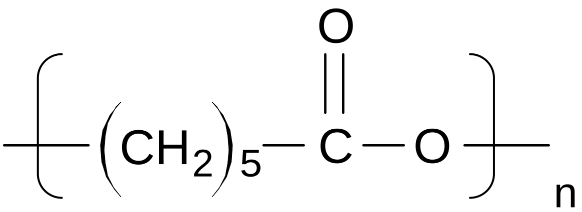
$$\left[-\overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - O - \right]_n$$

Fig. 1.1 Chemical structure of PHB.

PHB is a naturally occurring polyester, which has been synthesized by several microorganisms as intracellular carbon and energy storage compounds under conditions of nutrient limit [50-51]. It is commercially produced by bacterial fermentation and can be harmlessly biodegraded to water and carbon dioxide by a wide variety of bacteria in the environment [50, 52]. Since first discovered by Lemoigne in 1920s, it has been the most studied and easily produced member of PHAs family [52]. This microbial polyester demonstrates exceptional stereochemical regularity and crystallinity as high as 60 - 90% [51]. This material is brittle owing to the progressive crystallization upon ageing with the formation of large size spherulites [53]. PHB possesses useful physical characteristics comparable to those of some widely used polyolefins such as PP [2, 54]. In addition, more recently, the inherently biodegradable, biocompatible and natural origin properties of PHB have also made this biopolyester one of the promising candidates in the preparation of biomaterials for many biomedical applications [17]. Specifically, much attention has been given recently to the applications of PHB in combination with bioceramic such as HAP in orthopaedic and dental applications [31, 38-39, 42].

Despite its interesting biodegradability and biocompatibility, the high price, excessive brittleness and narrow processing window of PHB have limited its introduction in the market as a valid ecologically useful alternative to the currently widespread non-biodegradable conventional thermoplastic materials and larger commercial usage [51]. Therefore, research in improving the properties of microbial PHB has attracted a great deal of attention. Among the various strategies developed, polymer blending and copolymerization have been largely employed and reported [9, 17-22]. For example, blending of PHB with component having lower melting point may result in a decrease of the melting temperature that can improve the processability of the microbial thermoplastic, as demonstrated by PHB blends with poly(ethylene oxide) (PEO) [18]. Furthermore, the cost of the resulting materials can be very attractive as compared with the rather expensive PHB matrix. To retain the biodegradability of PHB in the resulting materials, a suitable choice of the PHB partner in the system such as biodegradable polymer and natural fillers should be taken into consideration.

1.5 Poly(ε-caprolactone) (PCL)



$$-\!\!\left[\left(\mathrm{CH_2}\right)_5-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}\right]_n\!\!-$$

Fig. 1.2 Chemical structure of PCL.

PCL, a popular aliphatic polyester produced synthetically from ring opening polymerization of ε-caprolactone, is a low glass transition temperature semicrystalline polymer with a well recognized biodegradability [55]. Similarly to PHB, PCL releases non-toxic by-products upon hydrolytic *in vivo* degradation. Owing to its well-known biodegradability, non-toxicity and permeability properties, homopolymer and copolymers of ε-caprolactone have widespread applications in industry and fields of medicine [56-57]. Because of its remarkable properties and ability to be miscible with many polymers, PCL has also been emphasized in developing novel materials. Consequently, polymer mixtures and also composites comprising PCL as one constituent have been studied extensively over the past few decades [9, 55, 22, 27, 30, 58-63]. Nevertheless, low mechanical strength and melting temperature ($\approx 60\ ^0C$) of this synthetic polyester restrict it from many large scale industrial applications [3, 61].

1.6 Calcium Hydroxyapatite (HAP)

HAP is one of the bioactive calcium phosphates, which exhibits excellent biocompatibility, osteoconductivity and bioactivity [32]. Due to its significant chemical and physical resemblance to the mineral constituents of human bones and teeth, it has been extensively used as a bone implant material in either sintered block or granular forms. Stoichiometric HAP has the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ and a calcium to phosphorus (Ca/P) ratio of 1.67 [64]. It is not a compound of fixed composition and may be characterized in terms of varying Ca/P ratio. Unfortunately, wide applications of HAP have suffered some limitations from their mechanical and degradation properties. HAP monoliths are non-biodegradable, brittle, with low tensile strengths as well as low resistance to impact loading [23, 28, 30]. Several studies had showed that incorporation of HAP resulted in distinct improvement and changes to various properties of biodegradable polymers such as PCL, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(L-lactide) (PLLA), including their mechanical performance, crystallinity, melting and crystallization behaviours as well as bioactivity and osteoconductive behaviour [26-27, 30, 32]. Thus, the use of HAP can be expected to induce improved properties of the PHB matrix in certain aspects as well.

