Doctoral Dissertation

ポリエチレンカーボネート/ポリ乳酸ブレンドの物性および分解性評価

Physicochemical and degradation properties of poly(ethylene carbonate)/ poly(lactic acid) blends

Tokyo University of Agriculture and Technology (September, 2019)

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TABLE OF CONTENTS

Abstract

The great effort in fulfilling the environmental concerns and rapidly increasing demand for poly(lactic acid) (PLA) in the applications such as packaging, biomedical, textiles, and others, showing that new techniques are required that solve the physicochemical properties problems of low toughness due to brittleness, slow hydrolysis and crystallization. The polymer blend is a compromising method due to its processibility more efficient and cost-effective. Many attempts have been made to improve PLA toughness and degradability by mixing PLA with other various polymers. However, the properties of modified PLA, consisting the mechanical strength and degradability, are still limited by the miscibility, phase's morphology and non-biodegradable additives factors. In this dissertation, the physicochemical and degradability properties of poly(ethylene carbonate) (PEC)/poly(lactic acid) (PLA) blends, were studied. PEC is a remarkable aliphatic polymer material can be synthesized by the copolymerization of carbon dioxide (CO_2) gas with epoxides. It has remarkable features such as the high stress-strain hardening profile, possesses better degradability properties and to some extent, the PEC and PLA are compatible due to the chemical structure resemblances. These studies reveal that PEC/PLA blends were successfully prepared by alternative solution casting and melt quenching techniques. Intermolecular forces between the oppositely charged ends (δ^+, δ^-) of carbonyl groups in PLA and PEC gives a rise of compatibility and thermal stability. Furthermore, this study demonstrates the possibility to take benefit of high strength PLA and ductility PEC, based on the enhancement of toughness properties PEC/PLA blends. At certain circumstances, the degradability of PLA is remarkably improved with the addition PEC. Finally, additional of melt-quenching proved to be an effective method modifying the physicochemical, crystallinity, structural and thermal properties. Addition of PEC to PLA is for seen an easy strategy for creating a new PLA binary system with biodegradable polymer with well-defined physicochemical and degradation properties.

Chapter 1

Introduction

1-1 Demands and applications of poly(lactic acid)

Polymer has become essential in certain industries as a raw material for packaging films, textiles, automotive and transport, consumers' goods, agriculture and horticulture, coating and adhesives, building and construction as well as electric and electronics. Therefore, the highly usage raised a significant growth in the demand for petrochemical polymers such as polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), polybutadiene (PB) and nylon. The consumption of these polymers has brought an environmental concern in which the polymers would take a long time to be degraded if the wastes are dumb into the sea. Table 1-1 lists the degradation time for several commodity products from various polymer types.

Table 1-1 Degradation time for several commodity products [1].

Products	Degradation Time
Banana peel	2-5 weeks
Newspaper	6 weeks
Cigarette but	1-5 years
Waxed milk carton	3 months
Plastic bag	10-20 years
Nylon Fabric	30-40 years
Foamed plastic cup	50 years
Plastic beverage bottle	450 years
Disposable diaper	450 years
Fishing net and fishing line	600 years

The consequences from this event; marine life are threatened, which require further action to clean up the plastic pollution incurring more time and cost, land pollution that affects plant growth and crops yield as well as air pollution due to open burning. As a result, together with the influences of a lack of oil assets motivated an effort directed towards the biodegradable biobased polymer production. Pathways of biobased polymer

are extensively shown in Fig. 1-1. Evidently, alternative approaches are available to produce more than 30 types of biobased polymer such as poly(lactic acid) (PLA), polyurethanes (PUR) and polyhdroxylalkanoates (PHAs) for substituting petro-based polymers in the future.

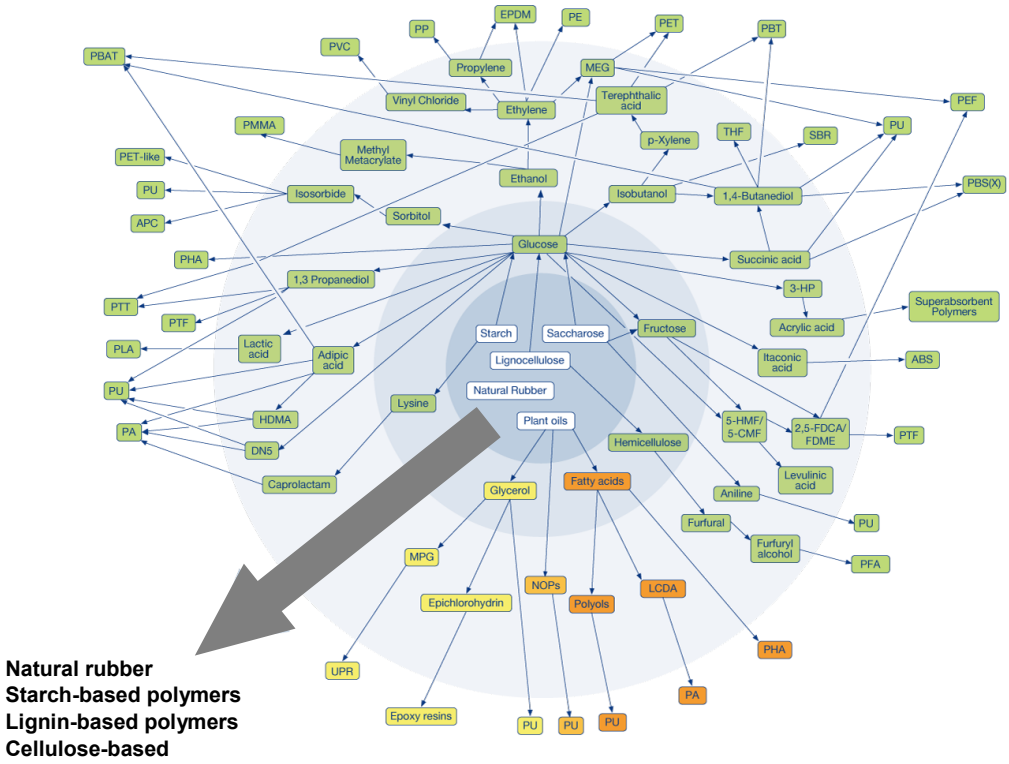


Fig. 1-1 Pathways to biobased polymers [2].

In general, biobased polymers are synthesized from several biomass resources including natural rubber, plant-oils, starch, lignocellulose and saccharose. According to a report of biobased blocks and polymer-global capacities and trends from 2018 to 2023 published by Nova-Institute GmbH (2019) [2], the production capacity of biobased polymer will continue to be developing as depicted in Fig. 1-2. Biobased polymers that are in demand is led by PUR based on natural-oil polyols (NOPs), cellulose acetate (CA), starch blends, PLA, PHAs, polyethylene furanoate (PEF) and aliphatic polycarbonates (APC)-cyclic. The production of biobased polymer is forecasted to rise to more than 6

million tonnes by 2023. Some of these polymers are synthesized from different feedstocks and processes designed to meet application specifications as illustrated in Fig. 1-3.

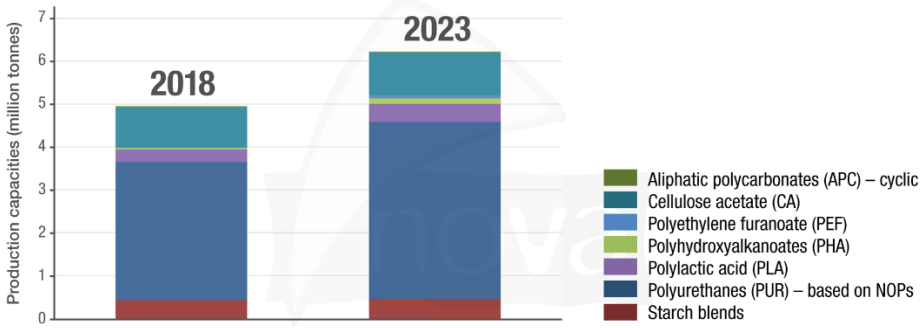


Fig. 1-2 Biobased polymer production capacities in 2018 and 2023 [2].

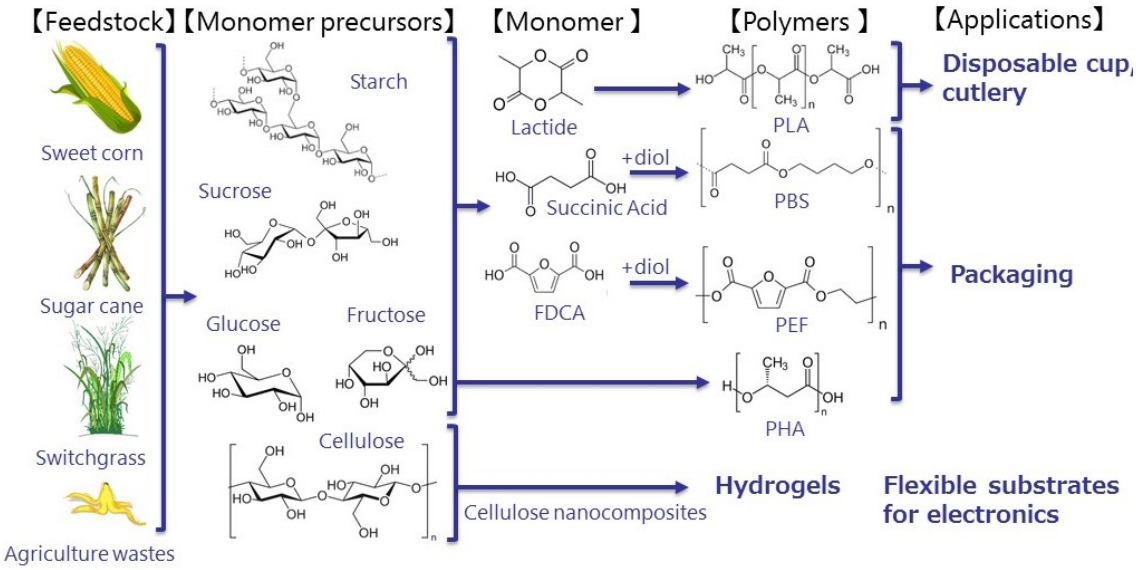


Fig. 1-3 Process design of biobased polymers [3].

According to Garlotta [4], PLA becomes the utmost investigated biobased polymers, which comprises several excellent properties such as renewable, biodegradable and recyclable [5–7]. In 2018, PLA was in demand, placing at the second highest of global

biodegradable bioplastic after starch blends as depicted in Fig. 1-4. It can be clearly observed that PLA contributes 10.3% to the worldwide production capacities of bioplastics in 2018, which is equivalent to 0.2 million tonnes. PLA has been considered to be a safe polymer according to Food and Drug Administration (FDA) [8].

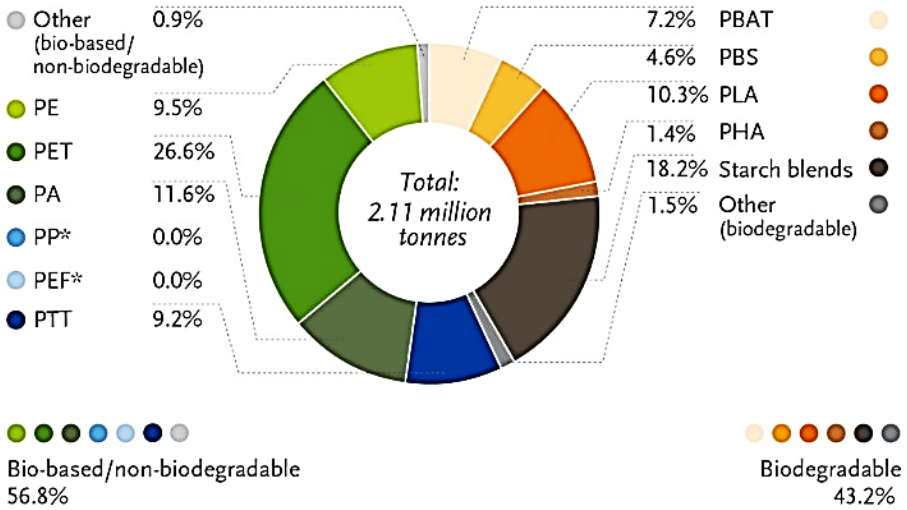


Fig. 1-4 Worldwide production capacity of bioplastics 2018 (by material type) [9].

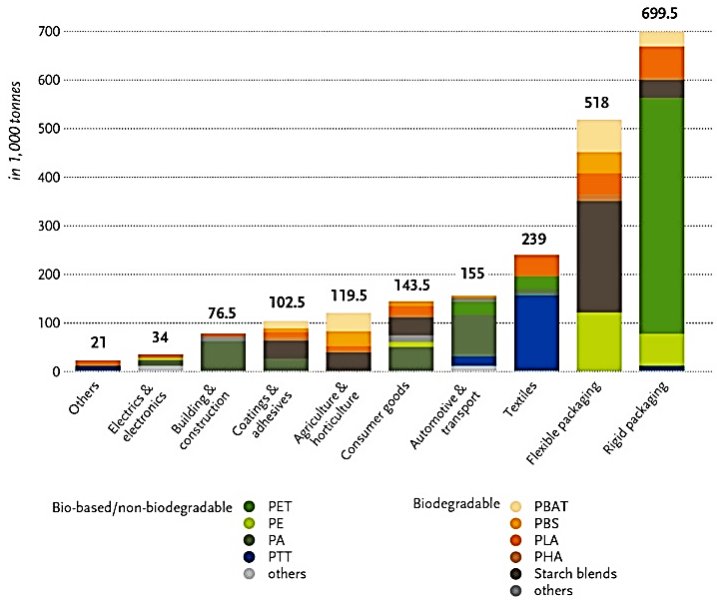


Fig. 1-5 Worldwide production capacities of bioplastics 2018 (by market segment) [9].

Due to biodegradability, demand for PLA is relative higher as for a flexible and rigid packaging, as well as for textiles and consumer goods as shown in Fig. 1-5. Nevertheless, PLA is also becoming an important material in other fields including electrics and electronics, building and construction, coatings and adhesives, agriculture and horticulture, as well as automotive and transportation [4,6,10–14]. On top of that, PLA shows its biocompatibility when the degraded products of PLA are harmless for living organisms comprising the human body [15], allowing it the greatest appropriate polymer to the substitution for biomedical uses. Alternatively, PLA has been utilized not only for tissue engineering and scaffolds but also suitable as for drug transporter and blood vessels [16–18].

1-2 Fundamentals and properties of poly(lactic acid)

Poly(lactic acid) (PLA) is a typical biodegradable thermoplastic polyester produced from monomers including lactic acid and lactide using alternative polycondensation and ring opening polymerisation routes as illustrated in Fig. 1-6.

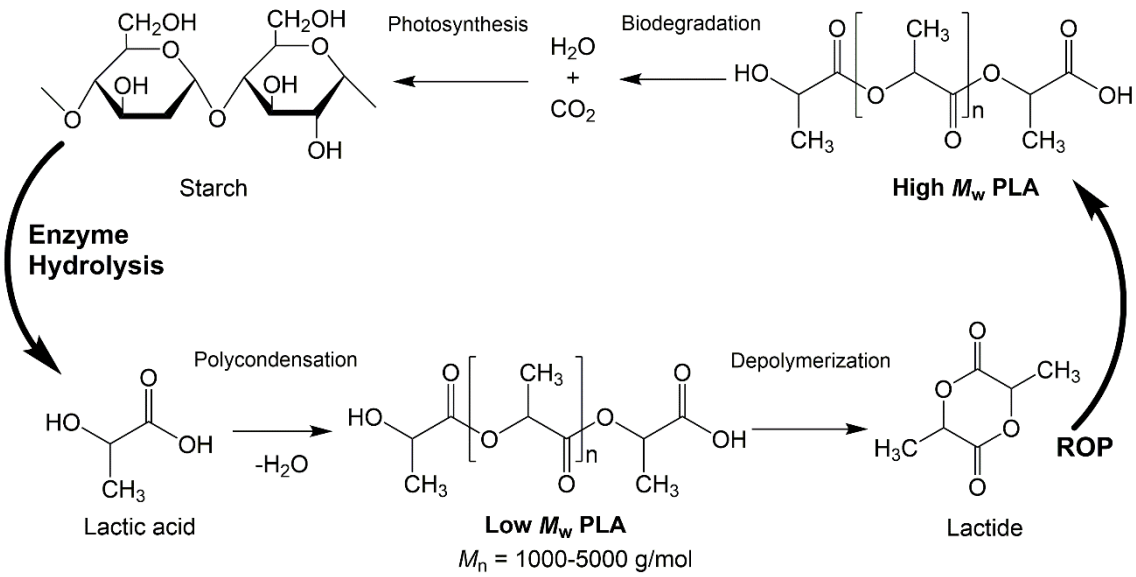


Fig. 1-6 Typical synthesis and circulation of poly(lactic acid) (PLA) [19].

Monomer lactic acid basically comes from corn starch, wheat and sugar beets [20]. Lactic acid leads to the formation of poly(L-lactic acid) (PLLA) and its enantiomers poly(D-lactic acid) (PDLA) depending on the types of catalyst involved in the synthesis. Meanwhile, the ones prepared from lactide by ring opening polymerisation (ROP) is mentioned as polylactide. Both types are commonly referred to as PLA.

After a life time, PLA is degraded and the biodegradability of PLA has led to produce eco-friendly carbon dioxide (CO_2) and water (H_2O) when it is finally degraded. It is well known that CO_2 and H_2O are the vital feedstocks for plants and crops growth via photosynthesis. The cycling process of PLA is as shown in Fig. 1-6. In addition, there are three stereoforms of lactide that are possible; L-lactide, D-lactide and meso-lactide [21]. All structures of beginning stereoisomers of lactic acid and lactide are summarised in Fig. 1-7.

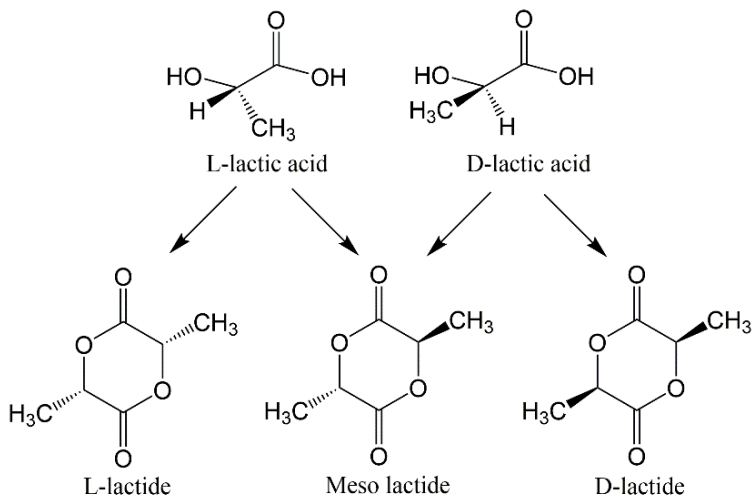


Fig. 1-7 Beginning stereoisomers of lactic acid and lactide [21].

PLA is a type of semi-crystalline polymer with the level of transparency that is dependent on the crystalline phase. Less crystallinity will show high transparency level. It has becoming increasingly popular as a biodegradable engineering plastic [22] owing to its high mechanical strength instead of the thermal properties as summarised in Table

1-2. Depending on its molecular weight variation and composition of stereo chemical, the tensile strength and elastic modulus of PLA are as high as 28-70 MPa and 1.2-4.0 GPa, correspondingly [4,19]. Among other types of biodegradable polymers such as poly(hydroxyalkanoates) (PHAs), poly(ethylene glycol) (PEG), or poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS) and its copolymers, PLA has higher melting temperature around 170-180 ^{o}C that helps PLA to be easily treated by few types of processing method such as injection moulding, film extrusion, blow moulding and thermoforming [15,23].

Table 1-2 Typical PLA polymers physical properties [16].

Physical properties of PLA	
Crystallinity	Semicrystalline (PDLA)
	0-37% (PLLA)
	Amorphous (PDLLA)
Glass transition temperature, T_g	50-64 ^{o}C
Melting temperature, T_m	145-186 ^{o}C
Tensile strength	28-70 MPa
Young's modulus	1.2-4.0 GPa
Elongation at break	2-6%

PLA displays several attractive properties including the mechanical and physical comprising the high modulus, high strength, as well as the good clarity and barrier properties. Mechanical properties of PLA include the tensile strength and the tensile modulus, show comparable characteristics to some petro-based polymers type such as high density poly(ethylene) (HDPE), polypropylene (PP), polystyrene (PS) and poly(ethylene terephthalate) (PET). However, PLA inherits brittleness due to low toughness as demonstrated by the elongation at breakage and small impact strength limitations at less than 10% (as tabulated in Table 1-2) and 20 J/m [24], causing low toughness that establishes the greatest challenge for PLA. The processibility, formability and foamability of PLA are significantly impacted by the properties of low melting

strength and slow crystallization. Due to low service temperature including low heat deflection temperature (HDT), in some specific areas, these shortcomings of PLA will cause limitation especially related to the injection moulding processing.

The compostable, recyclable, biodegradable and biocompatible properties of PLA are undeniable [25] since PLA could be synthesized from renewable natural resources. However, PLA shows slow degradation upon hydrolysis, thereby limiting the PLA in case it is being used as a commodity material due to the degradation of PLA that influences the environmental concern following dumping. Rasal *et al.* [15] has clearly mentioned that PLA shows low degradation process upon hydrolysis neither by water and alkaline solution, forming two possible species namely carboxyl and hydroxyl end groups [26]. The process is controlled by pH, temperature and time [27–32]. Tsuji and Ikada [29] conducted a degradation based on the alkaline hydrolysis studies on PLA using low concentration of 0.01N sodium hydroxide (NaOH) solution. After 5 months, PLA was slowly degraded and the hydrolysis was influenced by the process conditions.

Thus, different approaches have been used since the last few decades to overcome the aforementioned disadvantages of physicochemical and biodegradability properties ascended by the existing PLA for targeted applications. Some of the methods used to modify PLA bulk include chemical copolymerisation, plasticization and polymer mixture [10,15,19,24,33–36].

1-3 Modifications of Poly(lactic acid)

Chemical polymerisation has been initiated more than two decades although it is expensive [22] in comparison with other techniques, which the PLA copolymers are extensively prepared by incorporating PLA with the other tough, ductile and/or elastomeric monomers [15,37,38]. These processes could be carried out through either polycondensation of lactic acid, producing low molecular weight copolymers or by the ring opening copolymerisation of lactide with cyclic monomers like glycolide, ε-caprolactone, δ-valerolactone, trimethylene carbonate as well as a linear monomers like

ethylene glycol, producing high molecular weight copolymers (see Fig. 1-8, showing the common polyester repeated units of PLA-based copolymers).

In early studies, excellent *in vitro* and *in vivo* degradation properties of copolymerised L-lactic acid and ε-caprolactone without any catalyst [39] and high toughness and ductility biodegradable elastomeric implant L-lactide and ε-caprolactone copolymers have been developed [40]. Other than that, L-lactic acid has also been polycondensed with D,L-mandelic acid and other α-hydroxy acids such as D,L-α-hydroxybutyric acid, D,L-α-hydroxyisovaleric acid and D,L-α-hydroxyisocaproic acid. Nevertheless, copolymerisation via polycondensation becomes a valuable tool to control the end groups of PLA, producing low molecular weight copolymers (M_w<10,000).