1.7 Literature Review

1.7.1 Polymer Blends

Due to their importance in both academic and technical aspects, there has been tremendous interest in the research of polymer blends and miscibility of various blend systems has been studied widely. One class of interesting polymer systems is formed by semicrystalline-semicrystalline blends. Nevertheless, semicrystalline polymer blends have received much less attention than fully amorphous or amorphous-semicrystalline systems. Morphologies developed in these blends are complex and still not well understood. Owing to the presence of other crystallizable component, constituent may crystallize differently in a more complex manner in the blend as compared to the neat polymer. Their properties such as crystallization and mechanical behaviours are inherently coined by their phase morphologies that are strongly affected by the processing history and miscibility behaviour [47]. Polymer blends containing crystallizable component may undergo different phase changes, liquid-liquid phase separation, and also transitions as crystallization and relaxational glass transition. All of them are paramount important for regulating morphologies developed in the blend [65]. The crystallization behaviour and morphology of such blend become even more complex in an immiscible system. For heterogeneous polymer systems, the evolution of morphology during processing is complex and influenced markedly by the miscibility of the blend components as well as blend features that include the blend composition, interfacial and rheological properties. Thus, investigations on the crystallization and melting behaviours are important for fully semicrystalline blends.

Among the conclusions drawn from the literature, it is evident that PHAs can form miscible blends with polymers containing the appropriate functional groups, e.g. with PEO by intermolecular hydrogen bonding [18], and with poly(vinyl acetate) (PVAc) via dipole-dipole interaction [19, 21]. Biodegradability, physical properties and crystallization behaviour of PHAs in the blend are significantly affected by the nature of the blend partner such as its crystallizability and miscibility with the microbial polyester. Increased miscibility of PHAs with non-biodegradable thermoplastics decreases the apparent biodegradability of PHAs due to the restriction of enzymatic access [19]. Whereas, the phase separated morphology of immiscible blends will form large pathways after degradation of the dispersed phase, allowing greater access of the PHA depolymerase to the matrix material. When compared with pure PHAs, blends of PHA with other biodegradable polymers also usually show improved biodegradability [21, 66].

Most of the PHAs blends studied in recent years have been focused on PHB and its copolymer, PHBV. Since last few decades, blending of PHB and also its copolymer with a variety of polymers (biodegradable or non-biodegradable, having similar or different characteristics, amorphous or semicrystalline) has been undertaken. Miscible blends containing PHB have been formed with amorphous polymers such as PVAc [19], poly(epichlorohydrin) (PECH) [20], atactic PHB (*ata*-PHB) [67] and poly(*p*-vinylphenol) (PVPh) [68], as well as semicrystalline materials including PEO [18], poly(vinyl alcohol) [69], poly(ethylene succinate) [70], low-molecular weight PHB (D-PHB) and PHBV with 12 mol% of hydroxyvalerate content (P(HB-co-12% HV)) [71].

Upon addition of the second component, a depression of the experimental T_m of PHB was reported for all these homogenous blends, illustrating the miscibility of the blend constituents in the molten state. Additionally, miscibility of these blends has also been demonstrated by other outcomes, including exhibition of a single composition-dependence of the glass transition temperature (T_g), depression of PHB equilibrium melting point (T_m^0), retardation of PHB crystallization rate and suppression of PHB crystallinity in the blend. For PHB blends with D-PHB and P(HB-co-12% HV) [71], microscopy observations showed that ring-banded morphology is observed when PHB is in excess. When the respective second component is the major component, fibrous textures of the spherulites develop. For blends with PVAc [19], PECH [20], *ata*-PHB [67] and PVPh [68], the other constituent appeared to be included in the interlamellar regions of the PHB spherulites and formed a homogeneous mixture with amorphous PHB molecules after crystallization of PHB from a one-phase melt.

Immiscibility has been reported for PHB blended with amorphous polymers including ethylene-propylene rubber (EPR) [19], poly(cyclohexyl methacrylate) [72], poly(hydroxyl ether of bisphenol A) (phenoxy) [53], poly(1,4-butylene adipate) (PBA) [21], poly(β-propiolactone) (PPL) and poly(ethylene adipate) (PEA) [66], as well as semicrystalline polymers such as PCL [8, 21, 58, 73-74], P(HB-*co*-76% HV) [66], poly(3-hydroxyoctanoate) [75], poly(tetramethylene oxide) (PTMO) [47], poly(methylene oxide) (PMO) [76], poly(butylene succinate-*co*-butylene adipate) (PBSA) and poly(butylene succinate-*co*-ε-caprolactone) (PBSC) [50, 77]. Miscibility behaviour of these blends has been studied extensively by means of various methods, including the determination of T_g, morphological observations, studies of melting and crystallization behaviours. Immiscibility for the blends of PHB with P(HB-*co*-76% HV), PBA, EPR, PCL, PPL and PEA blends had been demonstrated by the unchanged T_g values of the individual components. While, morphological examinations on the blends of PHB/EPR, PHB/PMO and PHB/PTMO exhibited biphasic appearance. For blends of PHB with

EPR, PBSA and PBSC, the presence of blend partner did not influence the radial growth rates of PHB spherulites in the blends. In immiscible blends of PHB and its copolymer, P(HB-*co*-76% HV), no depression of the experimental T_m was found for either polymer in blended state.

Despite the immiscibility of the system, a strong depression of PHB melting point was found in PHB/PMO blends due to a change of PHB lamellar morphology [76]. In blends, PHB crystallizes after crystallization of PMO upon cooling. Preceding crystallization of PMO in the blend leads to space restriction for subsequent growing of PHB spherulites causing PHB to adopt greater lamellar thickness morphology. Nevertheless, crystallinity of PHB was not affected by the presence of PMO. On the other hand, presence of liquid PHB slowed down the linear growth rate of PMO during isothermal crystallization owing to lower thermal conductivity of the molten heterogeneous phase, but did not significantly change the crystallinity and T_m of PMO. For blends of PHB with EPR, morphological changes of the crystalline component gave rise to a small depression in T_m of the PHB phase [19]. In these blends, PHB spherulites grew from a two-phase melt containing EPR domain as the dispersed phase. During spherulite growth, EPR materials were first rejected and then incorporated in the intraspherulitic regions.

Miscibility of PHB/PCL blends, comprising two semicrystalline aliphatic polyesters with remarkable biodegradability characteristic has been assessed differently by various approaches, including determination of T_g [21, 74], viscometric study [73], thermal analysis [8-9, 58], microscopy examination [8-9, 21, 58], and mechanical characterization [21, 58]. It is found that PHB and PCL are immiscible on the molecular scale regardless of the blending techniques. For the resulting blends of PHB and PCL, studies have been mainly made on their biodegradation behaviour, morphology and mechanical properties [21, 58, 78]. There is still very limited detailed investigation on the melting and crystallization behaviours of PHB and PCL in the blended state.

In several studies, thermal transitions as T_g and T_m of the blend constituents were almost constant and unaffected by the blend composition, inferring macrophase separation into PHB and PCL domains in the melt [8-9, 21]. In a recent study on polymer-blend solutions of PHB and PCL via solution viscometry [73], intrinsic viscosities of the blends were linear functions of blend composition to a good approximation. Negative deviations of Huggins coefficients from perfect behaviour were observed for blends of PHB and PCL indicating repulsions between the coils that lead to immiscibility. Miscibility, morphology, biodegradability and mechanical properties of PHB/PCL blends prepared via solution blending were investigated by Kumagai and Doi [21]. Microscopic observations and mechanical measurements indicated a macrophase-separated structure. Young’s modulus and the tensile strength of the blends decreased with increasing PCL content. The degradation of PHB/PCL films was greatly influenced by the blend morphology. For blends with a dispersed PCL phase, the weight loss increase was found to be greater than that of pure PHB. The release of PCL dispersed phase from the film surface increased the susceptible surface area, and therefore accelerated the degradation of PHB matrix caused by PHB depolymerase. In blends of PHB and PCL prepared from solution mixture of chloroform and trifluoroacetic acid, polarizing optical microscopy study showed that spherulites of PHB grow in the presence of two-phase melt [9].