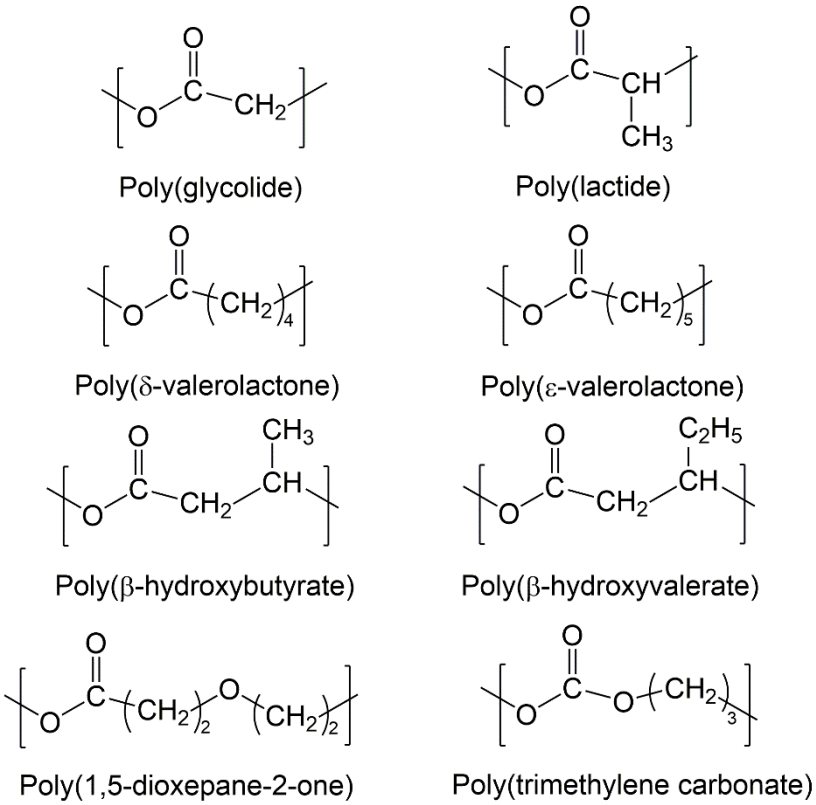


Fig. 1-8 Common polyester repeated units of PLA-based copolymers.

Ring opening copolymerisation (ROP) of L-lactide is a more common and strategized approach for PLA copolymerisation to improve its degradation, thermal and mechanical properties. For example, the introduction of ε-caprolactone to poly(lactide-co-glycolide) copolymers has brought super tough properties to PLA. The ductility and toughness of PLA have been seen to progress significantly when trimethylene carbonate (TMC) and caprolactone copolymers were introduced. Ethylene glycol is also another considerable and a common copolymer with PLA due to its biocompatibility and hydrophilicity [41].

Recently, studies conducted by Fan *et al.* [42,43] showed that flexible PLA copolymers are effective in biomedical treatments for drug delivery and oxygen carriers. However, this PLA modification technique is considerably expensive due to lengthy reaction period and rigorous copolymerisation with additional catalyst for the reaction, creating additional challenge for chemical copolymerisation. Even though this method is effective in enhancing PLA ductility, it brings losses in some advantages of PLA in reducing the mechanical strength and melting temperature evidently of several copolymers [19,44,45].

Plasticization is another approach to modify the glass transition temperature, improve ductility, and increase processibility of PLA by the introduction of either biodegradable or non-biodegradable plasticizers [46]. There are huge types plasticizer emphasized and introduced to PLA including lactide monomer, low molecule weight poly(ethylene glycol) (PEG), citrate esters, glyceryl triacetate, dibutyl sebacate, epoxidized soybean oil, liquefied wood flour ester, oligomers, and some combinations plasticizers [11,47,56–61,48–55]. The list of plasticizers, advantages and their disadvantages are summarised in Table 1-3.

It can be observed in Table 1-3 that most of these plasticizers are very efficient in enhancing the ductility of PLA, as demonstrated by the dramatic improvement in break elongation shown by plasticized PLA. The breakage of PLA at 10% significantly increased to 200-420% with the assistance of small amount for instance 20 wt% citrate esters, PLA oligomers, or dibutyl sebacate [47,51,54] to the PLA.

Table 1-3 Improvement and problem of PLA modification with various plasticizers.

Plasticizers	Improvement	Problem
Low molecular weight lactide [11,62]	-Increase in elongation at break.	-Stiffening with time. -Migration toward the surface.
Oligomers (glycerol, citrate esters, low molecular weight PEG, PEG monolaurate, lactic acid) [63]	-Lactic acid and low molecular PEG are efficient plasticizers. -Natural citrate ester is miscible with PLA at all compositions and improved elongation at break.	-Glycerol inefficient plasticizer to PLA. -Loss in tensile yield strength.
Triacetin Tributyl citrate [64]	-Lowering T_g PLA around 10 ^oC at 25 wt%.	-PLA underwent crystallization and migration of plasticizer molecules toward surface [65]. -Tributyl citrate oligomers causes phase separation with storage time [58].
Diethyl bis(hydroxymethyl) malonate (DBM)	-DBM oligomer demonstrated morphological stability with storage time [66].	-Phase separation and migration of DBM toward surface.
Multiple plasticizer systems	-Low molecular weight triacetin and poly(1,3-butylene glycol adipate) (PBGA) increased the elasticity and sustain the tensile strength [67].	
Low molecular weight PEG Low molecular weight PPG	-PPG miscible to PLA, plasticization effects better than PEG [68]. -Combination PEGs and acetyl tri-n-butyl citrate increased elongation at break.	-40 wt% PEG causes the PLA to be very ductile and PEG influences the miscibility and PLA crystallization behaviour [69]. -Acetyl tri-n-butyl citrate limits the miscible PEG in PLA and miscibility depending on the molecular weight of PEGs [52].

However, most of these plasticized PLA received similar problems related to the migration of the small molecules towards the surface of PLA, causing phase separation between PLA and the plasticizers. Furthermore, during storage time or service, the plasticized PLA may possibly become brittle following low migration rate of plasticizers from bulk to surface. In addition, incorporation of phthalate plasticizers to PLA [70,71] may create to potential environmental and health issues similar to many cases reported for PVC [72,73]. Another serious problem related to plasticization is the high content of plasticizers by 15-20 wt%, which is typically required to substantially enhance the tensile toughness, thereby causing a severe reduction in tensile strength and elastic modulus [47,49,57,74]. For example, the PLA break elongation improved considerably from 11% to 233% with 15 wt% glyceryl triacetate; however, the elastic modulus and tensile strength decreased significantly from 1.02 GPa and 65 MPa respectively to 0.59 GPa and 29 MPa [55].

Due to these constraints, addition of plasticizers to PLA is not the best approach for toughening PLA. It is therefore essential to develop distinct techniques for all while enhancing PLA's tensile toughness and durability impact, and in the interim to usually maintain a high amount of mechanical strength, flexible modulus, and durability. In comparison, polymer blend comprising the mixing of flexible or elastic polymers or copolymers has given an alternative way of considerably improving tensile strength and impact strength simultaneously if fine morphology and appropriate compatibility of blends are acquired [75–80].

1-4 Polymer blends

Polymer blend is defined as a mixture of at least two polymers or copolymers, which are physically mixed with or without any chemical bonding between them. Fig. 1-9 illustrates the schematic diagrams of morphology evolution of polymer blend for poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) when the content are varied at different ratios. Unique materials are generated through blending as far as its processibility and or performance are concerned. For instance, the properties of polymers

blends are superior to those of component homopolymers such as enhancing the mechanical, barrier and flame-retardant properties. Due to its simplicity, blending technologies provide attractive opportunities to reduce material cost with or without little sacrifice in properties especially for reusing and recycling polymer wastes.

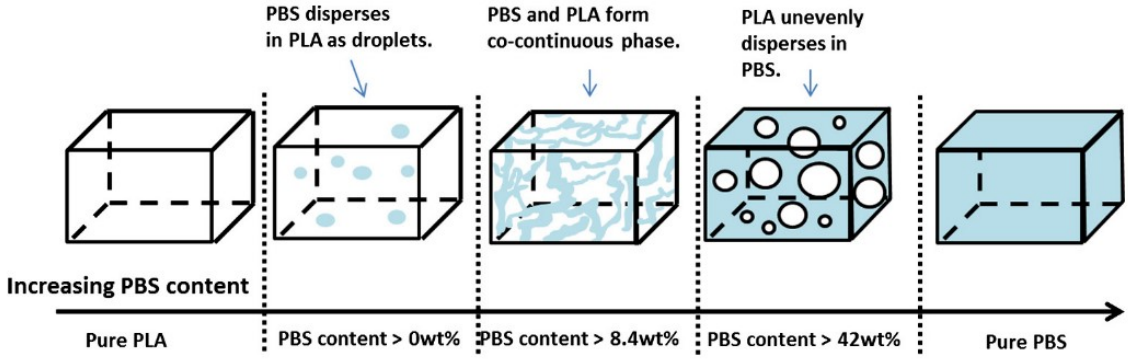


Fig. 1-9 Morphology evolution for PBS/PLA blends. PBS is shaded while PLA is white [81].

As shown in Table 1-4 summarised by Saini *et al.* [16], there are various blend techniques used for the PLA blend system such as solvent casting, melt extrusion, electrospinning, foaming and solution blending and emulsification. Thus, each of these PLA blend systems resulted a blend material with new properties through blending, which is suitable towards the suggested applications. For instance, the addition of poly(hydroxybutyrate) (PHB), poly(caprolactone) (PCL) and hyaluronic acid (HA) could enhance mechanical properties through melt extrusion and blending, respectively. In other cases, the incorporation of thermoplastic polyurethane (TPU) and poly(ethylene glycol) (PEG) to PLA increased the crystallinity, while PLA added to PCL decreased the crystallinity in the PLA/PCL blend system. Lignin introduced anti-oxidant and barrier properties to PLA film so that it is possible to be used as food packaging films. Morphologies of these blends are different to each other (as showed in Fig. 1-10), which are influenced by factors such as the blend techniques, initial properties of the polymers and interaction between polymers upon blending.

Table 1-4 PLA blends with suggestion applications [16].

Polymer	Technique	Suggested application	Properties affected	References
Poly(hydroxybutyrate) (PHB)	Melt extrusion	Packaging	Improved ductility, break elongation, barrier characteristics	[61]
Thermoplastic polyurethane (TPU)	Melt extrusion	Actuators, tissue engineering	Shaped memory, extended tensile strength, break elongation	[82,83]
	Foaming	Tissue engineering	Shape memory, greater crystallinity, porous morphology	[84]
Poly(caprolactone) (PCL)	Electro spinning	Tissue engineering, grafts	Elevated elasticity, fibre orientation, hydrophilicity reduced	[85]
	Solvent cast film	Nerve conduits	PLA offers reduced crystallinity and enhanced degradation compared to PCL alone, resulting in cell porosity	[86]
Poly(glycolic acid) (PGA)	Electro spinning	Soft tissue engineering	Mechanical properties similar to structural soft tissue materials	[87]
Poly(ethylene glycol) (PEG)	Nanoparticles/ microparticles	Drug delivery	Higher hydrophilicity, improved degradation	[88]
	Foaming	Scaffolds	Reduced viscoelasticity, enhanced crystallinity and hydrophilicity	[89]
Hyaluronic acid (HA)	Melt blending/ Compression moulding	Bone grafts, wound healing, tissue engineering	PLA offers greater break strength and elongation than HA alone	[90]
Chitosan (CHI)/PCL	Solution blended PLA/PCL emulsified into CHI solution/ solution cast film	Antimicrobial, haemostatic wound dressing	Combination of PLA mechanical strength, PCL flexibility, and CHI swelling behaviour	[91]
Lignin	Melt extrusion/ compressed film	Food packaging	Lignin introduces anti-oxidant and barrier characteristics	[92]

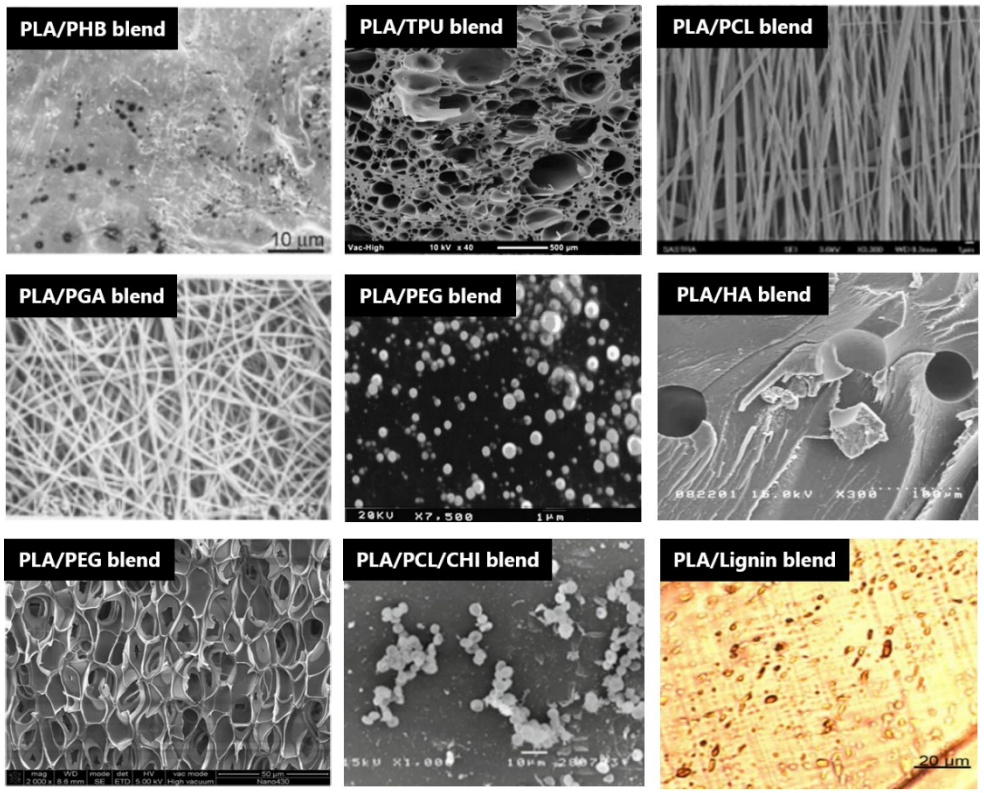


Fig. 1-10 Morphologies of various PLA blends prepared by melt extrusion [61][82,83][92], electrospinning [85][87], solvent casting [86], foaming [84][89], solution and emulsification [91] and nanoparticles [88].

Polymer blends have been widely implemented to enhance PLA's toughness [15,24,34]. According to the studies conducted by Nofar *et al.* [10], the number of research related to PLA blend is increased as shown in Fig. 1-11, comprising various blend systems such as binary system of PLA with non-biopolymers, biodegradable polymers, biobased polymers, biobased-biodegradable polymers, ternary polymer blends of PLA with two other polymers, ternary combination of PLA nanocomposites with a polymer and a nanofiller, as well as foams prepared by PLA-based blend.

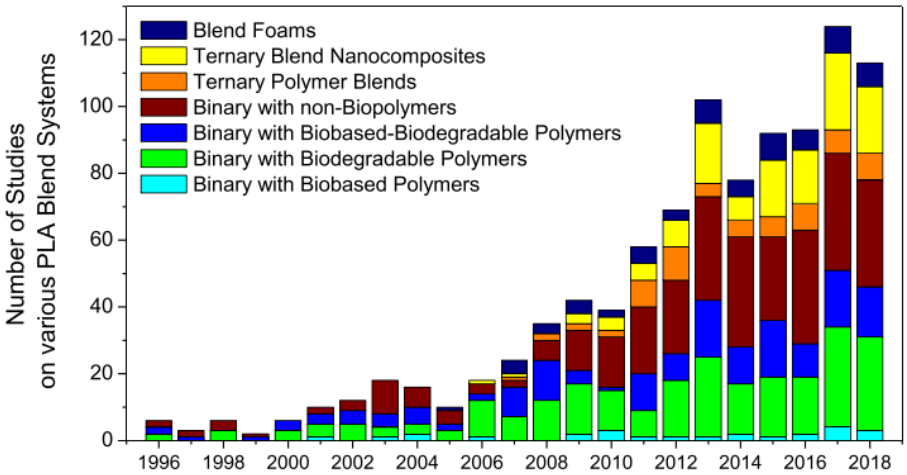


Fig. 1-11 Number of researches reported over the past two centuries on different PLA-based mixing technologies [10].

Based on Fig. 1-11, research work related to PLA blend initially begins with the non-biopolymers binary system before the importance of PLA binary system with biodegradable polymers is considered, activating the number of studies related to the research on biodegradable polymers binary system with a signified development from the year 2000. The development of polymer blend processing is also resulted from its simplicity, and it has been suggested by Nagarajan *et al.* [93] that the high molecular weight and low mobility of the blending components have increased the durability of polymer blends as a result of evaded plasticizers migration.

In early studies, the flexible or elastic non-biopolymers were added to PLA, which are usually produced from petroleum resources comprising polyethylene (PE) [94], polypropylene (PP) [95–97], polystyrene (PS) [98,99], acrylonitrile-butadiene-styrene (ABS) copolymer [100], poly(methyl methacrylate) (PMMA) [101–105], polyethylene terephthalate (PET) [106–112], poly(butylene terephthalate) (PBT) [113–115], poly(trimethylene terephthalate) (PTT) [116–118], polycarbonate (PC) [119], polyamide (PA) [120,121], poly(vinylphenol) (PVPh) [122–125], poly(ethylene glycol) (PEG)

[69,126–133], poly(ethylene oxide) (PEO) [129,134–137] and poly(oxymethylene) (POM) [138–140].

These approaches showed smaller losses on tensile strength and elastic modulus in comparison with plasticization for plasticized PLA at similar compositions. For instance, PLA incorporated with 20 wt% poly(ethylene glycol) (PEG)-based crosslinked polyurethane (CPU) showed elongation at break and impact strength to more than 200% and 400 J/m with the respect of PLA, which at only 10% and 16 J/m. In the meantime, the elastic modulus and tensile strength of PLA were not affected much by PEG based-crosslinked CPU which only reduced by 29% and 41%, respectively. However, mechanical properties become weak for PLA plasticized by 20 wt% PEG, demonstrated elastic modulus and tensile strength, by contrast, were significantly decreased by 82% and 67%, respectively.

Furthermore, the addition of several types of compatibilizers and copolymers such as those listed in Table 1-5 to these binary PLA blend with non-biopolymers has subsequently enhanced some of the compatibilized PLA blends properties including the ductility, toughness and rheological properties. These are because domain sizes significantly reduced with the presence of compatibilizers, causing increased interfacial adhesion between PLA and the polymers and lowered the interfacial tension.

Few of these materials have improved mechanical characteristics such as by adding a petroleum-based polymer and poly(ethylene octene) grafted with glycidyl methacrylate (POE-g-GMA) where the PLA's toughness effectiveness was accomplished by reactive mixing [141] with impact resistance exceeding 530 J/m due to the reduced domains size upon the addition of POE-g-GMA to PLA/POE blend as shown Fig. 1-12.

Table 1-5 List of compatibilizers and copolymers for PLA/synthetic non-degradable thermoplastics.

PLA blend	Compatibilizers/Copolymers	Ref.
PLA-PE	PE-b-PLLA, reactive PE-glycidyl methacrylate (GMA), LDPE-g-maleic anhydride (MA), ethylene-co-GMA (EGMA), ethylene-GMA-vinyl acetate (EGMA-VA), EMA-GMA, ethylene-butyl acrylate-GMA (EBA-GMA)	[94,142–148]
PLA-PP	PP-g-MA, styrene-ethylene-butylene-styrene-g-MA (SEBS-g-MA), PE-g-MA, PP-g-MA/PE-g-MA, EGMA-methyl acrylate terpolymer (PEGMMA)	[149–153]
PLA-PS	PS-b-PLLA, oxazoline-carboxylic acid	[154,155]
PLA-ABS	Styrene-acrylonitrile (SAN)-GMA, GMA-g-SAN, PE-epoxy, MA-g-ethylene propylene rubber (EPR), MA-g-SAN, Joncryl ADR-4368C CE	[100,156–158]
PLA-PMMA	PS-co-GMA	[159]
PLA-PET	PLA-g-MA	[160]
PLA-PBT	Paraphenylene diisocyanate (PPDI)	[161]
PLA-PTT	Ethylene-methyl acrylate (EMA)-GMA	[162]
PLA-PC	SAN-g-MA, poly(ethylene-co-octene) (EOR)-MA, tetrabutyleammonium tetraphenylborate (TBATPE), triacetin, random copolymer of styrene and GMA and N,N,N',N'-tetraglycidyl-4,4' diaminodiphenyl methane (TGDDM), ethylene-butyl acrylate (EBA)-GMA	[163–166]
PLA-PA	polyethylene-octene elastomer grafted maleic anhydride (POE-g-MA), alkenyl-succinide-anhydride-amide (ASAA), alkenyl-succinic anhydride-imide (ASAI)	[120,167–169]
PLA-PEG	PEG-co-citric acid (PEGCA)	[170]

It should be noted, however, that the addition of elevated levels of these altered petroleum-based polymers, compatibilizers, and high-off copolymers sometimes destroys PLA's sustainable characteristics. To overcome the sustainability issue for binary PLA system with non-biopolymers and due to public and environmental concerns, greater attention has been paid on the biobased (even if non-biodegradable) and biodegradable polymers to modify PLA.

It is noteworthy that some polymers based on petroleum are biodegradable or biocompatible such as polycaprolactone (PCL), poly(butylene succinate) (PBS), poly(butylene succinate-co-adipated) (PBSA), poly(butylene adipate-co-terephthlate) (PBAT), polyvinyl acetate (PVAc), polyvinyl alchohol (PVA), ethylene vinyl alcohol (EVOH), poly(ethylene succinate) (PES), poly(glycolic acid) (PGA) and aliphatic polycarbonates.

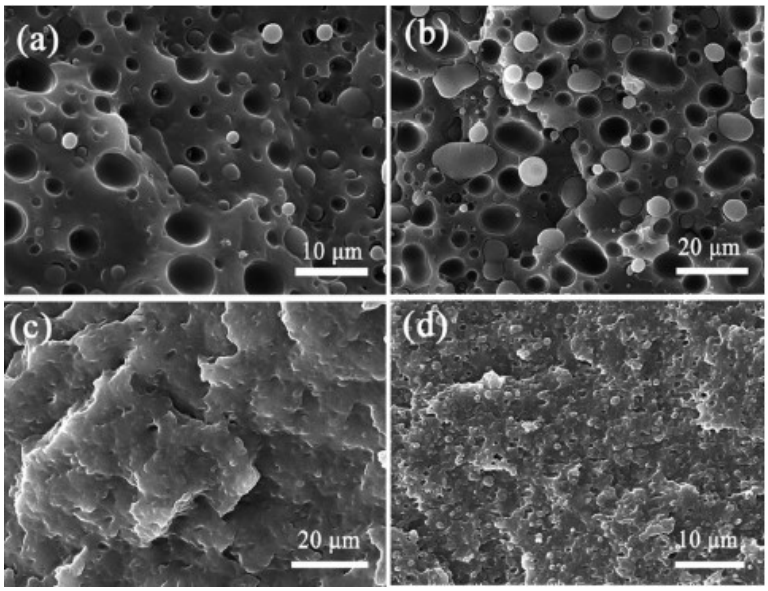


Fig. 1-12 SEM micrographs of the PLA/PEO blends freeze-fractured surfaces; (a): 10 wt% POE, (b): 20 wt% POE, (c): 10 wt% POE-g-GMA, and (d): 20 wt% POE-g-GMA [141].

1-5 Biodegradable polymer blends with poly(lactic acid)

Several studies on biodegradable polymer blends with poly(lactic acid) (PLA) explored the mechanical properties, crystallization of PLA, degradation; enzymatic and hydrolysis and other properties to suit in the applications such as materials for oxygen barrier layer [171], textiles filament [172], biomedical [173–175] and others [176,177].