Compression-moulded sheets of PHB blended with PCL were prepared and investigated by Gassner and Owen [58]. Despite the immiscibility of PHB and PCL, mechanical properties of the blends varied considerably with composition, implying that PHB and PCL form mechanically compatible films containing phase-separated partially crystalline domains. Besides, a small amount of solubilization of one component into the other caused a slight depression of T_m in the blends. For PCL-rich blends, dynamic mechanical measurements inferred that PHB spherulites embed in a continuous semicrystalline PCL matrix and the ductile PCL matrix dominates the mechanical behaviour of the blends. On the contrary, PHB phase forms the continuous matrix in the PHB-rich blends. Inclusion of PCL did not seriously lower the rigidity of the sample. As a result of the reinforcing effect of PHB, elastic modulus and maximum stress increased systematically with ascending PHB content. The mode of failure changed from ductile to brittle.

As reported, immiscible blends of PHB and PCL are formed independent of the blending methods. Despite that, various attractive features of the individual polymers have made the PHB and PCL polyester pair remains an important subject of research efforts for reasons of both industrial and academic interests. In this regard, compatibilization has been attempted to enhance miscibility of PHB/PCL blends. Being a polyester, PHB may form, in principle, via transesterification in the molten state, miscible blends with other main chain polyesters such as PCL. Nevertheless, it is a well-established fact that PHB is susceptible to thermal degradation at temperatures close to its T_m [51, 67, 71, 79-80], via a random chain scission mechanism involving a six-membered ring transition state [79-80]. To avoid this unfavourable condition, transesterification of PHB/PCL blends has been commonly carried out by means of a catalyst or by addition of a compatibilizing agent.

In a study by Impallomeni et al., copolymers of (R)-3-hydroxybutyric acid and ε-caprolactone were synthesized upon transesterification of the corresponding homopolymers in the presence of 4-toluenesulfonic acid [59]. Random and block copolymers were obtained depending on the experimental conditions. After transreaction, T_g of PHB decreased dramatically as the ε-caprolactone content was increased from 0 to 72 mol%. Whereas, significant T_m depression was observed for both polymers with increasing content of the second component. Also, Immirzi et al. reported formation of interfacial agents during reactive blending of PHB and PCL in solution of chlorobenzene [81]. The interfacial agent formed via radical reaction catalyzed by dicumyl peroxide, exerts a compatibilizing action towards the mixed polyesters, improving dispersion degree of the components.

Whereas, Kim and Woo increased the miscibility of PHB/PCL blends by using PHB/PCL copolyesters formed after transesterification, as a compatibilizer [9]. PHB/PCL copolyesters were synthesized in solution phase using dibutyltin oxide as catalyst at 160 ^{0}C. The added copolyesters compatibilize the heterogeneous PHB/PCL blend to form a homogeneous phase on which the chains of PHB/PCL copolymers act as a bridge between the two different phases in the blend. With ascending amount of compatibilizers incorporated to the blend, T_m depression of both blend components increased and crystallization temperature (T_c) of the two polymers shifted toward each other. It was found that the copolyester of low randomness is more effective for increasing the miscibility of the blend. For system with compatibilizer, microscopic observations showed that the spherulites of PHB grow in equilibrium with one phase melt. Molecules of PCL and copolyesters could be easily incorporated into the interlamellar regions of PHB where they form a homogenous phase. Besides that, Shuai et al. added block copolymers of PCL and poly(ethylene glycol) (PEG), PCL-*b*-PEG, as a compatibilizer to the blends of PHB/PCL [5]. An improvement in mechanical properties of PHB/PCL blends was achieved upon addition of the block copolymers.

Similar to blends of homopolymer PHB and PCL, binary PHBV/PCL pairs are immiscible [60]. Compared to the neat polymer, T_m and crystallinity of PHBV in the blends were almost unchanged. Nevertheless, addition of PCL decreased the T_c of PHBV about 8 - 12 ^{0}C despite the immiscibility of these blends. Besides, presence of PCL also slowed down the overall crystallization rate of PHBV in the blends, indicating a negative effect of PCL on the primary nucleation of PHBV. To improve the compatibility of PHBV and PCL, PHBV has been melt-mixed with PCL in the presence of dicumyl peroxide at 160 ^{0}C for 10 min [55]. Organic peroxide added during melt processing induced the formation of integrafted species responsible for the interfacial activity and compatibilization in the blends. Crystallinity of PCL increased with its decreasing percentage in the blends. Treatment with peroxide in the melt induced some structural alteration in PHBV that increased significantly its T_m and crystallization rate in pure state and blends. Formation of a graft copolymeric phase in the interfacial regions between the blend constituents upon treatment with peroxide was further evidenced by the spectroscopic and morphological investigations.