Enhancements on mechanical properties such as elongation at break and toughness of PLA have been demonstrated for several blends together with additional compatibilizers and chain extenders including PLA/polycaprolactone (PCL), PLA/poly(butylene adipate-co-terephthlate) (PBAT), PLA/poly(butylene succinate-co-adipated) (PBSA), PLA/ poly(butylene succinate) (PBS), PLA/polyvinyl alchohol (PVA), and PLA/poly(ethylene succinate) (PES) blends. For instance, the introduction of low content of PBAT to PLA around 10~25 wt% has increased the ductility of PLA up to 300%. Further addition of plasticizers and reactive compatibilizers such as 30 wt% acetyl tributyl citrate (ATBC) and dicumyl peroxide (DCP) to PLA/PBAT blends showed insignificant increase in strain at break by 300%, while reduced domain size and tensile strength remained unaffected. Two types of CEs namely Joncryl and 1,6-hexanediol diglycidyl ether) as well as the mixture of insignificant amounts of phtalic anhydride (PA) and bioxazoline (BOZ) have been applied to PLA/PBAT blends. In the existence of CE to PLA/PBAT blends, giving breakage rate at 515% following the PLA-co-PBAT copolymers in-situ development, whereas the presence of PA/BOZ mixture has reduced the domain size without affecting the tensile strength as claimed by Dong *et al.* [178]. More complex PLA/PBAT/ethylene-methyl acrylate-glycidyl methacrylate copolymer EMG-GMA (75 wt%: 10 wt%: 15wt%) blend system with super tough properties reported by Wu *et al.* [179], showing high content of plasticizers relative to PBAT for this multicomponent blend; nevertheless, it showed 13 timers larger notched impact strength of 62 kJ/m^2 than 90 wt% PLA/10 wt% of PBAT blend.

Meanwhile, for PLA/PBSA blends as reported in early study, added PBSA to PLA caused a decrease in tensile strength modulus and no impact on breakage elongation due to poor miscibility. Pivsa-Art *et al.* [180] established similar outcomes where elongation

at break of PLA has only increased by 6% with the addition of 30 wt% PBSA. Nofar *et al.* [10] however suggested that mechanical properties including elongation at break of this blend could be achieved by 150% with a proper mixing time. In other studies, miscibility of PLA/PBS blends was questionable when Park *et al.* [181,182] successful to elucidate the miscibility of PLA/PBS blend that only miscible in their amorphous states, after characterizing the blends with few techniques comprising the differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and small angle X-ray diffraction (SAXS) techniques as well from the negative value determined by Flory-Huggins interaction parameter. However, Bhatia *et al.* [8] differed that the blends were immiscible based on the modulated DSC and partial miscibility from their rheological results. The immiscibility of PLA/PBSA blends has been also confirmed by Yakohara *et al.* [183], Wu *et al.* [184] and, Deng *et al.* [81] at similar 20 wt% PBS. Hence, additional modification is necessary, which has been revealed by compatibilization using Jonycrl epoxy-based CE and TPP for PLA/PBS blend at 70/30 weight ratios. The former has increased the elongation at break to 200% whereas the impact strength has increased 8 times and later reduced the PBSA domain sizes, improved the impact strength (~3 times) and elongation at break (up to 200%). Similar to PLA/PBS blend system at 80/20 blend ratio, compatibilization by DCP, small amount of lysine triisocyanate (LTI) and methylenediphenyl diisocyanate (MDI) would not increase much higher the elongation at break in comparison to the effects of 10 wt% PBS to PLA, which is at 250%. However, reactive compatibilizers including PLLA-g-MA have capably increased strain at break from 240% to 390% with 20 wt% PBS.

Several studies reported the crystallization of PLA prior to the addition of the biodegradable polymers such as PCL, PBAT, PBS, PVA and PES. However, Kim *et al.* [185] exhibited decrease PLA and PCL crystallization with the rise of P(LA-co-εCL) copolymer content to PLA/PCL blends, which is contrary to a result reported by other researchers. PCL dispersion in PLA may act as heterogeneous crystal nucleating spots. With a more uniform spherulites morphology of PCL/PLA blend with even dispersed PCL within PLA, the crystallization rate would be further improved. Wang *et al.* [186] also revealed that octavinyl POSS and epoxy cyclo hexyl POSS have enhanced the PLA crystallization rate in the PLA/PBSA blends. Meanwhile for PLA/PBS blends during melt

crystallization, PBS at the molten phase was lubricated, enhancing the crystallization of PLA and PBS was capable to nucleate during cold crystallization of PLA [81,183,187].

Apart from the mechanical properties enhancement, the incorporation polycaprolactone (PCL) into PLA has been widely studied owing to the biodegradability and harmless characteristic of PCL. Most of the PLA/PCL blends have shown life-time control ability, degrading and forming safe by products for biomedical uses, therefore these blends are suggested for controlled drug release system, tissue engineering, scaffolds, and transplants. Several studies investigated the hydrolysis and biodegradation behaviour of PLA/PCL blend films. Tsuji *et al.* [188] reported more terminal groups of carboxyl groups in the 25wt%PCL/75wt%PLA blend, allowing for higher degradation of PLA. Apart from that, Fukushima *et al.* [189] found that PDLLA phase influenced the PCL to degrade, in which water can be easily diffused through the PDLLA amorphous matrix, thereby catalysing PCL degradation. Nevertheless, enzymatic degradation of PLA/PCL blend study done by Liu *et al.* [190] has confirmed that enzyme and PLA types are able to control the rate of degradation. In another study, the lipase-catalysed-catalysed-enzymatic has been easily degraded and became more significant by decreasing the PLLA content [191]. On the contrary, Sivalingham *et al.* [192,193] claimed that PCL has better thermal stability in relative to PLA; therefore, adding PLA to PCL would not influence PCL degradation neither thermally nor by enzymatic activities. Cai *et al.* [194] revealed the behaviour of discharged drug of PLA/PCL blends, showing faster drug release generated by the high water absorption at rough surface of phase separated PLA/PCL blends. In addition to these observations, Gaona *et al.* [195] examined reduced molecular weight for degrading PLA/PCL blends after these blends were executed for hydrolysis in phosphate buffer solution. Due to faster crystallization rates, reduced molecular weight of degraded PLA molecules, increased molecular mobility and shaped crystals, PLLA became more resistant to hydrolysis. On the other hand, 20 wt % PCL in PLA/PCL blends degraded slower than neat PLA and PCL [188,189,196].

Other than PCL, poly(glycolic acid) (PGA) is another form of biodegradable and biocompatible aliphatic polyester commonly used in biomedical applications despite its excellent mechanical characteristics. PLA/PGA nanofibres have been successful prepared

by You *et al.* [197] using electrospinning with non-porosity and unfortunately, slower degradation of PLA than PGA caused a decrease in degradation rate of PGA. Similar observation by Mahalik *et al.* [198] demonstrated enzymatic degradation that was decreased significantly with polyvinyl acetate (PVAc). Therefore, enhancement of PLA toughness could be done by incorporating several non-biopolymers, compatibilizers and copolymers. On the other hand, the addition of these polymers to PLA could not further tolerate the biodegradability and biocompatibility aspects.

Attempts on PLA binary blends with biobased and biodegradable have been alternatively carried out with natural starch, thermoplastic starch, lignin, polyhydroxylalkanoates (PHAs). Despite the improvement of mechanical characteristics, the extra feature of these biobased polymers including biodegradability has attracted excellent interest in food packaging and biomedical applications. Similar towards PLA binary system with non-biopolymers, the addition of compatibilizers has been further investigated as an alternative way to improve miscibility between PLA and the biobased as well as biodegradable polymer blends. In other studies, epoxidized soybean (ESO) has been used in the reactive compatibilized PLA/starch blends, giving rise of up to 42 kJ/m^2 for the impact strength and elongation at break at 140% as reported by Xiong *et al.* [199]. The addition of the chain extender multifunctional epoxy-acrylic-sytrene to PLA/thermoplastic starch (TPS) has increased the viscosity of the mixture and its melting resistance, enhanced ductility by up to approximately 340 % and hence the processibility. [200]. Whereas in Bartczak *et al.* study [201], the introduction of 20 wt% poly(3-hydroxybutyrate) (PHB) to PLA demonstrated an improvement of up to 4 and 2 times for ductility and impact strength, respectively. Ma *et al.* [202] also demonstrated 20 wt% polyhydroxybutyrate-co-valerate (PHBV) with a high hydroxyvalarate content where the strain at break and impact strength of PLA was increased to 230% and 150 kJ/m^2, respectively.

Furthermore, the degradation behaviour of these blends has been explored in several studies in terms of biodegradability. Gattin *et al.* [203] summarised that the PLA/starch blends have the greatest degradation in a liquid medium, moderate when they are in the composting medium and slowest in the inert solid. The study included moisture

uptake and enzymatic degradation affecting PLA/starch mixtures. The starch particles have been leached out from the PCL/starch interface following water sorption during the hydrolysis of PLA. Enzyme (α-amylase) has resulted in surface erosion and significantly deteriorated the mechanical properties of PLA/starch blends [204]. Several studies reported PLA/PHAs blends' degradability, showing dissimilarities in the degradation rate depending on the phase structures and could be measured by molecular weight of the PHB [205] as well as blending polymers [206]. Kikkawa *et al.* [207] elucidated that there were enzymatic degradation dissimilarity on the miscibility PLA/PHA blends, it progressed well for fully miscible than in immiscible and partially miscible blends. Meanwhile, as referred to Zhang *et al.* [208], high PHB content has increased the crystallization of PLA and improved the biodegradability even the PLA/PHB blends were found immiscible. In several other studies, the incorporation of PHB and poly(hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) to PLA have delayed the degradation of PLA [209,210], which is unfavourable; therefore, poly(ethylene glycol) (PEG) and acetyl tributyl citrate (ATBC) as plasticizers were incorporated to PLA/PHB blend, accelerating the hydrolysis rate [211–214]. Whereas PHB copolymer namely poly(hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)) [215–217] has successfully increased the biodegradability of PLA. Studies on biodegradation are quite limited for other biobased/biodegradable PLA blends such as PLA/PBAT, PLA/PBSA, PLA/PBS, PLA/PVA, PLA/EVOH and PLA/PES blends.

Based on previous numerous attempts via different polymers and techniques made to improve PLA brittleness due to its low toughness, crystallization and degradability directing to the developing biobased and biodegradable blend with PLA, polymer blend offers a wide range of opportunities for PLA. The characteristics of altered PLA such as mechanical strength and degradability are still restricted by the miscibility and morphology, which are formed by the distinctiveness of PLA blends and additional non-biodegradable additives may delay or/and deteriorate the biodegradability properties of PLA.

1-6 Aliphatic polycarbonates: Fundamentals and applications

The alternative approaches for PLA blend have been directed toward aliphatic polycarbonates due to their superiority in the biodegradability and also strain hardening mechanical properties. Synthesis of aliphatic polycarbonates (Fig. 1-13) via copolymerisation of carbon dioxide (CO_2) with epoxides has attracted many researchers in extending the potential of these polymers in comparison to the ones prepared via polycondensation between polyols with dimethyl carbonate and ring opening polymerisation of cyclic carbonate monomers.

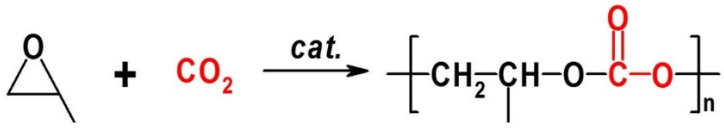


Fig. 1-13 Copolymerisation of CO_2 with epoxides towards aliphatic carbonate yields [218].

CO_2 is one of the most abundant and renewable sources of energy and the selective conversion of CO_2 with epoxides into degradable polycarbonates has been considered a promising green and viable route to polycarbonates [218–222]. Since its discovery by Inoue and co-workers in 1969 [218], this technique of copolymerisation has become one of the most well-studied and innovative techniques for the extensive use of carbon dioxide in chemical synthesis as a result of low cost manufacturing in the industrial scale. Various kinds of polycarbonate such as poly(ethylene carbonate) (PEC), poly(propylene carbonate) (PPC), poly(trimethylene carbonate) (PTMC), poly(butylene carbonate) (PBC), poly(2-alkoxymethylene carbonate), poly(2-alkoxymethyl-2-ethyl-trimethylene carbonate) as well as alternating copolymers with different side chains have been investigated. Table 1-6 shows the summary on type of polycarbonates in relevant studies.

In previous study, a series of polycarbonates comprising PEC, PPC and poly(cyclohexene carbonate) (PCC) were investigated for impermanent device wafer adhesives. These polycarbonates have shown sufficient adhesion strength to wafer-wafer bonding during the mated wafers processing. Interestingly after thermal decomposition of the carbonates, wafers were spontaneously released without or with little amount applied mechanical force as shown in Table 1-7 and free from residual after wafer debonding as shown in Fig. 1-14 [223] in comparison with commercial adhesive and Furukawa UV tapes. Patent on development of oxygen barrier laminate films by Dixon and Ford in 1977 [224] also emphasised polyalkylene carbonate adhesive.

Table 1-6 Functional aliphatic carbonates architectures.

Applications	References
Thermoplastics and binder	[223–225]
Solid polymer electrolytes	[226,227,236–240,228–235]
Coating resins	
Surfactants and foams	
Tissue engineering scaffolds	
- Electrospun fibres	[241]
- Biodegradable elastomers	[242–246]
- Hydrogels	[247–250]
- Drug delivery carriers (micelles/polymersomes/polycomplexes)	[251–258]

Table 1-7 Average adhesive strengths for bonded polycarbonates and adhesive tape, and in wafer debonding for polycarbonate residue and UV exposed tapes [223].

Material	Bonding Adhesion strength (N/mm)	Debonding Adhesion strength (N/mm)
PEC	0.01±0.005	0
PPC	0.03±0.02	0
PCC	0.05±0.02	0.0035±0.02
PPC/PCC	0.05±0.01	0.0035±0.02
Scotch	0.09±0.02	-
Furukawa tape #1	0.05±0.02 (unexposed)	0.024±0.001 (exposed)
Furukawa tape #2	0.15±0.03 (unexposed)	0.024±0.0005 (exposed)

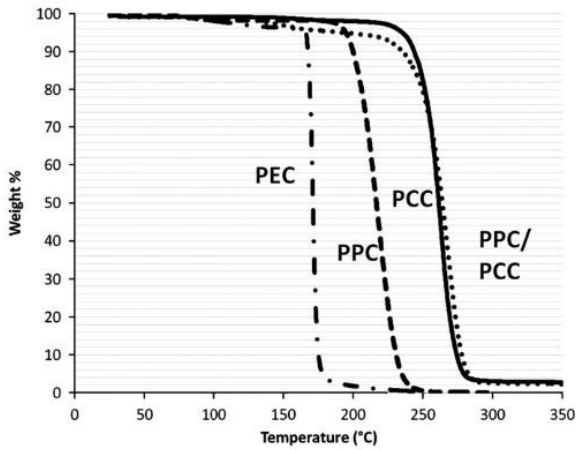


Fig. 1-14 Dynamic thermal gravimetric analysis of polycarbonates at rate of 1 ºC/min [223].

For solid polymer electrolytes (SPE), it has been well reported that the addition of salts to PEC shows great ion-conductive properties than the well-known SPE for batteries application including poly(ethylene oxide) (PEO), following better ion-transport mechanism [227,229,259]. In comparison with PEO, PEC allows a high content of salts

addition; thus, high ion conductivity could be achieved for the PEC-based electrolytes system as shown in Fig. 1-15. Further, extensive studies related to PEC-based electrolytes have been carried out by blending PEC with PTMC [239] filled with electron spun silica nanofibers [240] and TiO_2 nanoparticles [226] besides introducing an end-capping poly(ethylene carbonate)-based concentrated [233] to establish electrochemical stability for all-solid state Li battery.

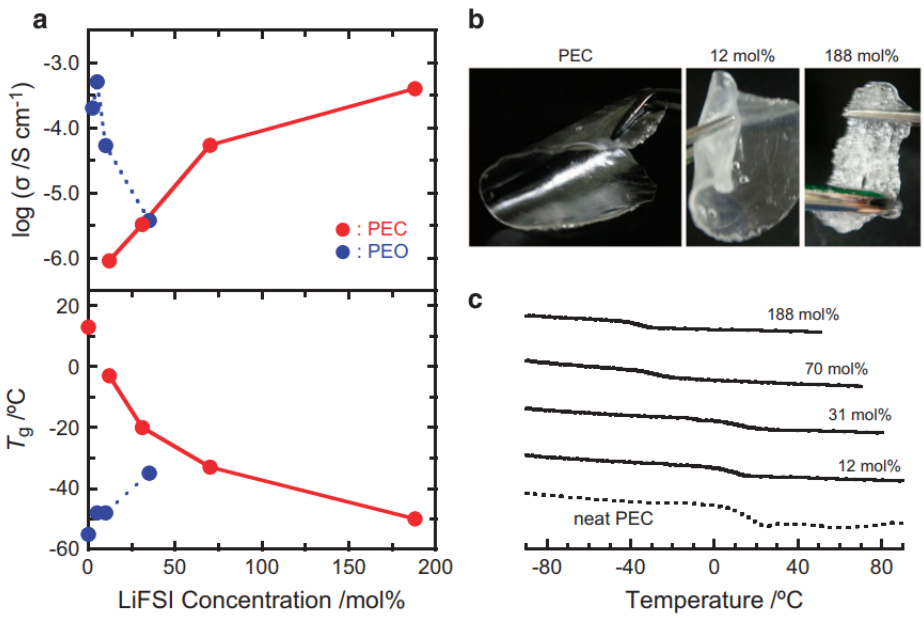


Fig. 1-15 (a) Dependence of conductivities for PEC and PEO-based electrolytes at 60 ºC on the LiFSI (lithium bis(fluorosulfonyl)imide) concentration; (b) photographs of neat PEC and electrolytes with 12 and 188 mol% LiFSI; and (c) DSC curves of neat PEC and electrolytes with different concentrations of LiFSI [260].

In biomedical field, oligomers and high-molecular weight poly(trimethylene carbonate) (PTMC) have been vastly studied for tissue engineering scaffolds including electronspun fibres, biodegradable elastomers, hydrogels and drug delivery carrier. For instance, soft biodegradable hydrogels with compression modulus values of lower than 100 kPa have been successfully prepared by photo-crosslinking aqueous solution of macromonomers such as PTMC-poly(ethylene glycol), (PEG)-PTMC and nanoclay

particles. The compressive strength, toughness and in vitro degradation of these hydrogels are influenced by TMC content and more significantly by the addition of Laponite nanoclay. Ultrafine fibres of PPC (Fig.1-16) and PCC have been successfully obtained by electrospinning. Upon UV irradiations, nanofibres PPC underwent photochemical bulk modifications, allowing for the control of progression of host/implant interactions *in vivo*.

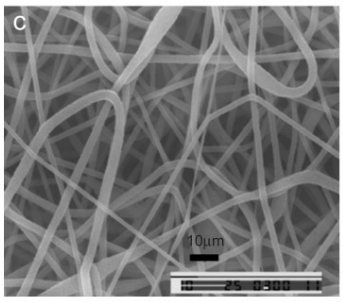


Fig. 1-16 SEM micrographs of electron spun PPC nanofibers (4 wt%) from dichloromethane solution [241].

There are studies done on the toughness enhancement of PLA blend related to aliphatic polycarbonates including poly(propylene carbonate) (PPC). The earliest study on PLA/PPC blends was reported in 2006 by Ma *et al*. [261], showing a partial miscible blend and concluded that both PLA and PPC are partly compatible following the resemblances in their chemical structures. Gao *et al.* [262] confirmed a phase inversion for PLA/PPC blend as shown by PLA/PPC blending ratio of 60/40 with a co-continuous morphology formed. In consideration of low miscibility of PLA/PPC blend contributing to low enhancement for PLA toughness properties, further studies have been carried out incorporating various types of compatibilizer such as maleic anhydride (MA), homopolymer PVAc, 1-2-propanediol isobutyl POSS (P-POSS) [263] and catalytic transesterification using tetra-n-butyl titanate (TNBT) as a catalyst [264]. PLA/PPC blend has shown the highest toughness achieving 1355% adding with the 0.9 wt% MA in comparison with PLA/PPC blend at ratio 70/30 with the strength remained unchanged,

suggesting that MA allowed for PPC domain size reduction, giving more interaction of PLA and PLA at the interphases [265].

Meanwhile, another studies reported by Gao *et al.* [266] demonstrated that homopolymer PVAc has been selectively localised at the interphases PLA/PPC, thus refining the morphology of these blends. PVAc enhances the interfacial adhesion by acting like a bridge that corresponds to the substantial increase in the PLA/PPC blend mechanical properties. However, studies on biodegradation related to this blend are not well investigated in the previous report.

Poly(ethylene carbonate) (PEC) is another type amorphous aliphatic carbonates with T_g around 13 °C, making it rubbery at room temperature and the thermal degradation of PEC at 198 °C. PEC has stress-strain ductile profile (Fig. 1-17). PEC shows a low modulus and high elongation ratio (at room temperature) suggestive for elastomeric materials. The mechanical properties can change considerably at 37 °C. The Young's modulus is reduced four times with temperature at 37 °C, suggesting that PEC undergoes softening process during heat treatment. The elongation measurable can reach more than 600% without film rupture.

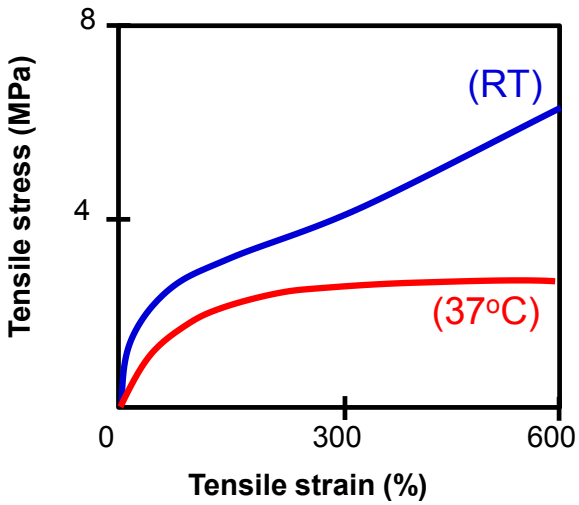


Fig. 1-17 Stress-strain curves of poly(ethylene carbonate) [267].

The relatively low thermal stability and poor mechanical properties associated to PEC still limit them to applications that are less demanding in these properties in general. However, tremendous research works on PEC have been increasingly explored for solid polymer electrolytes and biomedical applications, which were mentioned earlier as a result of good ionic conductivity and biodegradability (Fig 1-18) due to back-biting mechanism as illustrated by Stoll *et al.* [268] in Fig. 1-19.

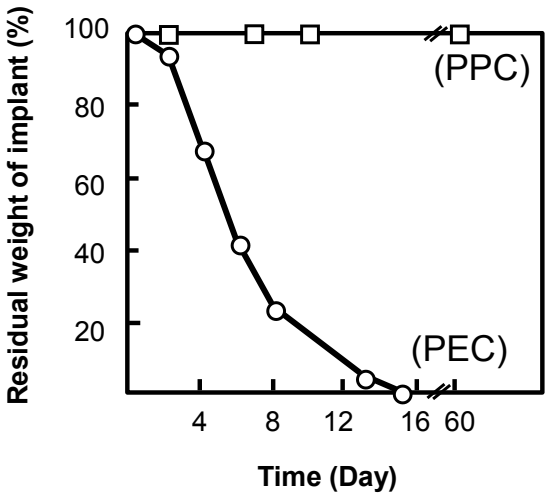


Fig. 1-18 Biodegradation profiles of poly(ethylene carbonate) and poly(propylene carbonate) in vivo (rat peritoneal cavity) [269].

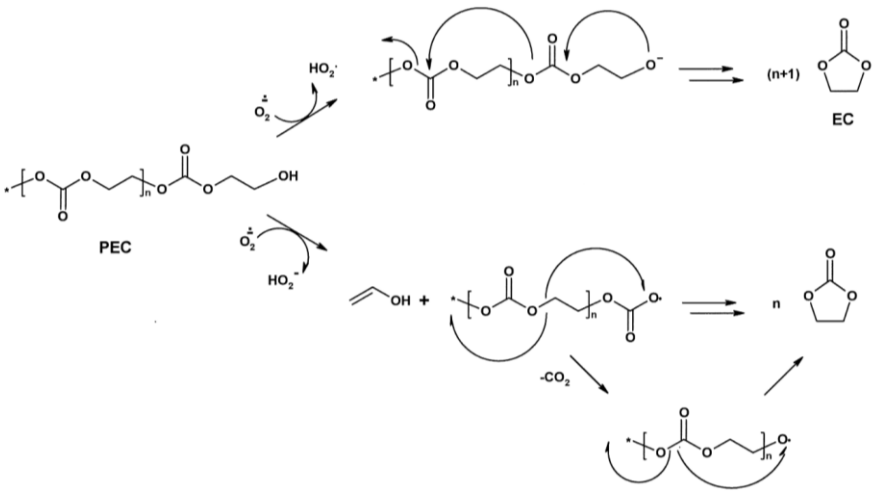


Fig. 1-19 Formation of ethylene carbonate (EC) initiated by a radical or anionic mechanism as suggested by Stoll *et al.* [268].

As observed by Stoll *et al.*, PEC tablets were stable in all aqueous solutions between pH 1-12. However in strong base of KOH solution at pH 13.5, rapid degradation of PEC was observed. PEC showed faster biodegradation rate in comparison with another type of aliphatic polyalkylene carbonate such, PPC. PEC was completely degraded after 2 weeks as shown in Fig. 1-18.

In the early 2000s, PEC was effectively mixed with poly(vinyl chloride) (PVC) to solve issues regarding the use of harmful chemical additives such as phthalates with synthetic polymers PVC to soften or stabilize the plastic, which was widely used as a raw material in producing children's toys and food products [270]. The first report on PEC and PLA blend emphasised the preparation towards an eco-friendly packaging film when the oxygen transmission rate of PLA has significantly decreased with the addition of 10 mol% PEC (Fig. 1-20).

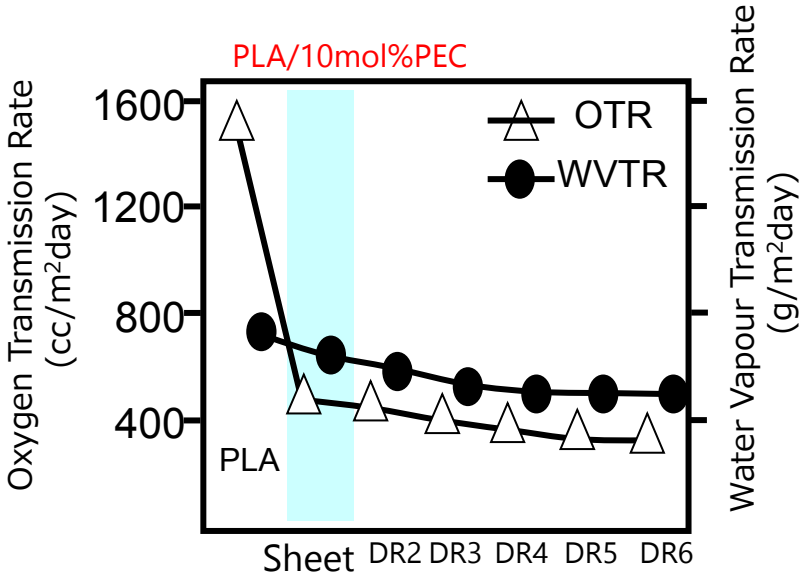


Fig. 1-20 Oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) of PLA/PEC blending films with various draw ratios [271].

However, as clearly mentioned earlier that PEC is thermally weak, the preparation of PEC/PLA blend at high temperature influences the blend profile. Characterization on PEC/PLA blend done by Mi *et al.* [271] remained disputable; limitations on the PEC/PLA blend ratios and the intention of their work were solely on the draw ratio (DR) aspects of extrusion process to produce a film. Therefore, an alternative method was suggested in this present work to elucidate the physicochemical of PEC/PLA blends prepared at room temperature by a simple solution casting technique.

1-7 Objectives

In this study, an alternative polyethylene carbonate (PEC)/poly(lactic acid) PLA blends were prepared based on 3 main considerations associated to the remaining challenges presented by various PLA blend systems regarding blend miscibility, toughness enhancement and degradability following the incorporation of various non-biopolymers and biobased/biodegradable polymers to PLA.

Poor miscibility influenced the PLA blend morphology, hence significantly restraining the mechanical properties due to poor interfacial adhesion or high interfacial tension at interphase between polymers. The mixing of compatibilizers to the PLA blend is an option to improve the interfacial adhesion, whereas additional cost is incurred and partly reduces the sustainability in the case for PLA binary system with biobased/biodegradable polymers.

In light of this, the establishment of partial miscible and compatible at some extent, between PLA and PEC resulted from the similarities in chemical structure of PLA and PEC were considered. Due to high stress-strain hardening properties of PEC, PEC in the PLA-rich blends toughened the PLA, while the PLA in the PEC-rich blends reinforced the PEC. Preparation towards an eco-friendly packaging film of PEC/PLA blend was successfully developed by Mi *et al.* [271]; however, the thermal history due the high thermally blend mixing for these PEC/PLA blends have an influence to the blend profiles. Furthermore, studies on degradation related to these blends were not investigated in detail.

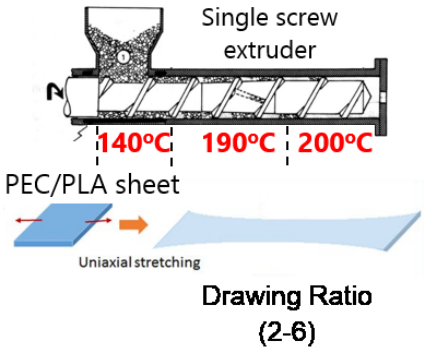
In this respect, PEC was introduced to PLA by simple solution casting at room temperature with different blend ratios. The preparation of these blends by solution casting was to provide an alternative approach to the preparation method. As mentioned earlier, the increasing attention on the aliphatic poly(alkylene carbonate)s derived from CO_2/epoxide copolymerisation has been increased due to their various functionalities and concept of CO_2 utilisation. Therefore, to elucidate the miscibility of PEC/PLA blends following the solution casting technique, the preparation and physicochemical characterization of these blends at different blend ratios were firstly investigated as discussed in Chapter 2.

In contrast to PPC, the biodegradability of PEC is much superior as successfully described earlier by Kawaguchi *et al.* [269]. Therefore, the incorporation of PEC to PLA can possibly control the degradation rate of PLA. The mechanical and degradation properties based on the alkaline solution were further investigated and characterised for the first time as in Chapter 3.

Due to the thermal stability shown by the PEC/PLA blends (as casted), transformation on the crystallization of PLA and phases morphology for PEC/PLA blends (as casted) was carried out introducing the melt quenching technique. The shift in the PEC/PLA structure and morphology of the melt-quench phase may result in distinct heat and mechanical characteristics. Further assessment on the impact of the melt-quench method on the structural and physicochemical characteristics of PEC/PLA blends has therefore been discussed in detail as in Chapter 4.

Based on each scope of study as discussed in Chapter 2, Chapter 3 and Chapter 4, summary of this research work is concluded comprehensively in the Conclusion part. The approaches of this present work are simplified and presented in the Fig. 1-21 accordingly.

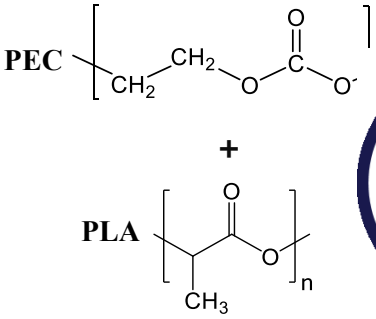
Existing Preparation of PEC/PLA blend as reported by Mi *et al.* [271]

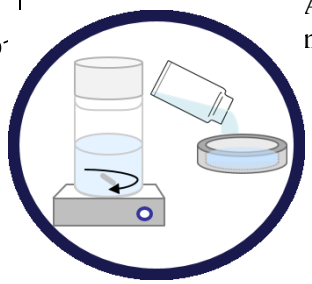


- Single screw extruder
- High thermal processing
- Stretching influenced PLA crystal formation

Our approaches

Solution cast preparation





Advantages of solution casting method;

- Low temperature processing (room temperature)
- Simple techniques
- Thin film

PEC/PLA blend (as casted)

[Chapter 2]

Characterized unique physicochemical, morphological and structural properties influenced by; miscibility, crystallinity of PLA and interfacial adhesion between PEC/PLA phases.

[Chapter 3]

Mechanical properties and hydrolysis in alkaline solution of PEC/PLA blend are examined microscopic and macroscopically.

[Chapter 4]

PEC/PLA blend (as casted)

- Thermal stable
- High crystallinity

Introduce to additional melt-quench technique

Modification by melt-quench technique to improve PEC/PLA blends film uniformity. Effect of the melt-quench process on the structural and physicochemical properties of PEC/PLA blends are characterized.

Fig. 1-21 Present research work approaches.

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Chapter 2

Preparation and characterization of poly(ethylene carbonate)/ poly(lactic acid) blends

2-1 Introduction

Poly(ethylene carbonate) (PEC) is a biodegradable polymer that is currently known as a new polymeric material. Inoue *et al.* in 1969 [1] have synthesised PEC where carbon dioxide (CO_2) can be produced through copolymerisation by reacting with epoxides. Therefore, PEC's broad development has been linked to economic problems and probable potential shortages of oil assets. PEC has been previously used as an ion-conducting material for strong electrolytes [2–9] and a layer impermeable to oxygen [10] in researches, and has been found to be useable in multiple applications including pharmaceutical and drug coating [11–14]. These applications take advantage of its excellent mixture of features relative to other materials; crystallinity deficiency, lightness, transparency, easy handling and colour-compatibility [15]. PEC could also be a tool to reduce CO_2 in the atmosphere as an alternate technique to capture carbon. Due to its small glass transition temperature (T_g), PEC unfortunately uses a rubber-like shape with a poor heat strength, which make it less appropriate.

Separately, due to its low strength and impact of brittleness [16–18], poly(lactic acid) (PLA) has been altered in a number of ways [19–21] such as through copolymerization and plasticization. Alternatively, polymer blend can be used to modify the features and efficiency of original polymers such as PEC and PLA in a more-cost effective and easier way. PLA blend studies have been successful from the perspective of sustainability, but certain blends posed miscibility challenges in stage separation with the introduction of biological-based/biodegradable polymers poly(3-hydroxybutyrate) [22,23], poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] [24], poly(butylene succinate) [25], poly(ε-caprolactone) [26–30] and polycarbonate [31].

According to equilibrium thermodynamics, the miscibility of two polymers is ascertained once the blending free energy of the Gibb is reduced, which results in a standardised single phase item with ordinary characteristics obtained from the mixable two materials. The majority of the blend polymers for all purposes instead, are immiscible and the presence of interphase and interfacial links between polymer parts assume a remarkable work in the characteristics of the mixing structure. As an indication of the

presence autonomous phases, the glass transition temperature, T_g for each element occurs individually. For this reason, the ultimate features of the melting might be soft in incomplete miscible blend owing to elevated interfacial tension with each polymer showing its own T_g [32] when two polymers are not consistent. Nonetheless, if these two polymers are more aligned or known as partial miscible polymers in some studies, interfacial adhesion will increase, thus reducing the interfacial tension. Thus, the T_g estimates are closer to each other in such cases and the final properties of the polymer blending could be more synergistically prominent than those of the constituents [32–35]. Kalogeras and Brostow [36] have showed this situation well as displayed in Fig. 2-1.

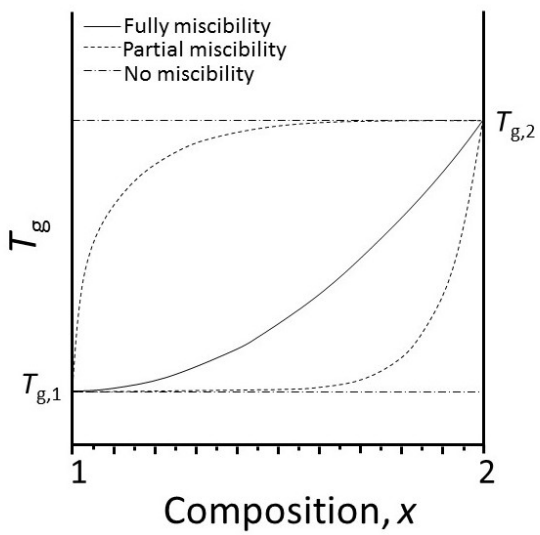


Fig. 2-1 A schematic representation of the dependence of T_g on composition, x in binary polymer blends: —— fully miscible system; – – – compatible system (partial miscible); – · – · – immiscible system [36].

A single glass transition temperature for all blends is distinguished by full miscibility. Two T_g values that represent a compatible system would depend on the composition of both polymers given by x (Fig. 2-1) in the region of upper and lower limits. In contrast, in the case of immiscible polymers, T_g values for pure components do not

change with the composition. The blend miscibility of polymer has been estimated in several models based on the polymer blend's structure as outlined by a few studies such as those by Fox [37], Gordon Taylor [38], Kwei [39] as well as Kalogeras and Brostow [36].

The easiest model design by Fox, as shown by Eq. (2-1) in his previous study, defines a weighted-average connection between T_g and the component's mass fraction.

$$1/T_g = (1\text{-}x_1)/T_{g,1} + x_1/T_{g,2} \qquad \text{Eq. (2-1)}$$

where $T_{g,1}$ and $T_{g,2}$ (in unit Kelvin) are the glass transition temperatures of the pure components with the lower and higher T_g, respectively, and x denotes the mass fraction of the higher T_g component. Significantly, x_2, x_2= 1-x_1, which is the second component in Eq. (2-1), is symmetrical with regards to parts and allows only characteristics of sheer component to be estimated.

Gordon and Taylor (GT) in their study included a parameter known as $k_{G\text{-}T}$ (in Eq. (2-2)) to properly depict the unbalanced contributions of elements in a blend to total T_g in the weighted-average relationship. The test data must be used to evaluate $k_{G\text{-}T}$ [36].

$$T_g = (x_1 T_{g,1} + k_{G\text{-}T}\,(1\text{-}\,x_1)T_{g,2})\ /\ (x_1 + k_{G\text{-}T}\,(1\text{-}\,x_1)) \qquad \text{Eq. (2-2)}$$

Kwei has established the T_g behaviour in several resin mixtures such as polymethylmethacrylate (PMMA) and phenolic resins, which has significantly deviated from the Gordon Taylor model. This variation was caused by the input of hydrogen bonding between parts; to solve this problem, Kwei inserted a second parameter q, as shown in Eq. (2-3), altering the Gordon Taylor mathematical model. The parameter k in Kwei model the same physical denotation as $k_{G\text{-}T}$, whereas q is referred to the effects of interactions between components like the hydrogen bonding on the T_g value.

$$T_g = [(x_1 T_{g,1} + k_{KW}\,(1\text{-}\,x_1)T_{g,2})\ /\ (x_1 + k_{KW}(1\text{-}\,x_1))] + qx_1\,(1\text{-}\,x_1) \qquad \text{Eq. (2-3)}$$

Index 2 is the greater T_g component in all formulas. Kalogeras and Brostow proposed a change to the mathematical model to conform with the difficulty shown in Eq. (2-4) for a more complicated binary systems such as PEO and epoxy resin (ER) blends.

$$T_g = x_1 T_{g,1} + (1- x_1)T_{g,2} + x_1(1- x_1) \text{ x } [a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2 + a_3(2x_1-1)^3] \quad \text{Eq. (2-4)}$$

The amount of a_i parameters representing the laboratory information determines how complex is the scheme for polymer blends and copolymers.

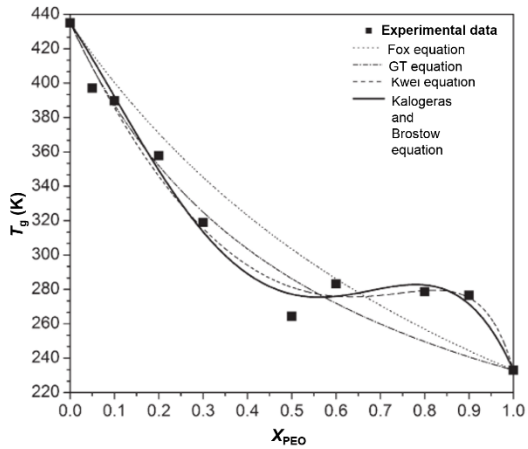


Fig. 2-2 Results for the binary PEO+ER blends as a function of composition. ■ Experimental results; …… Fox equation; – – –Kwei equation (k_{KW}=7.0, q=−514); – · – · – Gordon–Taylor equation ($k_{G\text{-}T}$=0.36); — Kalogeras and Brostow equation (a_0=−227, a_1=284, a_2=316) [36].

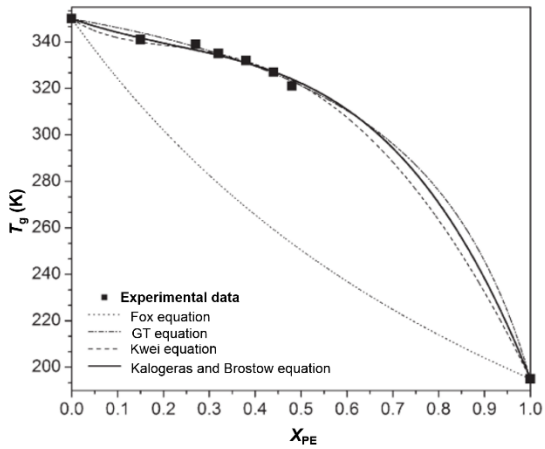


Fig. 2-3 Results for the PVA/PE copolymers as a function of composition. ■ Experimental results; …… Fox equation; – – – Kwei equation (k_{KW} =0.32, q=356); – · – · – Gordon–Taylor equation ($k_{G\text{-}T}$=4.38); — Kalogeras and Brostow equation (a_0=199, a_1=126, a_2=13.2) [36].

Fig. 2-2 and Fig. 2-3 demonstrate the examination of every model fitted to the test esteems for complex binary systems of PEO and ER blends as well as polyvinyl alcohol (PVA)/polyethylene (PE) copolymers [36]. As illustrated in the Fig. 2-2 the mathematical template proposed by Kalogeras and Brostow in 2008 is able to estimate the difficulty

of T_g behaviour for PEO and ER blends. The Fox design may be sufficient for very well-powered miscible systems. The increasing system diversity can no more make the Fox model suitable and alternative methods for measuring the miscibility features of a binary system can be used including the one-parameter model of Gordon Taylor, two-parameter model by Kwei as well as the model by Kalogeras and Brostow as presented in Fig. 2-3. These models have been used extensively for the evaluation of polymer miscibility as well as in relevant studies as outlined in Table 2-1 for PLA copolymers and blend systems.

Table 2-1 Summary of miscibility estimation PLA copolymer and blend system.

Copolymer and blend system	Estimation Model	Ref.
Partial miscible PLA/polycarbonate (PC) blend	Gordon Taylor ($k_{G\text{-}T}$=0.85) Kwei (k_{KW}~0, q=-180) Kalogeras and Brostow (a_0=17, a_1=-258.3, a_2=370)	[40]
High miscibility PLA/PMMA blend	Gordon Taylor ($k_{G\text{-}T}$=0.4)	[41]
High miscibility PLA/poly(butylene succinate) copolymer	Fox $T_{gexp} \sim T_{g\text{-}Fox}$	[42]
High miscibility PLLA/PDLA blend	Fox $T_{gexp} \sim T_{g\text{-}Fox}$	[43]
High miscibility PLA/polyvinyl acetate (PVA) blend	Fox $T_{gexp} \sim T_{g\text{-}Fox}$	[44]
Partial miscible PLA/acrylic rubber (ACM) blend	Gordon Taylor ($k_{G\text{-}T}$=0.5)	[45]
High miscibility PLA/soy protein blend	Fox $T_{gexp} \sim T_{g\text{-}Fox}$	[46]
Partial miscible PLA/poly(hydroxyl ester ether) blend	Gordon Taylor ($k_{G\text{-}T}$=4.46) Kwei (k_{KW}~2.63, q=-11.76)	[47]

Mi *et al.* proposed in 2016 that an environmentally friendly packaging film could be designed using the PLA blends with PEC using melt extrusion, accompanied by a uniaxial orientation with distinct proportions to enhance the PLA properties [48]. The inclusion of 10 mol% PEC has been shown to increase PLA flexibility. Due to the poor thermal stability of PCE during the melt blending, an elevated processing temperature may restrict possible blends.

Thus, this current research examines a film-casting alternative technique and the optimum solution including solvent type and solution concentration. No scientific evidence of PEC/PLA blend characteristics using a straightforward solution casting technique or its impact on physicochemical characteristics of items has been mentioned before. The current research examines the production of PEC/PLA blends by wet process with distinct PEC and PLA mixing proportions and assesses for the first time, their physicochemical, miscibility characteristics and morphology.

2-2 Experimental Procedure

2-2-1 Materials

A poly(L-lactic) acid (PLA, M_w=57,000) of commercial grade was utilised in this study. Initially, the PLA was dried for 5 hours at 60 °C in a vacuum dryer to eliminate any moisture. Poly(ethylene carbonate) (PEC QPAC ®25, M_w=131,000) was bought from Empower Materials, USA. Gel permeation chromatography readings for PEC and PLA were produced using a two-column TOSOH ECOSEC HLC8320 scheme (TSK liquid GMHHR-H, TOSOH Co). Calibration using polystyrene standards was performed using HPLC grade chloroform as an eluent with a flow rate of 1.0 ml/min. Prior to being dried in a vacuum dryer for 24 h at 60 ºC, the PEC was dissolved in acetonitrile and washed with extra methanol. Before preparing the mixtures, both polymers were held in a glove box.

2-2-2 Sample Preparation

The Fig. 2-4 illustrates PEC and PLA where the default weights were dissolved in chloroform and stirred for 24 hours at room temperature. To prevent surplus solvent, the solution of PEC/PLA was then casted on a Teflon petri dish and put in a vacuum evaporator. The resulting film sample was dried for 24 hours at 60 °C in a vacuum dryer. PEC/PLA blends were selected for composition at PEC contents of 0, 10, 30, 70, 90 and 100 wt%.

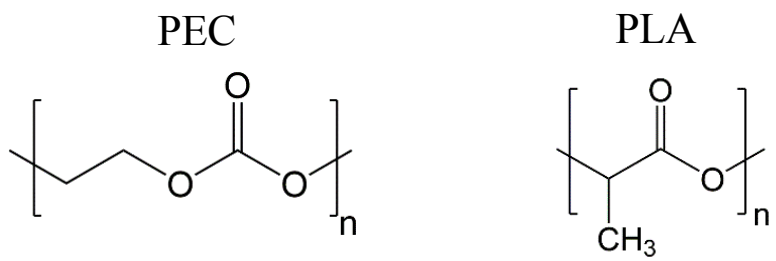


Fig. 2-4 Structure of poly(ethylene carbonate) (PEC) and poly(lactic acid) (PLA).