Due to the poor PHB thermostability close to its T_m, compatibilization of PHB-based blends by means of reactive blending is difficult and greatly limited. As compared to other immiscible polyester pairs, there is still relatively few studies on transesterification of PHB-based blends have been carried out. Miscibility and transesterification of PHB and phenoxy have been investigated by Yuan & Ruckenstein [53]. Depression of T_m and the existence of a single intermediate T_g indicated the formation of miscible blend. Transesterification occurred thru alcoholysis reaction and was notably affected by the blend composition, annealing time and temperature. For polymer mixture containing 10 wt% PHB, single-phase blend was obtained after annealing for a sufficient long time, a total of 60 min at 180 ^{0}C. At a higher annealing temperature, 190 ^{0}C, formation of a single phase was accelerated and achieved after a total of 30 min. For samples with higher PHB content, longer duration of annealing was required to achieve homogeneity, e.g. blend with 30 wt% formed a single phase after a total of 4 hours at 180 ^{0}C. Fourier transform infrared (FTIR) spectroscopy investigations demonstrated that the molecular structures of PHB moieties grafted to phenoxy are different for short and long annealing durations.

1.7.2 Transesterification

Flory first demonstrated transesterification reaction in 1942 [82]. It was found that if interchange did occur, the final distribution would be determined by the equilibrium between the various polymer molecules rather than by their initial rates of formation. The first attempt to establish the exact mechanism of transesterification reactions was carried out by Devaux and his coworkers, by studying a series of model reactions for bisphenol-A polycarbonate (PC) and poly(butylene terephthalate) (PBT) [83-84]. In addition to the preparation methods and characteristics of the blend system (components, initial compatibility and composition), proper choice of reaction conditions including blending temperature, intensity and duration of mixing, as well as type and concentration of catalyst are the determining factors for compatibilization of immiscible polyester blend via transesterification [53, 63, 85-90]. Specifically, high temperature usually above the T_m of the reactants and sufficient blending time are prerequisites for the occurrence of transreaction in many polyester blends [53, 86, 89-90]. These two processing parameters are closely dependent on each other. It means that at higher temperature the blending time can be reduced and vice versa [53]. Under these extreme reactive conditions, other reactions can take place concurrently with the transreaction [24, 88, 91-93]. These include decomposition, pyrolysis of ester groups and crosslinking. In some cases, it has been found that decomposition of blend component might be necessary in inducing the transesterification process [24, 92].

To avoid unfavourable side reaction that might be caused by thermal agitation, it is possible to reduce both extreme processing conditions by means of a catalyst [63, 94]. Hence, there has been a great interest in studying and determining appropriate catalysts for transesterification reactions [55, 59, 63, 84, 88-89, 94-96]. Catalysts like acid, base and organometallic compounds have been commonly employed to facilitate intermolecular exchange reaction. The activity of catalyst in the transreaction does not only depend on the catalyst itself, but also the compatibility of the reactants as well as their blend ratio.

For transesterification, the interplay between reaction parameters is complicated and change of any parameter may result in different miscibility behaviour and blend properties for the same polyester mixture [24, 59, 63, 85-86, 90, 92, 94]. Variation of the experimental conditions and competitive processes involved can result in a range of interchange degrees, reaction rates, and subsequently the resultant molecular chain microstructures. Relationships are yet to be developed between the transreaction degree in polyester blends with the reactant characteristics, blend composition, processing parameters and the role of catalyst. Clarification of these blending parameters implies the possibility to control the evolution of the chemical structure. Accordingly, a large number of polymeric materials with a wide range of desired morphologies and properties varying with transesterification extent during the blending process can be prepared from the same pair of initial polymers.

Among the studies of transreaction effect on the miscibility of polyester blends, extensive research has been focused on polyester systems consisting of PBT, PC, poly(ethylene terephthalate) (PET), and polyarylate [24, 83-84, 86-89, 91-92, 97-99]. Under suitable reactive conditions, significant enhanced miscibility via compatibilization has been achieved by means of transesterification. A considerable change in the thermal properties of the blends mainly in terms of glass transition, melting, crystallization kinetics as well as crystallinity of the blend constituents could be recognized after transesterification. A change of the blends from incompatible to partially compatible and finally to complete compatibility was observed with reaction extent. Interchange reaction between blend components presumably took place mainly in the mixed phase, producing a new copolymer, which altered from block to random copolymer with reaction progression.