2-2-3 Characterization

A polarised optical microscope (Olympus DP12 BX51) was used to produce morphological measurements on blend samples, whereas the size of PLA spherulites was determined at room temperature. All specimens' thermal characteristics were evaluated by Hitachi High Tec Co. system with dry N2, DSC7020 system. In the interval of 3-6 mg, a sample was measured and secured in an aluminium pan. It was then heated to 100 ºC at the speed of 10 ºC/min under the DSC procedure. Then, cooling process took place at -40 ºC with a speed of 10 ºC/min; from -40 ºC up to 200 ºC, a second heating was carried out again at 10 ºC/min. To determine T_{g1} for the blends, the first heating procedure was employed. As the maximum values of the melting peak, the melting temperatures of PEC, PLA and all PEC and PLA mixtures were measured. Eq. (2-5) was used to compute the crystallinity of PLA (X_c), which is normalised by the PLA weight portion (X_{PLA}),

$$X_c(\%) = \frac{\Delta H_m}{\Delta H^0{}_m} x \frac{100}{X_{PLA}} \qquad \text{Eq. (2-5)}$$

where ΔH_m (J/g) is the melting enthalpy of PLA, and $\Delta H^0{}_m$ is the theoretical melting enthalpy of a 100 % crystalline PLA, which is reportedly 107 J/g [49] considering the presence of α'- or α- crystal modifications or the influence of D-lactic acid units in the analysed poly(lactic acid). The melt-crystallization temperature of PLA in PEC/PLA blends was then calculated with another sample, that was first heated to 200 ºC at 10 ºC/min, then cooling at a rate of 5 ºC/min from 200 ºC to 40 ºC. XRD was measured using a Cu-K_α source at room temperature by Rigaku Smartlab. The scanning speed was 4º/min from 5 to 60º in range. Meanwhile, the current was 200 mA while the voltage was 40 kV. The thermogravimetric analyser (TGA, Hitachi High Tech) for PEC/PLA mixtures was used to measure their degradation temperatures. Samples were 6 mg in weight and heated with rate of 10 ºC/min from 30 ºC to 600 ºC. FT-IR measurements were performed for PEC, PLA, and all blend films using a type FT-IR JASCO FT/IR4100 with 32 scans at 4 cm^{-1} resolution under room temperature for each sample. measurements were taken ranging from 4000 cm^{-1} and 400 cm^{-1}.

2-3 Results and Discussion

2-3-1 Sample appearances (as cast)

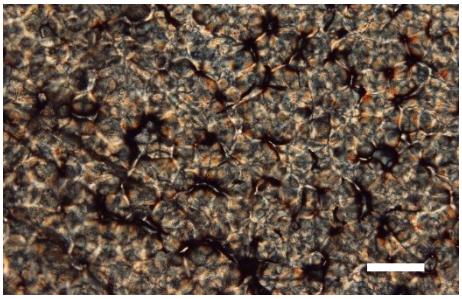
Fig. 2-5 depicts the pictures of the film (as cast) for blends of PEC/PLA. The elevated level of transparency of the PEC in relation to PLA was evident. With increasing PLA content in the blends, visibility of PEC was gradually reduced. PEC is amorphous while PLA is a semi-crystalline polymer; the principal reason for this decline was the crystallization of PLA in the amorphous phase.

Fig. 2-5 Images of PEC/PLA blends (as cast).

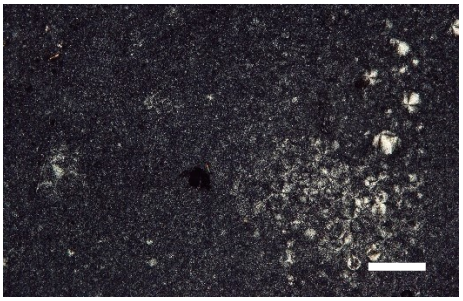
2-3-2 Polarizing Optical Microscope Measurements

PLA spherulites were observed in the blend samples utilising POM at room temperature. Besides, spherulites' formation was noted in the Fig. 2-6. Blends with a bar scale of 60 μm in length were seen in PLA, which include PEC70/PLA30 and PEC30/PLA70. According to an earlier study, the crystallization rate of PLA [50] is influenced by structural variables including molecular chain flexibility, molecular weight and the design of the branched-chain and mixing of polymers. An extremely organised spherulite structure was observed [51] in the event of the neat PLA as in Fig. 2-6 (a). In contrast, PLA spherulites with no-sphere shape were found as in Fig. 2-6 (b), since they are found in the amorphous phase that is rich with PEC.

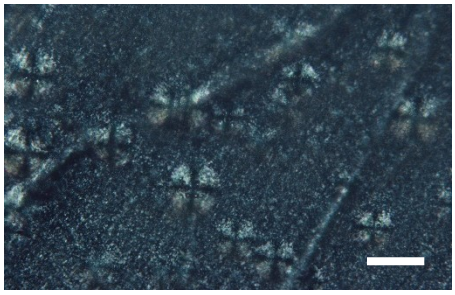
Transparent PLA spherulites with typical 30 μm spherical forms were seen in the blends of PEC30/PLA70 as demonstrated in Fig. 2-6 (c).



(a) PLA spherulites



(b) PEC70/PLA30



(c) PEC30/PLA70

Fig. 2-6 Observation of POM for (a) PLA, (b) PEC70/PLA30 blend and (c) PEC30/PLA70 blend. (Scale bar 60μm)

These findings are in accordance with the principle that PEC70/PLA30 began to melt at a lower temperature than PEC30/PLA70 as there were smaller amount of spherulites in the blend that completely formed as spheres. In the PEC-rich PEC70/PLA30 blend, the existence of non-spherical PLA spherulites shows that the flexibility of molecular chain by the amorphous stage affects the crystallization of PLA during PEC/PLA blend preparation. PLA's stereochemistry and thermal history are responsible for its crystallization behaviour [52].

2-3-3 Differential Scanning Calorimetry Measurements

PEC, PLA and PEC/PLA blends were evaluated in this study in terms of their thermal characteristics. This was to specify the glass transition temperature, PLA's degree of crystallinity, as well as the melting temperature and temperature of melt crystallization for blend films produced by the solution film-casting technique. The observed value of T_g is generally clarified by polymer's molecular chain mobility over T_g and significantly decreased chain mobility below T_g [53–56]. More precisely, T_g is defined by several variables, including chain stiffness (or flexibility), molecular symmetry, the existence of a side group, molecular weight, chain linkage, cross-linking and interaction between molecules [53–56]. Fig. 2-7 indicates the DCS curves of the second heating for PEC, PLA and PEC/PLA blends. Meanwhile, Table 2-2 provides the respective information regarding DSC.

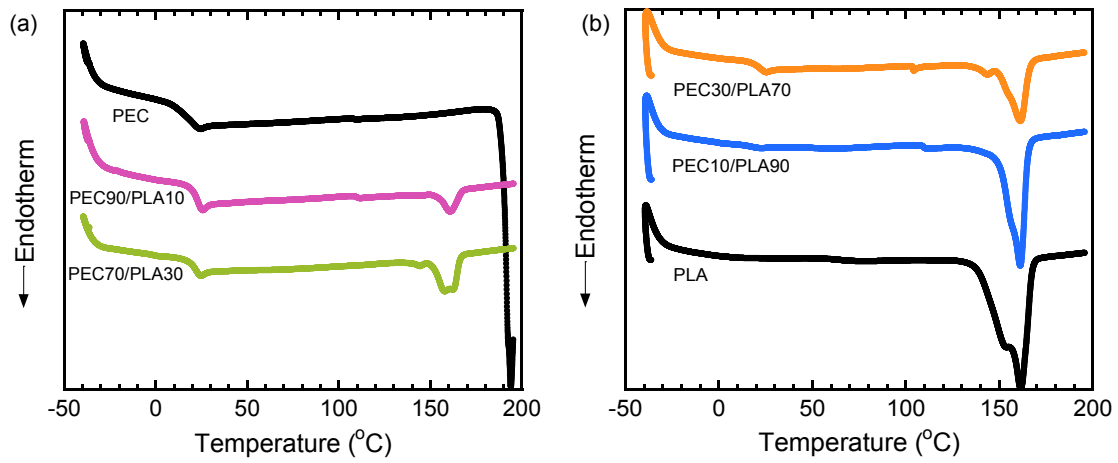


Fig. 2-7 DSC curves of (a) PEC-rich blends and (b) PLA-rich blends at the second heating.

In the Table 2-2, T_{g1} and T_{g2} tightly matched with those of PEC and PLA since the numbers were equal to the region of T_g for neat PEC and PLA. In the results of the first PEC/PLA blend heating from 30 °C to 100 °C, the value of T_{g1} for PEC/PLA blend initially shifted from neat PLA value to lower temperatures of more than 10 °C,

which was initially at 66 °C. These findings indicate that preparing PEC/PLA blends via the film casting solution would increase partly mixed PEC/PLA blends. As shown in Fig. 2-8 (a), T_{g1} was declined in PEC/PLA blends between 44 °C and 56 °C, which might be may be partly due to plasticization effect following the intermolecular interactions between PEC and PLA, since the carbonyl oxygens of PEC and PLA are the complexation sites similar to the C=O···O=C or C=O···O–C interactions for PPC/PLA blends [57]. The prevailing impact on T_g for the polymer is the intermolecular forces, which negate the influence on the reduced chain mobility by the backbone of aromatic polymer [56].

Table 2-2 DSC data of PEC, PLA and PEC/PLA blends.

Sample	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	T_{mc} (°C)	ΔH_m (J/g)	X_c (%)
PEC	-	11	-	-	-	-
PEC90/PLA10	54	18	161	107	5	47
PEC70/PLA30	56	17	158	109	10	31
PEC30/PLA70	56	17	161	98	19	25
PEC10/PLA90	44	13	161	98	40	42
PLA	66	-	161	99	56	52

The results of the second heating show that the T_{g2} corresponding to the PEC was increased from 11 °C to 18 °C in the PEC90/PLA10 blend as shown in Fig. 2-8 (b), which further confirmed the characteristics of the partly miscible PEC/PLA blends. T_{g2} value of the neat PEC was seen slightly lower than that of other blends. On the basis of the PLA (X_{PLA}) crystallinity computed by Eq. (2-5), the high crystallinity of the PLA in PEC amorphous phase for PEC90/PLA10 and PEC70/PLA30 blends could have decreased the amorphous PEC's chain mobility in the PEC-rich blends as well as significantly increased the value of T_{g2} for blends as displayed in Table 2-2. The alterations in PLA's crystallinity from 52% to 25%-47% in the PEC/PLA blends

were attributed, as in the PEC30/PLA70 and PEC10/PLA90 blends, to not only the effects of flexible PEC inserted into the blends, but also the high ratio of PLA. Higher PLA ratios offer more crystallinity in PEC/PLA blends. The 90 wt% PEC/PLA blend provides more crystallinity compared to that of 70 wt% PLA.

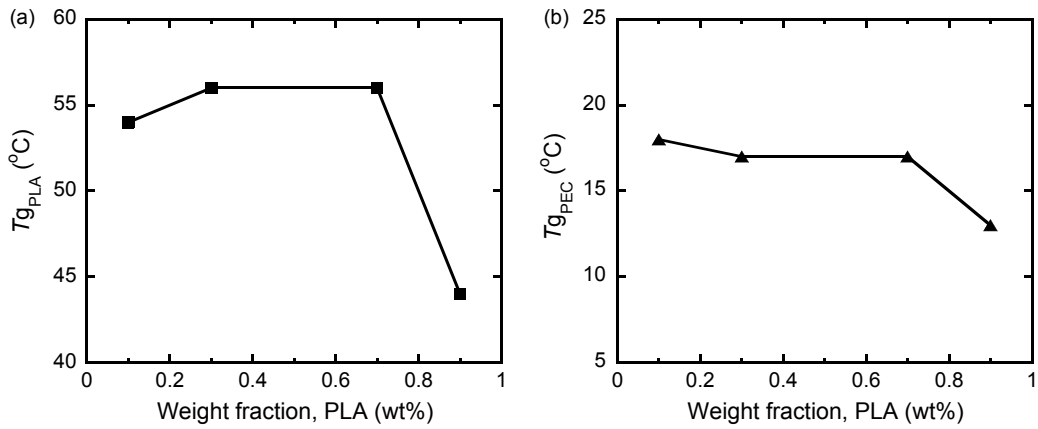


Fig. 2-8 Changes of T_{gPLA} (a) and T_{gPEC} (b) as a function of weight fraction of PLA for the PEC/PLA blends.

Distribution T_g of PEC and PLA for PEC/PLA blends are shown in Fig. 2-9, in which all T_g values present in the partial miscible boundaries comparable to the one suggested by Kalogeras and Brostow as shown in Fig. 2-1. The miscibility of PEC/PLA blends was evaluated using Fox, Gardon Taylor, Kwei and Kalogeras and Brostow models as given by the Eq. (2-1), Eq. (2-2), Eq. (2-3) and Eq. (2-4). Experimental data T_g for PEC and PLA are best fitted by Kwei equation using Eq. (2-3) with k_W=50, q=-45 and k_W=0.012, q=18 for upper and below boundaries, respectively. These results support that PEC/PLA blends are compatible and show partial miscible characteristic particularly at the amorphous phase for all compositions.

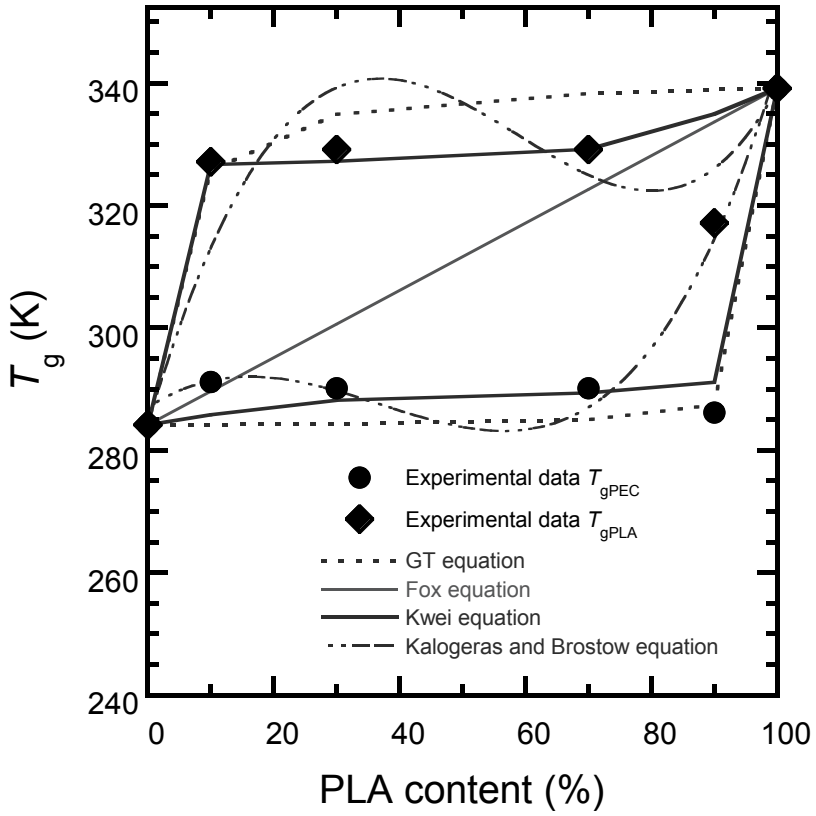


Fig. 2-9 Results for PEC/PLA blends as a function of composition. ● Experimental data T_{gPEC}; ◆ Experimental data T_{gPLA}; - - - - Gordon–Taylor equation ($k_{G\text{-}T}$=28 and 0.007); — Fox equation; ━ Kwei equation (k_W=50, q=-45 and k_W=0.012, q=18); Kalogeras and Brostow equation (a_0=0.10/0.11, a_1=0.18/0.11, a_2=-0.08/0.10, a_3=-0.18/-0.11, a_4=0.95/0.5 and a_5=-0.03/-0.3).

As can be seen in Fig. 2-7, with the aid of PEC, the melting temperature of PLA (T_m) was not altered substantially. The reduction in the first melting temperature of 110 °C in PLA-rich blends indicates that, until the ultimate PLA crystals melt, nearly 161 °C final melting temperature was observed for several blends [58]. During the cooling process for all films, a single exothermic peak was noted as shown in Fig. 2-10. The melt-crystallization of PLA components is ascribed to this finding as PEC is a completely amorphous structure. PEC has risen the frequency of PLA crystallization as shown in Table 2-2 during the melt-crystallization process.

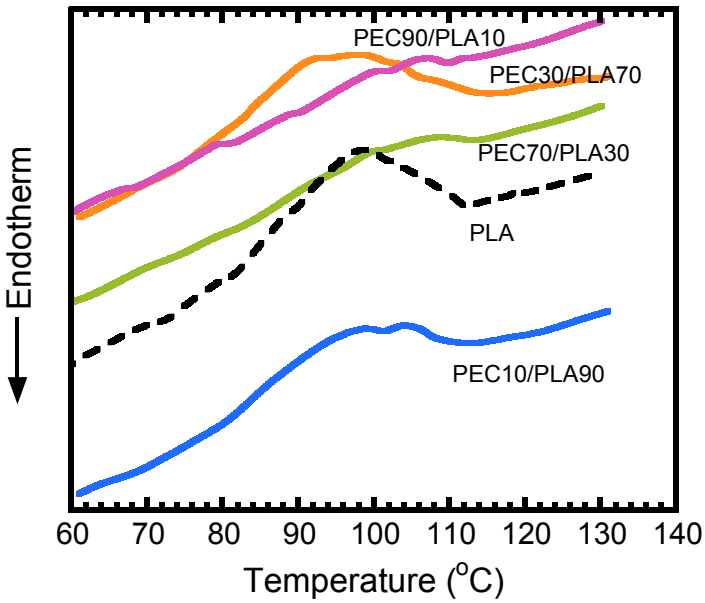


Fig. 2-10 Melt crystallization temperature of PEC/PLA blends upon cooling cycle from 200 °C to -40 °C.

T_{mc} values were 109 °C and 107 °C in PEC-rich blends of PEC90/PLA10 and PEC70/PLA30, which are greater compared to those in PLA-rich blends and neat PLA. Indeed, with reduced PEC concentration, the melt-crystallization moved to a reduced temperature. Melt crystallization temperature (T_{mc}) value is an indirect signal that indicates the PLA's crystallization rate and crystallinity, while a lower T_{mc} always corresponds to the lower crystallization rate and crystallinity [59]. This is owing to the increased PEC/PLA crystallinity compared to PLA-rich blends including PEC90/PLA10 and PEC70/PLA10.

2-3-4 Crystal structures

PLA crystals were confirmed using the XRD for the PEC/PLA blend, which resulted from the crystallization temperature (T_c) when a different crystal structure of PLA was formed in blends. At T_c values below 120 °C [60], a kinetically competitive α'

form of PLA appeared. PEC was determined by XRD in terms of its effects on the development of PLA crystals in PEC/PLA blend. The XRD features of PLA, PEC and PEC/PLA blends is shown in Fig. 2-11. At 16.76°, the highest peak can be seen, which is in line with the highest peaks in the profiles of PLA recorded by Kawai *et al.* [61] and Luo *et al.* [62]. These peaks are ascribed to the reflection by α' and α forms corresponding to (110)/(200) planes. Further reflection caused by (113)/(230) planes in the PEC10/PLA90, PEC30/PLA70 and PEC70/PLA30 blends, which is similar to the α' and the α forms' reflection, can be seen. Evidently, crystal formation was rather weak or absent particularly for blends rich in PEC in the PEC/PLA blends with reflections including (211) at 22.30° [49,63] and (011) located at 14.9° [64–66] that matched the features of the α. These results are supported with DSC observations at a melt-crystallization temperature under 120 °C for all blends as displayed in Fig. 2-10. The α-crystals produced at temperatures below 120 °C is substituted, according to Pan *et al.* [67] and Androsch *et al.* [68] by pseudo-hexagonal α' crystal. The α' form is thus ascribed to PLA crystals in the PEC/PLA blend.

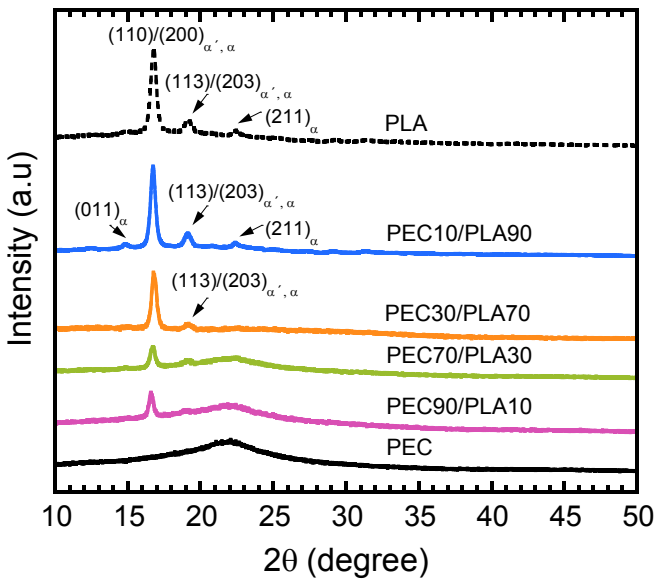


Fig. 2-11 X-ray diffraction patterns of PLA, PEC and PEC/PLA blends.

2-3-5 Thermogravimetric Analysis Measurements

Figs. 2-12 (a) and 2-12 (b) present the thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves for PEC, PLA and PEC/PLA blends.

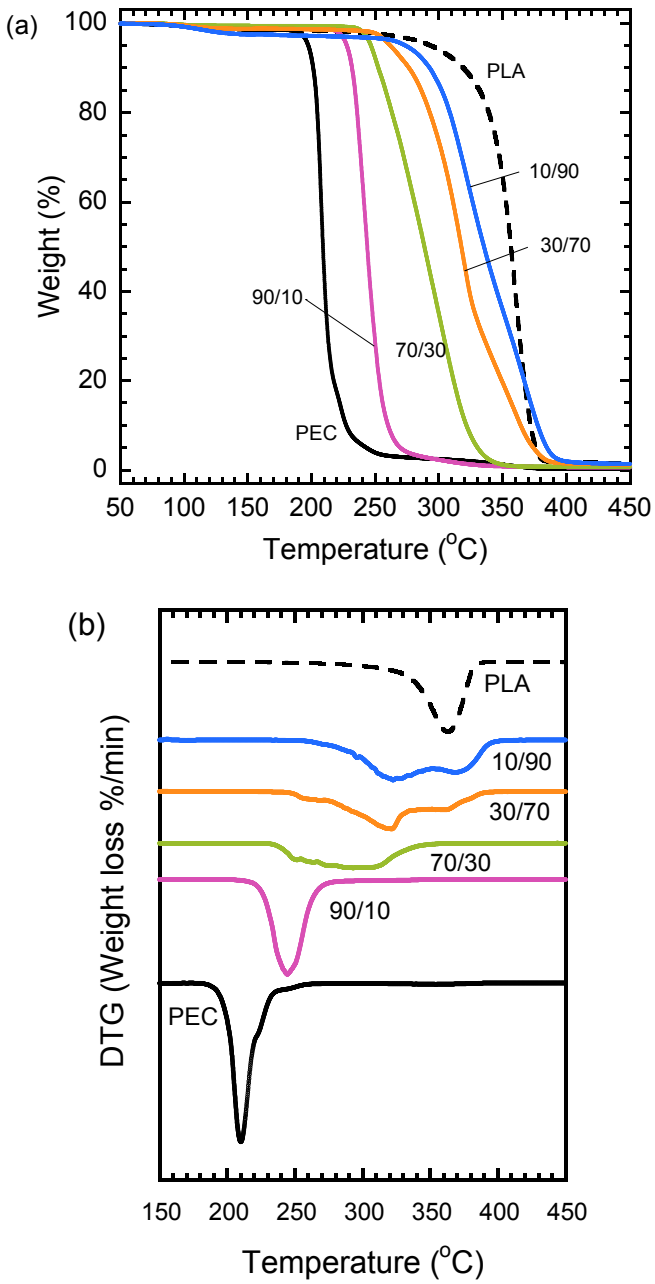


Fig. 2-12 (a) TG and (b) differential TG (DTG) curves of PEC, PLA and PEC/PLA blends.

Table 2-3 sets out the thermogravimetric data for all samples, including the temperature at 5 wt% weight loss (T_{d5}) from TGA and the maximum decomposition temperature (T_{max}) from DTG. PLA and PEC thermal degradation happened at 210 ºC and 364 ºC where PEC has a small T_{d5} compared to that of PLA. The PEC has already been degraded at 200 ºC for the respective cyclic carbonate, according to an earlier report [69]; subsequently, it was demonstrated that the degradation of PEC was caused by the original unzipping of the chains and is continued by chain scission at a greater temperature [70]. As observed in Fig. 2-12 (a), however, by adding just 10 wt% of PLA to the PEC, T_{d5} was increased by over 30 °C above that of the neat PEC.

The addition of PLA to PPC has also received similar results to that of previous study [57]. In addition, by adding PLA, the thermal stability of PEC was enhanced. This may be consistent with the structural illustration shown in Fig. 2-17 (a) and Fig. 2-17 (b) that reduced chain unzipping, slowed down the degradation of PEC and improved thermal degradation temperature for PEC-rich blends by the interaction between PLA and PEC in ester and carbonate units. PLA is subjected to a single-step degradation method according to past studies with complete decomposition at 400 ºC [71–73]. PLA is decreased by random chain scission or special chain-end split, which leads to a gradually decreased molecular weight [74]. However, thermal PLA degradation with the addition of 10 wt% PEC occurred in PEC/PLA blends at a reduced temperature of 323 °C rather than 364 °C since PEC has lower thermal stability than PLA. Thermal degradation of PLA may be facilitated by the graded PEC in the PEC/PLA blends.

Table 2-3 defines the decomposition temperature (T_{max}), where the temperature gave the maximum weight loss rate to PEC, PLA and PEC/PLA blends. The degradation of neat PEC and PLA occurred in a single step, starting at 190 ºC for PEC and 270 ºC for PLA through a final temperature of 260 ºC and 385 ºC with a DTG peak at 210 ºC and 364 ºC, respectively. In PEC/PLA blend, the T_{max} values of PEC and PLA were measured between the PEC and PLA values. In Fig. 2-12 (b), two neat polymers and blend of PEC90/PLA10 were observed in a single step decomposition; however, two-step decomposition of PLA-rich mixtures was obviously noted. The first phase is ascribed to PEC and the second to PLA in blends with two phases of degradation. Polycarbonate

(PC)/PLA blends have been found to show two phases of decomposition, which were related first to PLA and subsequently to PC [40]. In comparison to PEC90/PLA10 blend, a wide DTG peak existed for PEC70/PLA30 blend, which corresponds to the propagation of the reaction [75]. In PEC90/PLA blend, due to the elevated PEC concentration in the blend, a powerful sharp peak was found at 244 ^{o}C, which could be due to a rapid degradation response.

In contrast to PEC 70/30 blend, which was displayed in the following Fig. 2-12 (b), the reduction in PEC concentration with the addition of 30 wt% PLA, which initially has greater thermal degradation, influenced the degradation of the blend, which is slower and has an improved thermal degradation temperature of 301 ^{o}C.

Table 2-3 Thermogravimetric data of PEC, PLA and PEC/PLA blends.

Sample	T_{d5} (^{o}C)	T_{max} (^{o}C) of PEC	T_{max} (^{o}C) of PLA
PLA	294	-	364
PEC10/PLA90	274	323	373
PEC30/PLA70	262	322	363
PEC70/PLA30	246	252	301
PEC90/PLA10	229	244	244
PEC	198	210	-

The overall phase diagram of PEC/PLA blend, as it was established using thermal analysis of DSC and TG-DTA, is depicted in Fig. 2-13. Evidently, for pure PEC, undergo only single phase transition, a glass transition (T_g) and for pure PLA, two phases transitions that include glass transition (T_g) and melting transitions (T_m). Whereas, for the

PEC/PLA blends, in all range of compositions, show three phase transitions: two glass transitions as shown by (D) and (E) and single melting transitions as shown by (B). Raising the temperature further will eventually lead to thermal degradation of PEC/PLA blends with 5 wt% weight loss (T_{d5}) as shown by curve (A). Lowering temperature $T<T_{mPLA}$ and reaching melt crystallization as shown by (C), will cause the PLA component to melt crystallize and may be segregate from the amorphous PEC/PLA mixtures. In this temperature regime the PEC/PLA blends amorphous/crystalline, leading to two phase morphologies in which PLA crystalline phase co-exist with a mixed amorphous PLA and PEC phases.

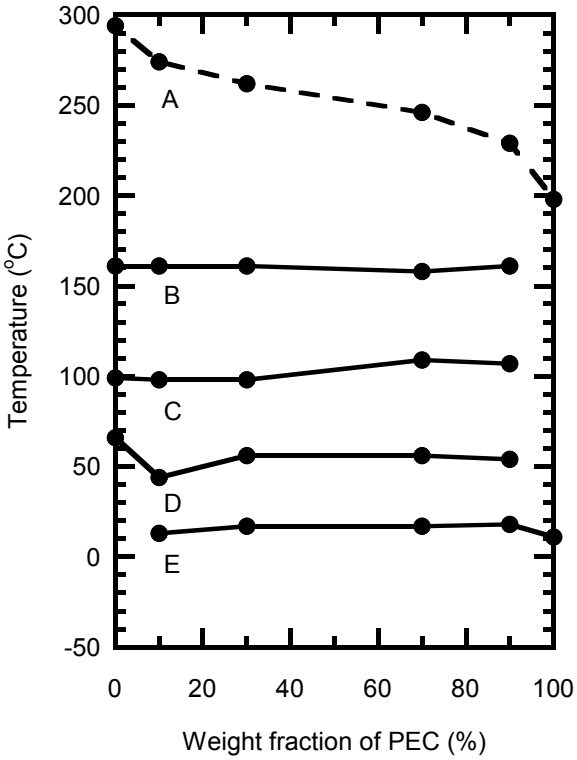
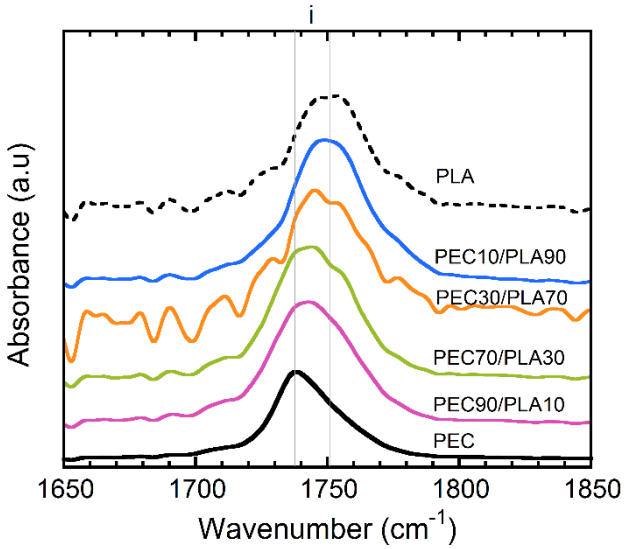


Fig. 2-13 Phase diagram of PEC/PLA blends presenting the temperature at 5 wt% weight loss (T_{d5}) curve (A), the melting temperatures of PLA (B), the melting crystallization temperatures of PLA (C), and two glass transition temperatures (D) and (E).

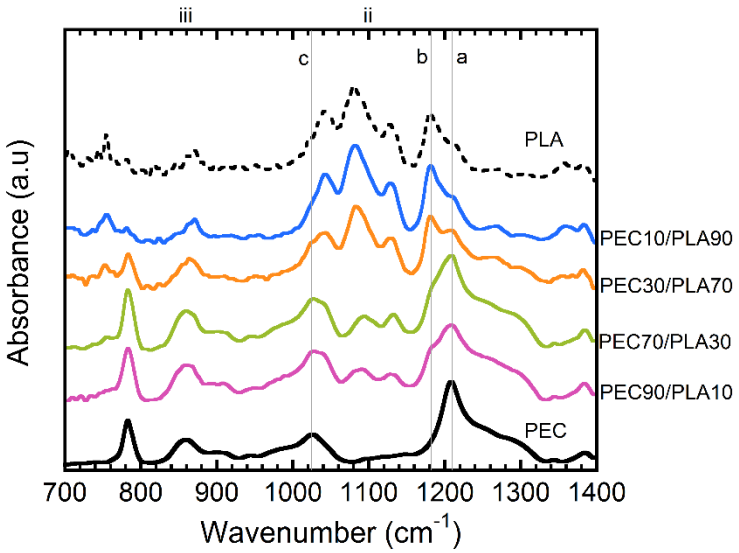
2-3-6 Fourier Transform Infrared Spectroscopy Measurements

To learn more about the interaction between PEC and PLA in the blend samples, FT-IR analysis was carried out. Fig. 2-14 (a) and (b) display the results obtained from the analysis. The values of carbonyl (–C=O), –O–C–O, –C–O– in–CH–O–, –C–O– in–CH_2–O– and –C–O– in –O–C=O allocated at each peak with different wave numbers are shown in Table 2-4. The extended vibrational mode of –C=O group ($\upsilon_{C=O}$) in the region of 1700-1800 cm^{-1} was obviously seen as shown in Fig. 2-14 (a). At 1738 cm^{-1} [57] and 1751 cm^{-1}, respectively, the $\upsilon_{C=O}$ peaks were observed for neat PEC and PLA [41,57]. Meanwhile, the peak between the two $\upsilon_{C=O}$ carbonyl peaks of neat PEC and PLA as demonstrated in region (i) in Fig. 2-14 (a) was followed in PEC/PLA blends. This is a powerful indication that these polymers have a significant interaction. Lots of studies in PPC blends with PLA on poly(propylene carbonate) resulted in similar peak shifts of $\upsilon_{C=O}$ [57,76] in carbonyl absorption. This change may result from the intermolecular forces that are based upon the Lewis acid-base nature between the oppositely charged ends (δ^+, δ^-) of carbonyl groups in PLA and PEC. For PCL/polyvinylphenol blends, the formation of hydrogen bonds resulted in a change of carbonyl peak as already indicated [77].

The interaction of the partial charges of –O–C–O–, –C–O– in –CH–O–, –C–O– in –CH_2–O–, and –C–O– in –O–C=O recorded in PEC/PLA blend could be considered responsible for the modifications in the spectrum of FT-IR shown in Fig. 2-14 (b). The vibration mode of the –O–C–O–group ($\upsilon_{-O-C-O-}$) in PPC has been reported to be 1223 cm^{-1} according to prior studies [57,78]. The absorbance peak at 1207 cm^{-1} as illustrated in Fig. 2-14 (b) could be equivalent to the O–C–O group in PEC. Increased concentration of PLA in PEC/PLA blend did not cause huge changes in the absorption of the PEC's –O–C–O–peak (as indicated on Line a); no interaction between δ^+ carbon in the –O–C–O–of PEC and δ^- oxygen in the –C=O group of PLA has obviously occurred. This observation is also aligned with the unchanged stretching vibration absorbing peak for –C–O– in –O–C=O of PEC in the PEC/PLA blend as stated in region (iii). It was difficult to reconcile the interaction between –O–C–O–in PEC and –C–O– in –CH–O– in PLA (Line b peak) with the undisturbed peak of Line b in PEC/PLA blend.



(a) Carbonyl groups



(b) Ether groups

Fig. 2-14 FT-IR spectra of (a) –C=O and (b) –O–C–O–, –C–O– in –CH–O–, –C–O– in –CH_2–O– and –C–O– in –O–C=O for PEC, PLA and PEC/PLA blends.

However, changes of the peak –C–O–in –O–C=O of PLA were situated in region (ii) where apparent peaks were seen at 1129 cm^{-1}, 1082 cm^{-1} and 1044 cm^{-1}, which may be

due to the partial charges between –C–O–in –O–C=O of PLA and the PEC's –C=O carbonyl group. In region (ii), for example, the –C–O–peak in –O–C=O of PLAs was 1082 cm^{-1} with increased PEC concentrations in the blend, which has slightly changed towards a greater wavenumber. The interaction between partial carbon charges in δ^+ on the carbon in –C–O–in –O–C=O of PLA, and δ^- on oxygen of the carbonyl group –C=O group of PEC in the PEC/PLA blend are illustrated in Fig. 2-17 (a).

The changes in vibrational peaks in region (ii) may also correlate to the interaction between –C–O–in –O–C=O of PLA and –C–O–in –CH_2–O–of PEC, as the –C–O–in –CH_2–O–vibration in PEC changed moderately to less wavenumber with increased PLA concentration in the blends of the PEC/PLA originally stretching to 1023 cm^{-1} (displayed in Line c) and also the peak strongly interacts with –C–O–in –O–C=O of PLA at 1044 cm^{-1} in the case for PEC-rich blend as shown by PEC90/PLA10 and PEC70/PLA30 blends. The interaction in Fig. 2-17 (b) can explain the increase in stretching vibration frequency of PEC/PLA blend's carbonyl presented in Fig. 2-14 (a).

Table 2-4 Characterization of FT-IR peaks for PEC, PLA and PEC/PLA blends.

Wavenumber (cm^{-1})	–C=O	–O–C–O–	–C–O– in –CH–O–	–C–O– in –CH_2–O–	–C–O– in –O–C=O
PLA	1751	-	1182	-	1129, 1082, 1044
PEC	1738	1207	-	1023	920, 856, 782
PEC/PLA	Region (i)	Line **a**	Line **b**	Line **c**	Region (ii), Region (iii)

To deeply analyse the interaction between PEC and PLA, deconvolution of the individual peaks originates from PEC and PLA were also determined. Fig. 2-15 shows the deconvolution of IR band of the –C=O stretching vibration frequency for (a) PEC and (b) PLA. From Fig. 2-15 (a), the –C=O stretching vibration frequency for PEC deconvolution consisting of three components of free –C=O appear at 1709 cm^{-1}, 1737 cm^{-1} and 1745 cm^{-1} following the intramolecular forces that presents for PEC. While due to crystallization of α and α' for PLA, giving five contributions apparently at about 1710 cm^{-1}, 1725 cm^{-1}, 1742 cm^{-1}, 1756 cm^{-1} and 1775 cm^{-1} (as shown in Fig. 2-15 (b)) with respect to the observation by Meaurio *et al*. [79] on the –C=O stretching band of the α-crystal of poly(L-lactide).

Each of these free –C=O peaks were used to determine the interacting –C=O peak between PEC and PLA for the PEC/PLA blend as shown in Fig. 2-16, after separating the individual free –C=O stretching vibration frequency of PEC and PLA as presented by blue line, from the original peaks. For all PEC/PLA blends, the interaction between PEC and PLA could be further explained by the appearance of new peak positioned between $\upsilon_{C=O}$ peaks of neat PEC and PLA appear at 1738 cm^{-1} and 1751 cm^{-1} except for PEC30/PLA70 blend with the peak appeared slightly higher at 1752 cm^{-1}. The wavenumber of the new peak position for interacting –C=O of PEC/PLA blends also display in the Fig. 2-16.

Based on the microscopically characterization, both PEC and PLA are compatible and not completely miscible. Illustration on the possibly schematic images of the PEC and PLA chains in the blends is shown in Fig. 2-18. The interaction between PEC and PLA may hold the PEC and PLA chains together more firmly, causing less able to move relative to each other, gives small changes in the glass transition temperature for PEC and PLA and increase resistance to thermal degradation as shown earlier.

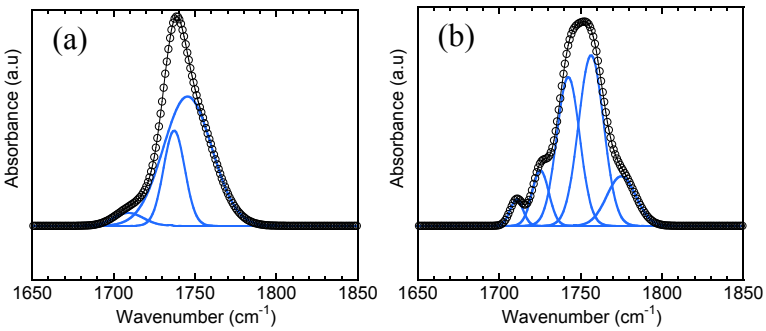


Fig. 2-15 Deconvolution of IR band of the –C=O stretching vibration frequency for (a) PEC and (b) PLA. (Plot: original data; blue: free –C=O; black: total of the peaks).

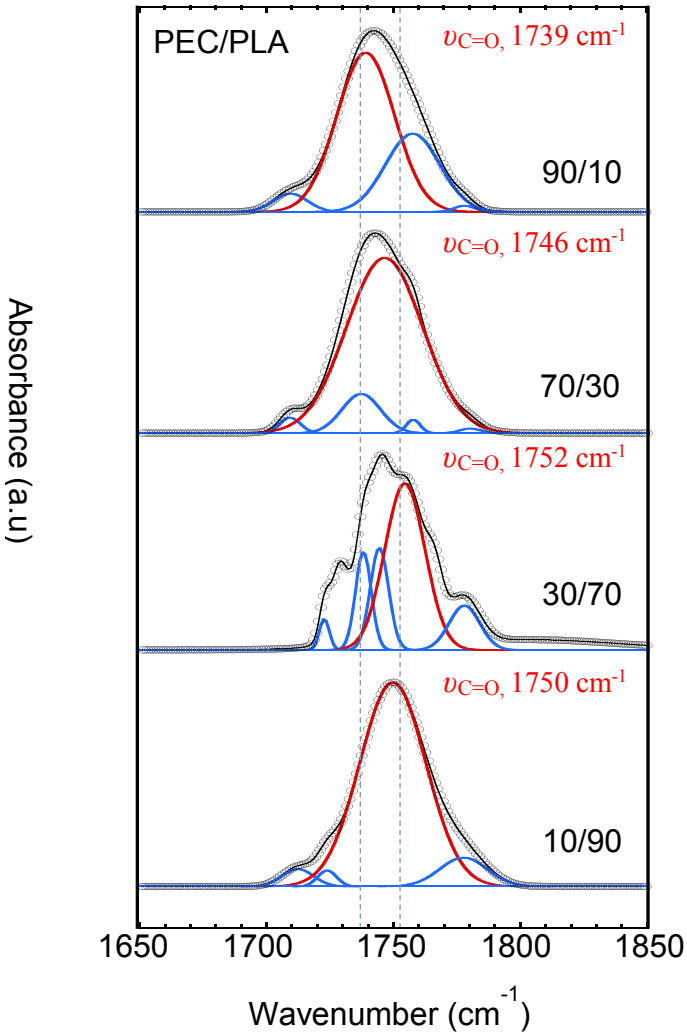


Fig. 2-16 Deconvolution of IR band of the –C=O stretching vibration frequency for PEC/PLA blends. (Plot: original data; red: interacting –C=O; blue: free –C=O; black: total of the peaks).

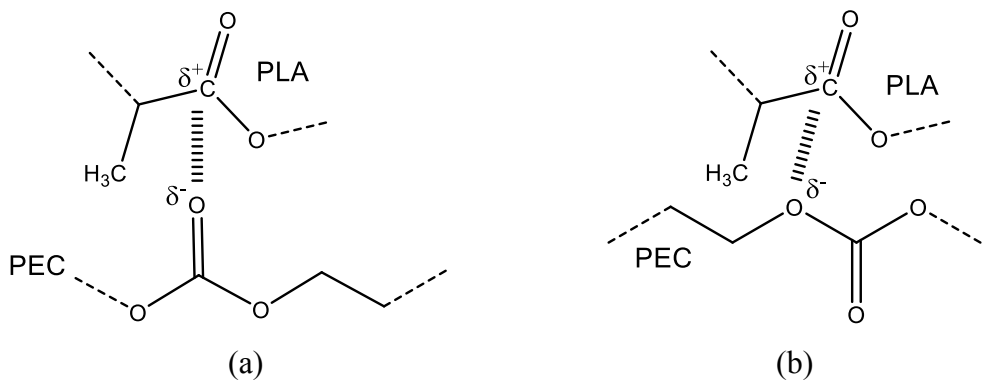


Fig. 2-17 Structural image of preassumed interactions between PEC and PLA (a) –C–O– in –O–C=O of PLA and carbonyl –C=O of PEC and (b) –C–O– in –O–C=O of PLA and –C–O– in –CH_2–O– of PEC.

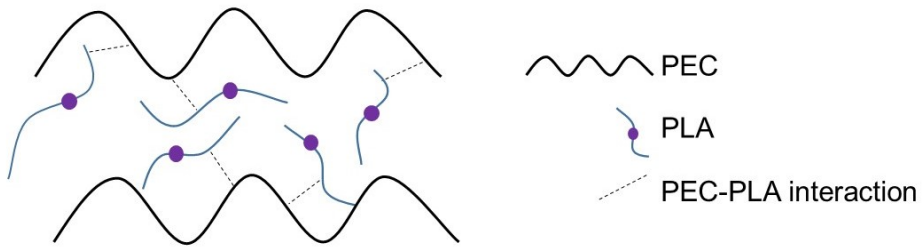


Fig. 2-18 Illustration of schematic images of interaction of PEC and PLA at the amorphous regions.

2-4 Conclusion

The solution casting technique has effectively produced PEC/PLA blend with distinct proportions of the biodegradable and biocompatible PEC and PLA. The blended specimens have been explored in terms of their physical appearance and crystallization of PLA spherulites, as well as thermal characteristics and relationships among polymers. The interaction between the ester and carbonic ester groups, primarily the interaction between partial charges, has been discovered to result in partially miscible PEC/PLA blend, which involved the interactions of –C–O–in –O–C=O of PLA and the carbonyl –C=O in PEC, as well as between the –O–C–in –O–C=O of PLA and the –C–O in –CH_2–O–of PEC. This study has also examined the changes in the T_g values across the blends. Adding PLA to at least 10 wt% in PEC has been seen to improve T_g value by over 10 ^oC when the PLA crystalline phase appeared in the blends in comparison to the neat PEC. The thermal stability has been also observed to change as a result of interactions between partial charges within PEC and PLA, with a weight loss in temperature (T_{d5}) by more than 30 ^oC at 5 wt%. In comparison to the blend PEC90/PLA10, the increase of PLA up until 30 wt% in the PEC/PLA blend has been seen to affect thermal degradation by slowing down the response, giving a high temperature at a 5 wt% (T_{d5}) weight loss of 246 ^oC. This blend includes a slight presence of (%) PLA crystallinity with a value of X_c of only 31%. Interestingly, X_c has been discovered in PEC to be highest in blends with just 10 wt% of PLA at 47%, which would aid in improving the mechanical characteristics of PEC that we propose to examine later.

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Chapter 3

Mechanical and degradation properties in alkaline solution of poly(ethylene carbonate)/ poly(lactic acid) blends

3-1 Introduction

Applications of bio-inspired polymers such as poly(lactic acid) (PLA) were first reported in the 1970s in the medical field as suture materials, as a result of the problems involved in obtaining surgical gut and the desire to have sutures which could be selected to degrade at different times after insertion [1]. The PLA synthesised from lactic acid and lactide via polycondensation and ring-opening polymerization respectively has become an alternative biobased material in view of the sustainability issue raised by petro-based polymers such as polyethylene and polypropylene.

Research on PLA has progressed, with work related to packaging film and tissue engineering [2] as a result of its properties including mechanical, biocompatibility, biodegradability and the function ability to hydrolyse in the presence of water. The low toughness of PLA is due to its brittleness, with elongation at breakage only 10% [3], while the low degradation rate upon hydrolysis, as mentioned in some reviews [4–7], is relevant to the suitability of PLAs as commodity materials. Degradation of PLA also has a bearing on environmental issues following disposal.