1.7.3 Calcium Hydroxyapatite

Various processes have been employed to prepare HAP ceramics, such as chemical co-precipitation [100], sol-gel process [101], spray-pyrolysis [102], hydrothermal synthesis [103], emulsion processing [104] and mechano-chemical method [105]. It is noted that the resulting properties of HAP obtained are process-dependent. Among the methods, chemical co-precipitation is reported to be the most promising technique because of its simplicity of experimental operations, low processing temperature and high yields of pure products [101].

Co-precipitation process was first proposed to prepare HAP ceramics by Hayek and Newesely [101]. The involved reaction of the process is as follows:

$$10\,Ca(NO_3)_2 + 6\,(NH_4)_2HPO_4 + 8\,NH_3{\cdot}H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6\,H_2O + 20\,NH_4NO_3$$

Based on this reaction, a derivative process was developed by Tas et al. to prepare nanosized and aggregated single-phase HAP bioceramics by using calcium nitrate tetrahydrate and diammonium hydrogen phosphate as starting materials [106]. Other modifications, for example, hydrolysis of a mixed solution of calcium nitrate and ammonium dihydrogen phosphate in the presence of hexamethylenetetramine [107] as well as replacing diammonium hydrogen phosphate with phosphoric acid [101], have also been performed to prepare stoichiometric and calcium-deficient HAP powders. However, preparation of fine HAP particles via co-precipitation process is reported to be very difficult [108]. To promote formation of fine particles, it is found that both calcium and phosphate ions which are involved simultaneously in the precipitation of HAP must be concentrated to favour high rate of nucleation than the rate of grain growth [101].

Because HAP is hydrophilic and most polymers are organophilic [109], there is usually lack of adhesion between HAP and the organic phase which in turn may result in inhomogeneous dispersion of fillers in the polymer matrix and an early failure at the interface of HAP/polymer. Therefore, the interfacial strength between HAP and the polymeric phase is one of the major factors determining the ultimate properties of HAP-filled polymer composites. Besides that, varying the amount of particulate HAP in the composite may result in a range of materials exhibiting different mechanical properties [110]. Also, the characteristics of filler particles, as discussed before, may influence markedly the properties of the resulting materials. Thus, as reinforcement for the polymeric phase, different shapes and sizes of stoichiometric and non-stoichiometric of HAP particles have been used [23, 26-28, 30, 33, 38-40, 42, 111-112].

With a well control of the fillers alignment in the polymer matrix during processing, the use of whiskerlike fillers has been demonstrated very recently as a promising way to enhance the reinforcing effect of HAP particles in composites [34]. Also, whiskers that are produced by calcinated at high temperature are found to possess more superior physical and chemical properties in terms of rigidity, hardness, stiffness, chemical and thermal resistance, than the raw inorganic materials [26]. Whiskerlike crystals of HAP have been synthesised over the past few years, largely by the precipitation and hydrothermal routes [113-117]. Recently, molten salt synthesis (MSS) technique has been reported to be one of the simplest methods for preparing ceramic powder bodies with whiskerlike, needlelike or platelike morphology and complex stoichiometry [106].

Preparation of HAP whiskers via MSS route based on the use of different low-melting salts as the medium of reaction has been extensively studied by Tas [106]. Along with the use of an appropriate fluxing agent, the results suggested that soaking time and temperature are the most significant variables in altering the morphology and size of whiskers. The use of fluxes as potassium chloride, potassium bromide, calcium chloride and sodium sulphate produced large single crystals of HAP, rather than whiskers, over the MSS temperature range of 850 - 1000 ^{0}C. Molten salt synthesis with a potassium sulphate flux was proved to produce short ($\leq$ 60 µm) HAP whiskers effectively in the temperature range of 1080 – 1200 ^{0}C. The bioceramic particles synthesized exhibited non-stoichiometry (i.e. calcium deficiency) that had a Ca/P molar ratio of 1.64. For MSS method, selection of the salt is critical for obtaining desirable powder morphology and characteristics [118]. The melting point of the salt should be low and appropriate for the synthesis of the required phase. In addition, the salt should have sufficient aqueous solubility to be eliminated easily by simple washing after synthesis. Other than MSS method, HAP whiskers have also been prepared through the hydrolysis of tricalcium phosphate in a binary mixture of water and isopropyl alcohol [111].