According to Rasal *et al.* [6], PLA has a slow biodegradation rate upon hydrolysis either by water or alkaline solution to form carboxyl and hydroxyl end group [8] (as shown in Fig. 3-1) according to hydrolysis environment such as pH, temperature and time [9–11] and also, depending on the PLA crystallinity. Both alkaline and acidic media accelerate the rate of hydrolysis, unfortunately hydronium ions have no significant and a very low catalytic effect on the hydrolytic degradation of PLA compared to that of alkalis. Among numerous degradation parameters, the effect of crystallinity (X_c) on autocatalytic, alkaline and enzymatic degradation of PLA have been intensively studied with respect to theirs applications in medical field.

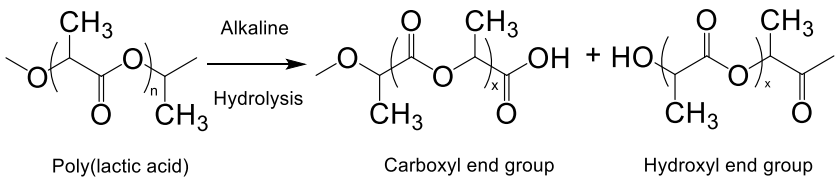


Fig. 3-1 Hydrolysis of poly(lactic acid) [8].

Referring to Tsuji and Ikada report [12], PLA with lower crystallinity showed slow rapid mass losses, whereas the mass loss of high crystallinity proceeds much slower for a longer time in the phosphate buffered solution as shown in Fig. 3-2.

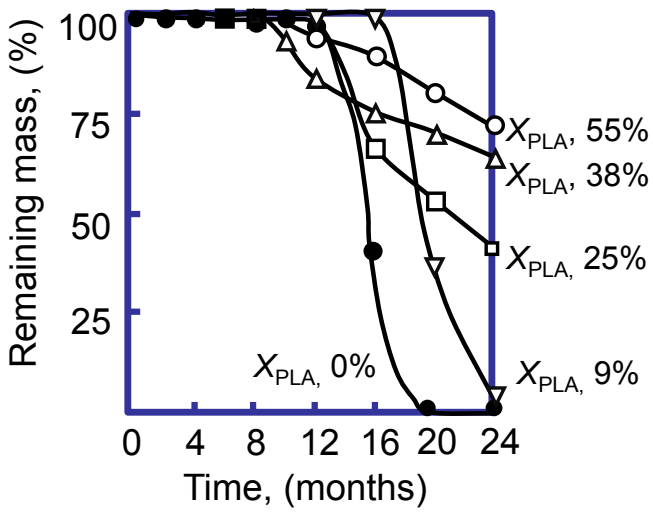


Fig. 3-2 Mass remaining for the PLA films with different PLA crystallinity as a function of hydrolysis time in 0.15 M phosphate buffered solution of pH 7.4 at 37°C [12].

PLA modification has therefore been studied using numerous methods such as polycondensation [13], ring-opening copolymerization [14], addition of plasticizer such poly(ethylene glycol), (PEG) as well as the addition of oligomer [15–17] and another polymer [18] so as to further modify the mechanical properties and the degradability.

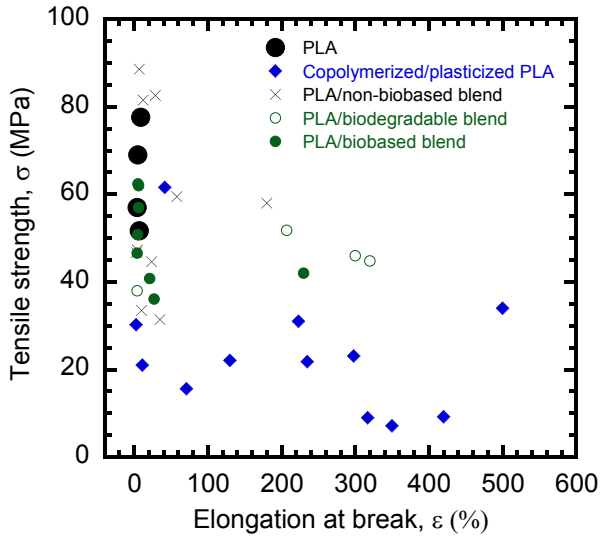


Fig. 3-3 Mechanical properties of modified PLA [16,19–34].

Fig. 3-3 shows the mechanical properties including tensile strength, σ (MPa) and elongation at break, ε (%) properties of PLA upon modification via copolymerization, plasticization and various type of polymer blends. Apparently, the mechanical properties of modified PLA transformed and decreased in some cases, depending on the modifications which further influence the miscibility, phase morphologies, and reduced sustainability due to the incorporation of non-biodegradable additives, however.

Recently, a poly(ethylene carbonate) (PEC) as an alternative biodegradable polymer synthesized from carbon dioxide (CO_2) has been considered in PLA modification. Unlike petro-based polymers, PEC is another type of aliphatic polycarbonate which has good biodegradability and biocompatibility in the *in vivo* environment [35]. The molecular structures of PEC and PLA are fairly similar and enhance their miscibility [36]. The glass transition temperature (T_g) of PEC is lower than that of PLA and is approximately 10 ^{o}C; this material is physically soft and rubbery at room temperature. PEC has stress-strain ductile profile and the elongation measurable reached more than 600% without film rupture. In previous studies, PEC was introduced so as to prepare PEC/PLA blends via the melt blending method [37] and the solution

casting method [36]. Addition of PEC to PLA clearly influences crystallinity, crystal formation and thermal properties.

Early studies on the degradability of PEC were performed by Imai *et al.* [38] and Kawaguchi *et al.* [39]. The mechanism of biodegradation of PEC has been extensively studied by Acemoglu *et al.* [40,41]. Stoll *et al.* [42] have reported further mechanistic aspects of the biodegradation of PEC for use as a drug carrier and coating [43]. As observed by Stoll *et al.*, PEC tablets were stable in all aqueous solutions between pH 1-12, however in strong base such KOH solution at pH 13.5, rapid degradation of PEC was observed as shown in Fig. 3-4.

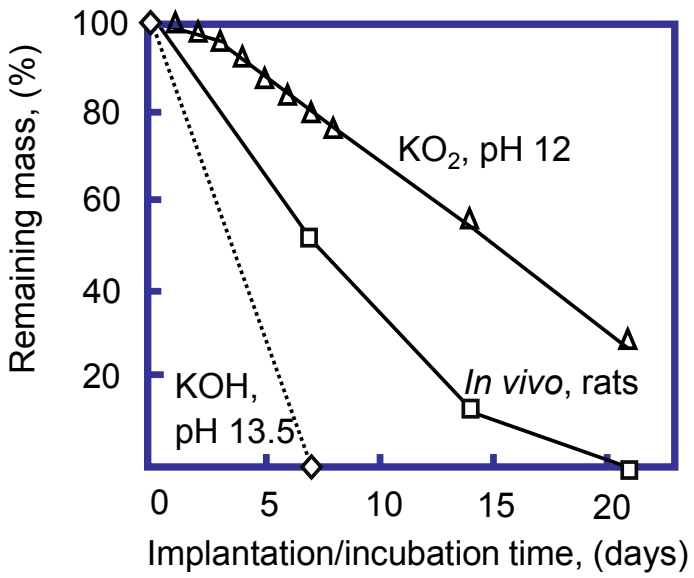


Fig. 3-4 In vitro and in vitro comparison of degradation of PEC tablets [42].

Addition of PEC to PLA promises control of hydrolytic degradation of the neat PLA in the PEC/PLA blend system. The mechanical and degradability properties of PEC/PLA blends have not yet been determined or discussed in detail, however. The addition of PEC to PLA possibly improves brittleness and contributes to the overall mechanical properties, including toughness, in PEC/PLA blends. In the present study, the

mechanical and degradability properties based on alkaline solution hydrolysis are studied and discussed for PEC/PLA blends. Although accelerated hydrolysis with the usage of high concentrated alkaline solution does not mimic the degradation in the physiological medium, this procedure may facilitate a basic study of morphological change of PEC/PLA blends during degradation.

3-2 Experimental Procedure

3-2-1 Materials

A commercial grade poly(L-lactic acid) (PLA, M_w=165,000) was used. The PLA was first dried in a vacuum oven at 60 ºC for 5 h prior to use. Poly(ethylene carbonate) (PEC QPAC®25, M_w=138,000) was purchased from Empower Materials, USA. The PEC was dissolved in acetonitrile and washed with excess methanol before being dried in a vacuum oven at 60 ºC for 24 h. The structures of PEC and PLA are shown in Fig. 3-5.

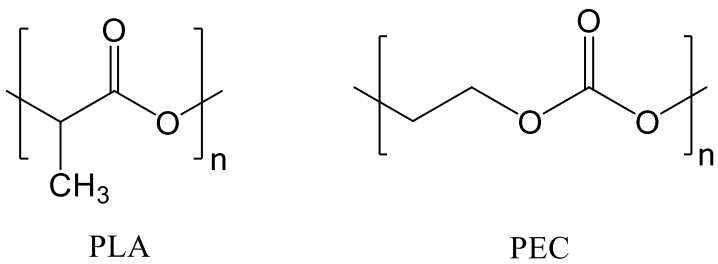


Fig. 3-5 Structure of poly(lactic acid) (PLA) and poly(ethylene carbonate) (PEC).

3-2-2 Sample Preparation

The PEC/PLA chloroform solution was cast onto a Teflon petri dish and then placed in a vacuum evaporator to remove excess solvent. The resulting sample, as film, was dried in a vacuum oven at 40 ºC for 24 h. Both polymers were kept in a glove box

prior to preparation of the blends. The compositions of the PEC/PLA blends were chosen as 0, 10, 40, 50 and 100 wt% PEC. Notation of PEC10, PEC40 and PEC50 are used to address PEC10/PLA90, PEC40/PLA60 and PEC50/PLA50 blends.

3-2-3 Characterization

A load test was carried out using an IMADA Force Gauge ZTA-DPU with an elongation rate of 10 mm/min. To confirm the reproducibility of the mechanical properties, at least five samples were measured, and the average values for each composition were taken as accurate. The modulus of resilience (U_R) and modulus of toughness (U_T) of PEC, PLA and PEC/PLA blends are based on the maximum energy which can be up to the elastic and rupture limits, which were determined by integrating stress-strain(S-S) curves which was calculated from the area under the S-S curves. An alkaline hydrolysis test was performed using films of controlled thickness of approximately 200 μm in 10 mL 1M NaOH aqueous solution pH 12. The films were placed in a glass vial filled with this NaOH solution, and the vial was covered. Hydrolysis was performed at 37 ^{o}C for a predetermined period. After hydrolysis, the films were washed with distilled water at room temperature and the NaOH solution was wiped off the surface, then the film was quickly weighed. The resulting films were dried at room temperature for 2 h followed by drying in vacuum for 48 h, then they were weighed (W_{dried}). The weight loss (W_{loss}) was calculated using Eq. (3-1),

$$W_{\mathrm{loss}} = \frac{W_{\mathrm{dried}} - W_{\mathrm{initial}}}{W_{\mathrm{initial}}} \times 100\% \qquad \text{Eq. (3-1)}$$

Morphological observations of the blend samples before and after hydrolysis were made using a scanning electron microscope (SEM, JEOL JCM600 Plus). Gel permeation chromatography measurements were made for all samples using a TOSOH ECOSEC HLC8320 system with two columns (TSK gel GM_{HHR}-H, TOSOH Co). HPLC grade chloroform was used as eluent, at a flow rate of 1.0 mL/min, and calibration took place using polystyrene standards.

3-3 Results and Discussion

3-3-1 Mechanical Properties

Neat PLA displays typical brittle behaviour upon tensile deformation. Neat PEC, conversely, has a typical ductile stress-strain profile, and can sustain elongation more than 400% elongation before rupture. Separated S-S curves of PEC and PLA are shown in Figs. 3-6 (a) and (b) respectively.

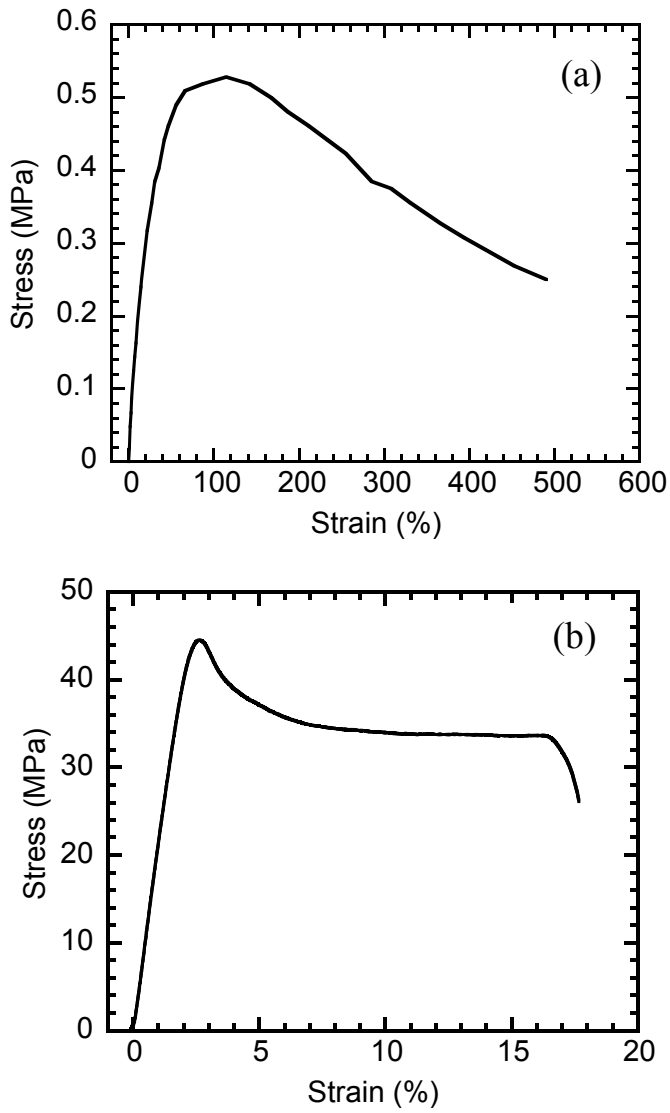


Fig. 3-6 Stress-strain curves of (a) neat PEC and (b) neat PLA.

Fig. 3-7 shows SEM images of cross-section fracture following quenching with liquid nitrogen of PEC and PLA, showing that the surface of amorphous PEC has smoother breakage and almost noticeable track lines than the surface of rough PLA that corresponds to brittleness in fracturing.

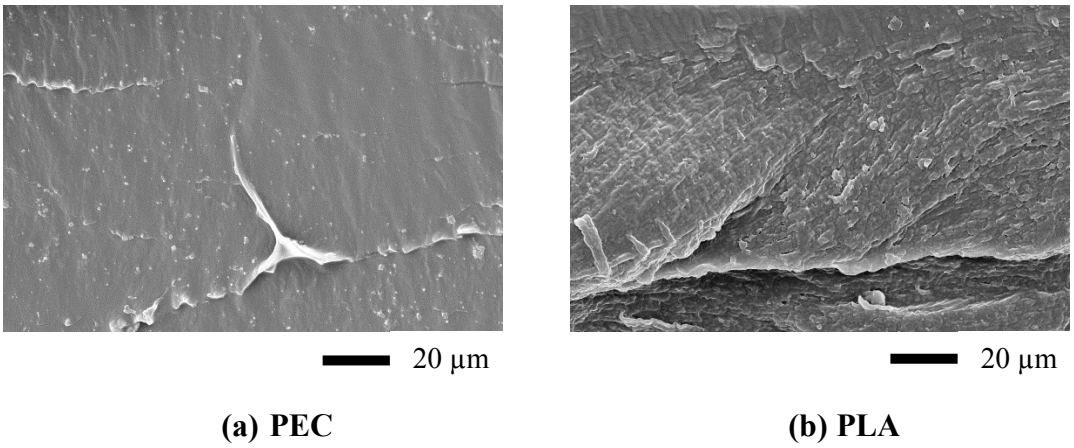


Fig. 3-7 SEM images of cross-section fracture under the quenched of liquid nitrogen for (a) PEC and (b) PLA. (Scale bar 20 μm)

Fig. 3-8 shows the stress-strain (S-S) curves of PEC, PLA and the PEC/PLA blends. Table 3-1 summarises the average mechanical properties for all compositions. For the PEC/PLA blends in Table 3-1, PEC10/PLA90 has the highest Young's modulus and tensile strength. These properties are fairly similar to neat PLA and the data reported previously by Lorenzo *et al.* [27]. Interestingly, at this composition, the highest value of the modulus of resilience (U_R) was obtained, before declining with addition of further PEC to the blends as shown by PEC40/PLA60 and PEC50/PLA50.

The addition of 50 wt% PEC improved the modulus of toughness (U_T) to its highest value of 45.8 MJ/m^3 and gave a Young's modulus similar to neat PLA. This value is fairly similar to the toughness characteristic of poly(propylene carbonate) PPC50/PLA50 blends reported by Ma *et al*. [44]. The findings by Di Lorenzo *et al.* [45]

that the PPC/PLA blends became more ductile with increasing PPC content also support our results.

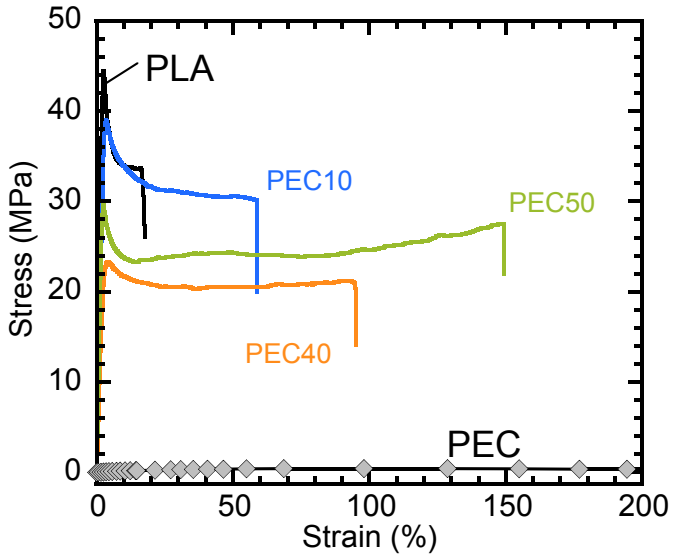


Fig. 3-8 Stress-strain curves of PEC, PLA and PEC/PLA blends.

Table 3-1 Mechanical properties of PEC, PLA and PEC/PLA blends.

Films	PLA	PEC10	PEC40	PEC50	PEC
Tensile Strength (MPa)	44.2	38.2	23.3	27.7	0.5
Elongation at Break (%)	17.3	60.2	94.8	150.9	490.5
Young's Modulus, E (GPa)	2.1	1.4	0.8	1.3	0.002
Modulus of Resilience, U_R (MJ/m^3)	0.33	0.43	0.16	0.25	0.05
Modulus of Toughness, U_T (MJ/m^3)	6.7	21.2	24.0	45.8	2.1

According to Ma *et al.*, the toughness or breaking energy is due to a complex interplay of several factors including the phase morphology, the relative modulus of the

phases, the chain structure and interfacial adhesion. Specific interaction in the surface area of attached phases such as hydrogen bonding (leads to the strongest interfacial adhesion), dipole-dipole interaction and ion-dipole interaction or repulsive interaction give enhancement to the interfacial adhesion between blend constituents. Upon the stress loading, stress transfer between two phases following strong interfacial adhesion between phases and the yield stress of the polymer blend (σ_{blend}) obeys the law of mixture given by Eq. (3-2) according to the Pukanszky's model,

$$\sigma_{blend} = \sigma_1 ø_1 + \sigma_2 ø_2 \qquad \text{(Eq. 3-2)}$$

where, σ and $ø$ are the yield stress and concentration of each components, respectively. While, for less interfacial adhesion between phases, the yield stress is depending on the separates phases of the matrix and dispersed phase that follows,

$$\sigma_{blend} = \sigma_m (1-ø_d)/(1+2.5ø_d) \qquad \text{(Eq. 3-3)}$$

where, σ_m and $ø_d$ are the matrix yield stress and the concentration of dispersed phase, respectively. In previous studies on PPC/PLA blend, Pukanszky's model has fit to characterize the yield stress for partial miscible PPC/PLA blends. The continuous PPC phase in PPC50/PLA50 therefore has a lower yield stress and favours the matrix, which requires more energy to break the materials [46].

In PEC/PLA blends, the rubbery properties of PEC lessen with decreasing PEC concentration in the PLA phase. Upon stress loading, the elongation of PEC/PLA blends is limited relative to neat PEC for which the strain is initially almost 491% (See in Fig. 3-6 (a)). Large strain properties, such as the yield behaviour and the elongation at breaking, are linked to the adhesion between the phases present in the material [47–49]. It proved impossible to determine the highest elongation upon stress loading for PEC due to equipment constraints. As a result of this constraint, the elongation of 491% at breaking for PEC reaches the value of U_T only at 2.06 MJ/m^3. Improvement in the mechanical properties of PEC/PLA blends might be due to the partial miscibility that is evident from the shift of T_g from neat PEC and PLA (See Fig. 3-9).

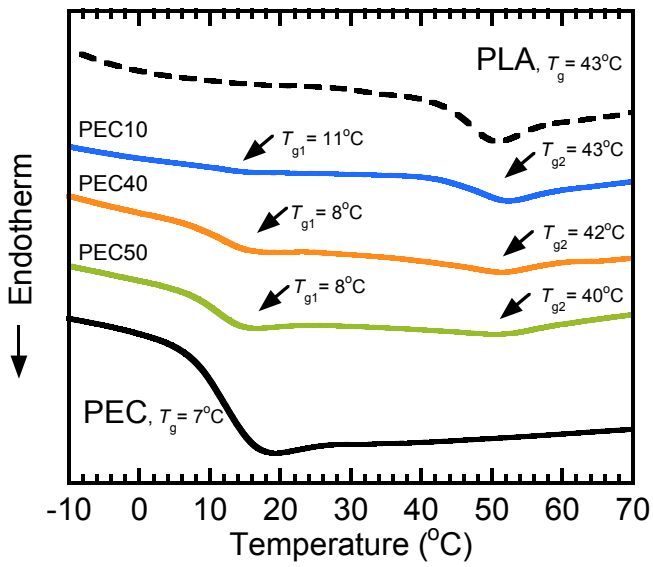


Fig. 3-9 Changes of T_{gPLA} and T_{gPEC} as a function of weight fraction of PLA for blends.

In the chapter 2, the partial miscibility characteristics of PEC/PLA blends was examined, which are presumably due to the intermolecular interactions between PEC and PLA [36]. Evidently, PEC and PLA phases show high interfacial adhesion based on the yield stress of PEC/PLA blends estimated by the Pukanszky's model as shown in Fig. 3-10, elucidating that stresses are transferred between PLA and PEC phases upon the stress loading, therefore increase the breaking energy PLA.

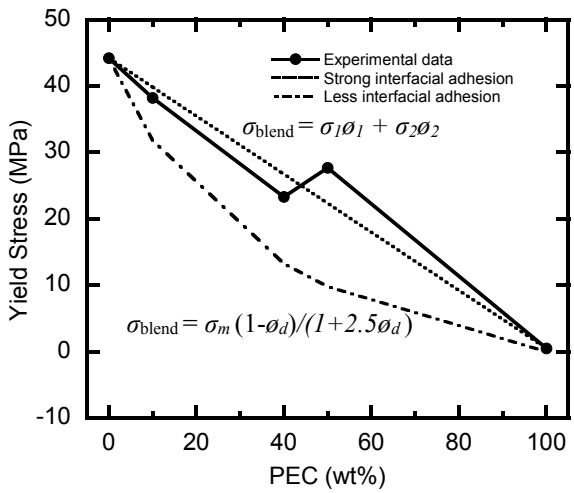


Fig. 3-10 Yield stress PEC/PLA blends.

Fig. 3-11 illustrates the simple schematic diagram of the interfacial adhesion for the stress transfer that is possibly happened at the interphases of domains PEC and PLA.