Depending on the properties to be evaluated, several techniques have been applied to characterize the HAP reinforcement particles and also the resulting composites. Among them, a few important techniques that have been widely used for characterization are scanning and transmission electron microscopy, X-ray diffractometry, mechanical testing and differential scanning calorimetry (DSC) [23, 25-28, 30, 38-40, 42, 101, 106]. For HAP, other methods that have been employed to characterize the bioceramic include inductive coupled plasma atomic-emission spectroscopy, energy dispersive X-ray spectroscopy, Brunauer-Emmett-Teller specific area measurement and FTIR spectroscopy [26-27, 101, 106].

Since the early 1980s, a variety of bioactive composites have been developed for hard tissue replacement [64]. The first bioceramic/polymer composite consisted of HAP reinforced high-density polyethylene (PE) was used clinically for orbital floor reconstruction and in middle ear implants. The original concept of using a bioceramic to reinforce a polymer was first discussed by Bonfield et al. [119]. Due to a current shift of emphasis in biomaterial engineering from materials that remain completely stable in the biological environment to materials that will biodegrade in response to the cellular and extracellular environments [32], combination of HAP with biodegradable polymers such as PHB and PHBV, PCL, PLLA and poly(D,L-lactide) has attracted a great deal of attention lately [26-28, 30-32, 38-39]. Ideally, biodegradable polymer/ceramic composites would combine the bone-bonding potential of HAP with the dynamic mechanical and degradability properties of the polymeric component. After recovery, the polymeric parts are metabolized and excreted, whereas the ceramic constituents are assimilated in the body.

1.7.4 Polymer Composites

The literature on biodegradable polymer composites is quite extensive [23, 26-28, 30, 32, 43]. HAP-filled polymer composites form a relatively new family of materials. To date, the studies concerning polymer composite based on PHB are, however, still very limited. A few reports have been published on the use of natural fibres and inorganic particulate fillers, such as wheat straw fibres, wood cellulose, maize starch, calcium carbonate, china clay and chopped glass fibres as reinforcement for PHB and its copolymers [25, 35-36, 44-45, 120]. For *in vivo* applications, PHB has been proposed as longer lasting biomaterial than PLA and its copolymer with glycolic acid that suffer from rapid degradation via hydrolytic depolymerization [121]. It has been demonstrated that materials based on PHB produced a consistent favourable bone tissue adaptation response with no evidence of undesirable chronic inflammatory response after implantation periods up to 12 months [39]. Furthermore, it has also been observed that PHB-based materials produce superior bone healing rate when compared with other thermoplastics, such as PE.

So far, there is still little works have been performed on the polymer composites comprising PHB and HAP bioceramic [31, 38-39, 42]. Different techniques have been used to prepare these composites and studies have been largely focused on their degradation behaviour, morphology, mechanical and biological properties. Among the studies, PHB powder has been compounded with particulate HAP powder (mean particle size of 8.6 µm) and then injection-moulded into plaques by Doyle et al. [39]. A direct positive correlation between filler content and Young's modulus of specimens could be observed where composite modulus increased linearly from 4 GPa for unfilled PHB to 11 GPa for composite with 40 % HAP content. In contrary, tensile strength and failure strain of the composites decreased with ascending HAP amount. The greater the amount of HAP present, the more rapid was the deterioration in properties as a consequence of the pathways introduced by the presence of filler particles for fluid ingress into the bulk material. For flexural properties, reinforced PHB exhibited a greater initial modulus but a smaller bend strength than those of neat specimen. However, *in vitro* studies showed that addition of fillers increased the rate of modulus decrease as compared to unfilled polymer.

Similar results were obtained for injection-moulded PHB composites with HAP added in proportions varying from 0 to 50 % [38], in which an inverse relationship could be recognized between their tensile strength and percentage strain at failure with HAP content. These outcomes were related to the reduction in the amount of the ductile polymeric phase and also flaws and stress risers introduced by HAP crystal granules. The observation that composites with smaller amount of HAP maintained its structural integrity even beyond the point of compressive failure would be of importance for orthopaedic implant applications. For PHB scaffolds prepared via salt-leaching, mechanical properties of PHB including compressive elastic modulus and maximum stress showed improvement after 10 % of HAP blending [31].