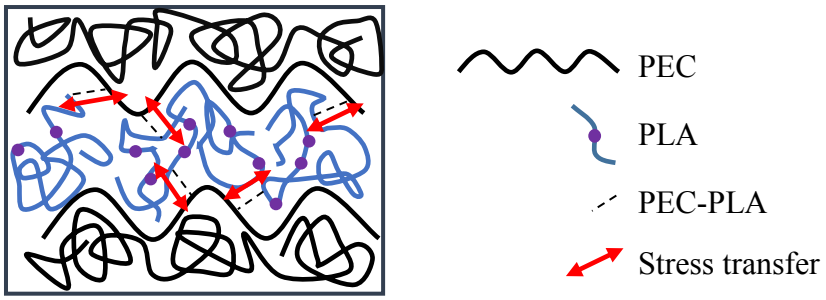
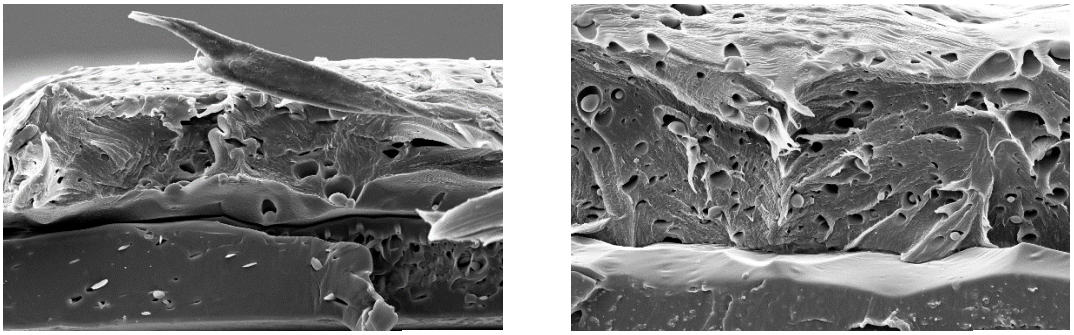


Fig. 3-11 Schematic diagram of the interfacial adhesion at PEC/PLA interphases.

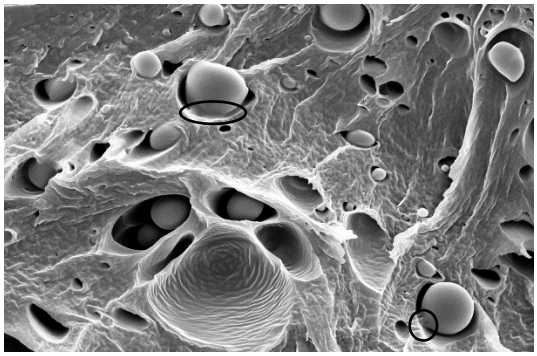
Also, as mentioned by Di Lorenzo *et al*. [45], the mechanical properties of polymer blends depend on the composition, the morphology and the level of segregation resulting from phase separation in the amorphous phase. From the photographs of SEM images in Fig. 3-12, sea-island morphology for PEC40/PLA60 and PEC50/PLA50 blends with small domains PEC and PLA in PLA-rich and PEC-rich phases was confirmed which correspond to the influence of rate of solvent drying [50] causing to nucleation growth from the phase inversion [51]. The sea-island structure, in which the continuous amorphous phases between PEC and PLA are partly responsible for the improved toughness of both compositions of PEC/PLA blends. However, low interfacial adhesion at the interface between PEC-rich and PLA-rich phases is observed in the PEC40/PLA60 blend (as shown in Fig. 3-12 (a)) which may contribute to low mechanical properties in comparison with the PEC50/PLA50 blend (see Fig. 3-12 (b)).



(a) PEC40/PLA60 **(b) PEC50/PLA50**

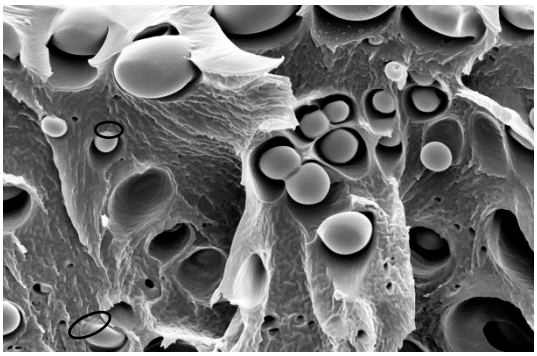
Fig. 3-12 SEM images of cross-section fracture under the quenched of liquid nitrogen for (a) PEC40/PLA60 and (b) PEC50/PLA50 blends. (Scale bar 50 μm)

Similar observations have been reported for partially miscible systems such as PPC/PLA blend, with the addition of more than 40 wt% of PPC, for which the crystalline phase and two or more amorphous phases occur, the PPC/PLA blends showed good homogeneity from two amorphous phases, with domains that are small in size and well dispersed within the other continuous phase, giving good properties at breakage [28]. Apparently, domains of PEC and PLA are dispersed in the continuous PLA-rich and PEC-rich phases for PEC50/PLA50 blend (see Fig. 3-13). The size of PEC domains for PEC10/PLA90 blend are in between 1 μm to 8 μm, whereas the domains size are much bigger; 3 μm to 10 μm for the PEC50/PLA50 (PLA-rich phase) blend. However, there is also slightly interphase adhesion (as shown in a black circle in Figs. 3-11 (a) and (b)) could be seen at the domains PEC interphase. Possibly, stresses are transferred at these sites causing improve toughness properties for the PLA. Schematic diagram at these sites is shown in Fig. 3-11.



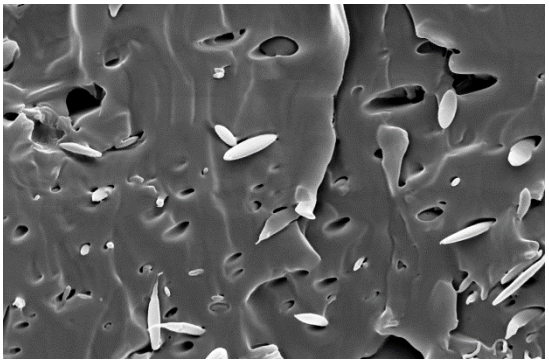
20 μm

(a) PEC10/PLA90



20 μm

(b) PEC50/PLA50 (PLA-rich phase)



20 μm

(c) PEC50/PLA50 (PEC-rich phase)

Fig. 3-13 SEM images of cross-section fracture under the quenched of liquid nitrogen for (a) PEC10/PLA90 (b) PEC50/PLA50 (PLA-rich phase) and (c) PEC50/PLA50 (PEC-rich phase) blends. (Scale bar 20 μm)

The morphologies of PEC/PLA blends observed from the SEM images may be further explained from thermodynamics point of view. The Flory-Huggins interaction parameter (also known as χ parameter) could be used to explain the interaction between polymer and solvent for the preparation of solution casting technique applied for PEC/PLA blends. The Flory-Huggins interaction parameter of polymer-solvent system $\chi_{p\text{-}s}$ is expressed by Eq. (3-4),

$$\chi_{p-s} = (V_s/RT)\left(\delta_s - \delta_p\right)^2 + 0.34 \qquad \text{(Eq. 3-4)}$$

where V_s the molar volume of the solvent, R is the universal gas constant, T is the temperature, and δ_s and δ_p are the Hansen solubility parameters of the polymer and solvent respectively. High interaction between solvent and polymer is indicated by small $\chi_{p\text{-}s}$ (when $\chi_{p\text{-}s} < 0$) , in which polymer is highly dissolved and expanded in the solvent. While, when $\chi_{p\text{-}s} > 0$, the polymer avoid to get in contact and become much more compact and show high immiscibility with solvent.

The Hansen solubility parameter, δ values of PEC, PLA and chloroform are 24.7 $MPa^{1/2}$, 20.2 $MPa^{1/2}$ and 17.8 $MPa^{1/2}$, respectively. The $\chi_{p\text{-}s}$ of PEC and chloroform is higher than $\chi_{p\text{-}s}$ of PLA and chloroform ($\chi_{PEC\text{-}chloroform} > \chi_{PLA\text{-}chloroform}$), which suggests that chloroform is greater solvent for PLA than for PEC. From these values, the PEC may firstly solidified from the blend solution. Additional to the solvent-polymer interactions, the wetting effect between PEC and the teflon substrate may also imply to the formation of PEC-rich blend under layer on the teflon substrate during the vacuum drying. After the PEC-rich blend under layer formed, the solution continuing evaporates and solidifying to form the PLA-rich blend upper layer as observed for PEC40/PLA 60 and PEC50/PLA50 blend as illustrated in Fig. 3-14. Similar to a bilayer structure consisting of under poly(methyl methacrylate) (PMMA) layer and upper polystyrene (PS) layer forms due to vertical phase separation of immiscible PS/PMMA blend in the toluene solvent during the spin-coating process as reported in Zhang *et al.* [52].

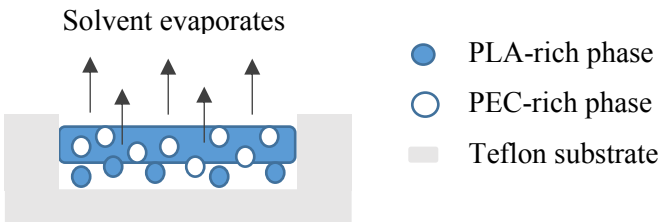


Fig. 3-14 Illustration of PEC/PLA film bilayer multiphase morphologies formation during vacuum drying.

Based on the mechanical properties of PEC/PLA blends prepared by the solution casting technique, these blends have shown better toughness properties for modified PLA in comparison with the one modified with the plasticization method. The toughness properties also are comparable to other modified PLA blends as shown in Fig. 3-15. Therefore, PEC is an alternative polymer to provide an acceptable toughening effect to PLA.

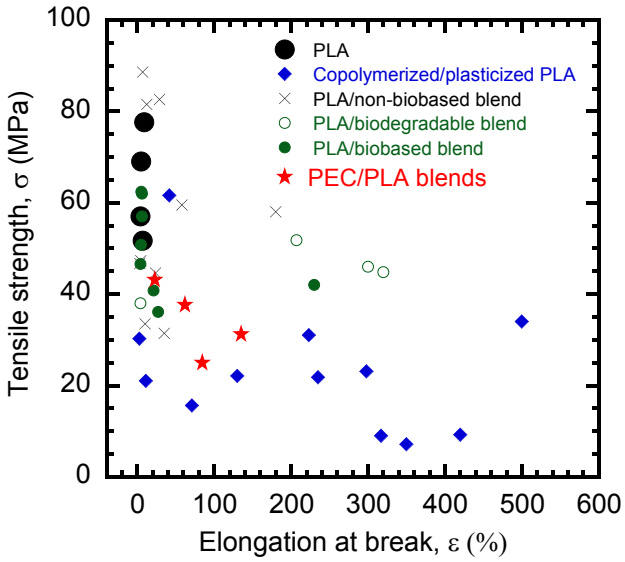


Fig. 3-15 Mechanical properties of PEC/PLA blends and various modified PLA system [16,19–34].

3-3-2 Alkaline Hydrolysis Measurement

Fig. 3-16 shows the weight loss (W_{loss}) of PLA, PEC and PEC/PLA blends as a function of time immersed in 1M NaOH solution in the hydrolysis test. In this study, the values of W_{loss} refer to the weight loss of PEC, PLA and PEC/PLA blends. The thickness of each sample was controlled to be less than 2 mm by homogeneous hydrolysis [53–56]. The neat PLA and PEC are hydrolysed in 1M NaOH solution, and PLA gave the highest weight loss relative to the PEC for each chosen degradation time. PLA was completely hydrolysed in the alkaline solution after 48 h, whereas approximately 10 wt% remains in the case of PEC. In the alkaline solution, depending on the change in the molecular weight, the PEC is reportedly biodegraded by surface erosion [40] and the reaction proceeds from the chain ends [42] to produce ethylene glycol and carbon dioxide. In PLA, the amorphous phase undergoes hydrolysis preferentially [57] to form either a carbonyl or hydroxyl end group [9].

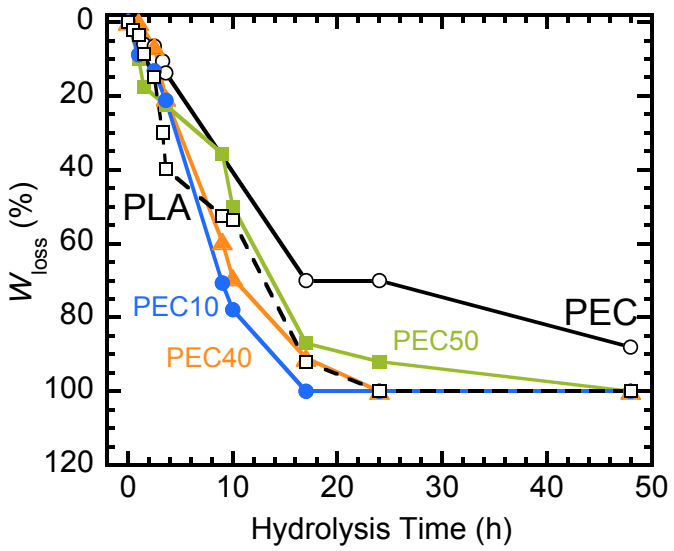


Fig. 3-16 W_{loss} changes of PEC, PLA and PEC/PLA blends degraded in 1M NaOH solution at 37 °C.

The PEC10/PLA90 and PEC40/PLA60 blends were clearly hydrolysed faster than the neat PLA. The PEC50/PLA50 blend is more stable in the alkaline solution, however, with slower degradation and evidence of the least weight loss in comparison with other blends. Before hydrolysis, the crystallinity of PLA for each blend composition is almost constant, between 36-39 % (See Table 3-2 and Fig. 3-17). The crystallinity of PLA (X_c), which is normalized by PLA weight fraction (X_{PLA}), was calculated using Eq. (3-5) as follows;

$$X_c\,(\%) = \{(\Delta H_m - \Delta H_{cc})/\Delta H^o_m\} \times (100/X_{PLA}) \qquad \text{Eq. (3-5)}$$

where, ΔH_m (J/g) is melting enthalpy of PLA and ΔH^o_m is theoretical melting enthalpy of a 100 % crystalline PLA, which is reported as 107 J/g [36,58]. The value is referred base on the presence of α' or α crystal modifications or the influence of D-lactic acid units in the analyzed poly(lactic acid).

Table 3-2 Thermal Properties of PEC, PLA and PEC/PLA blends.

Films	PLA	PEC10	PEC40	PEC50
Glass Transition Temperature, T_{g1} (°C)	43	43	42	40
Glass Transition Temperature, T_{g2} (°C)	-	11	8	8
Melting Temperature, T_m (°C)	181	179	180	179
Heat of Fusion, ΔH_m (J/g)	38	36	25	19
Crystallinity of PLA, X_c (%)	36	37	39	36
Melt-Crystallization Temperature, T_c (°C)	104	105	101	105
Heat of Melt-Crystallization, ΔH_c (J/g)	-18	-31	-13	-6

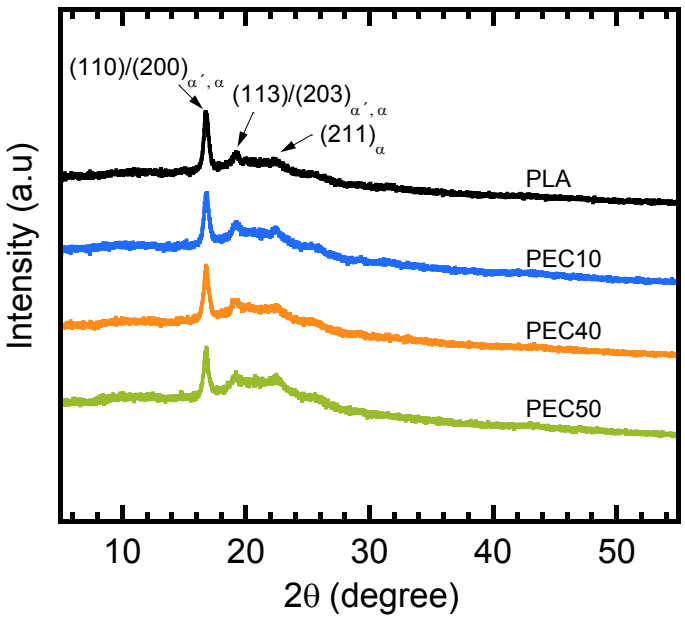


Fig. 3-17 XRD profile of PLA and PEC/PLA blends.

From XRD measurement, presence of α' or α crystal can be observed in the PEC/PLA blends with high intense peak showing reflection of α' and α crystals form of a typical semi-crystalline PLA which the peak located at 16.70° and 19.2° attributed to (110)/(200) planes and (113)/(203) planes, in well agreement in the profiles of PLA reported by Kawai *et al.* [59] and Li *et al.* [60]. Reflections of (211) planes located at 22.30° [58,61] which corresponds to the characteristics of α form crystal are also presented but at very low intensity. Apparently, the T_c values presented in Table 3-2 indicate the crystallization for all blends occurs at temperature below 120 °C as a results of kinetically competitive α' form of PLA [62].

DSC curves of PLA and PEC/PLA blends after degradation for 2 h and 10 h are shown in Fig. 3-18. Upon degradation for 2 h, the heat of fusion of PLA for all PEC/PLA blends slightly increased in relative to pure PLA. The slight increase in the heat of fusion (See Table 3-3) might be due to the progressed degradation of amorphous phases of PLA and PEC which cause the increase in the crystalline phase of the PEC/PLA blends. From

the Fig. 3-18, the melting temperature of degraded PEC/PLA blends for 10 h is slightly decreased as a result of decreasing PLA crystalline thickness.

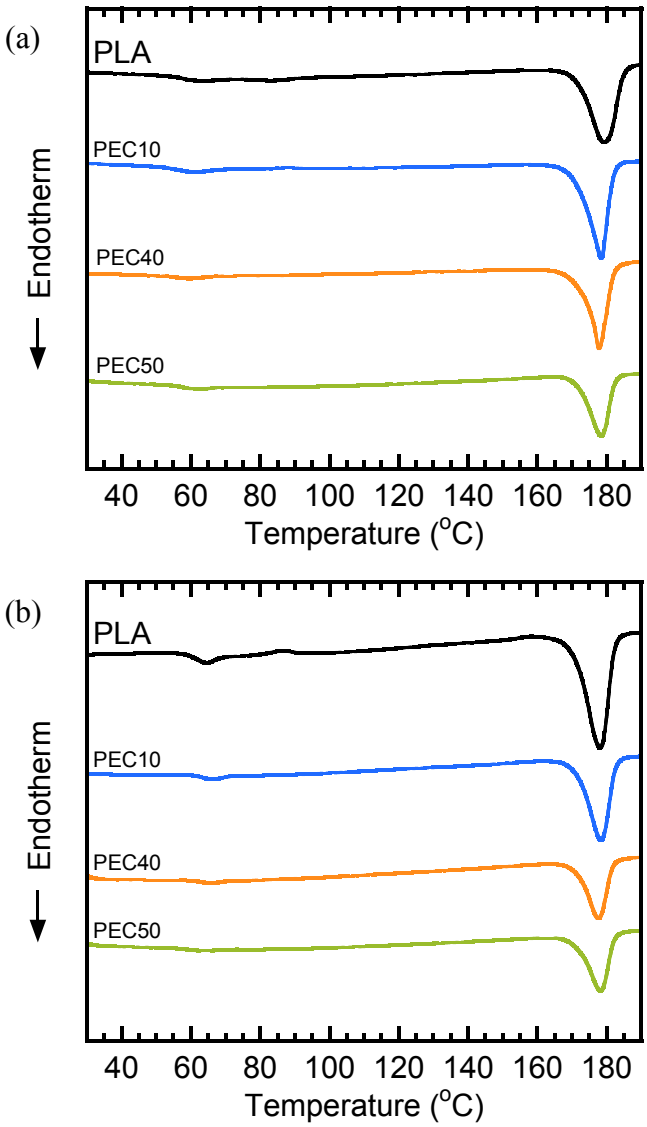


Fig. 3-18 DSC curves of PLA and PEC/PLA blends after (a) 2 h and (b) 10 h hydrolysed in 1M NaOH solution at 37 ºC.

However, after 10 h, the heat of fusion is non-linearly increased as observed for PEC40/PLA60 and PEC50/PLA50 blends in comparison with samples before degradation. Slight drop in the crystallinity might be due to partial dissolution of PLA

crystals that leached out and dissolved in the alkaline solution as a result of the weight loss at 50 % for PEC50/PLA50 and 60 % for PEC40/PLA60 blends (in Fig. 3-16). Indeed, PEC40/PLA60 blend shows slightly higher heat of fusion contrary to the PEC50/PLA50 blend after 10 h corresponds to higher weight loss. As the degradation progressed, the variation of crystallinity of PLA in the PLA phase and the ratio of PEC and PLA may influence on the change in weight loss upon alkaline hydrolysis for the hydrolysed PEC/PLA blends.

Upon hydrolysis for 2 h and 10 h, the changes in physical appearance of PEC, PLA and PEC/PLA blends are shown in Fig. 3-19. Relative to the original samples, the transparency of PLA and PEC/PLA blends were much more opaque, and the sample were more brittle and broke easily while handling, as seen with the hydrolysed PEC40/PLA60 blend after 10 h.

Table 3-3 Heat of melting PLA in PLA and PEC/PLA blends degraded in 1M NaOH solution at 37 ^{o}C.

Sample/ ΔH_m (J/g)	0 h	After 2 h	After 10 h
PLA	38	38	44
PEC10/PLA90	36	38	38
PEC40/PLA60	25	32	22
PEC50/PLA50	19	23	20

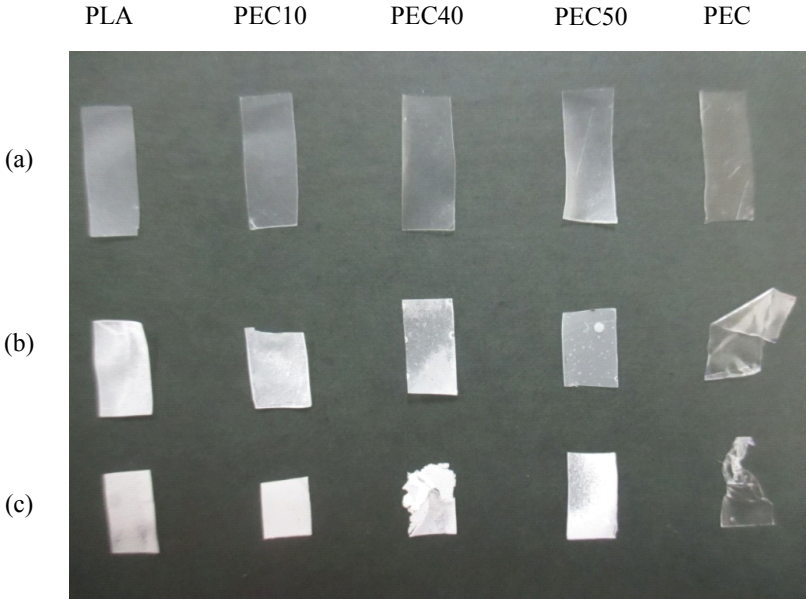


Fig. 3-19 Changes of physical appearance of neat PLA, neat PEC and PEC/PLA blends by hydrolysis at (a) 0 h (b) 2 h and (c) 10 h in 1M NaOH at 37 ºC.

At early stages of the alkaline degradation, there was no noticeable accumulation of crystalline residue in the solution. After 17 h, however, an accumulation of crystalline residues was clearly observed, which largely disappeared after 48 h; this is due possibly to the small-sized crystalline residues formed from PLA, which may promptly degrade to water-soluble oligomers or monomers [63].

3-3-3 Scanning electron microscopy observation after alkaline degradation

As shown in Fig. 3-20, upon hydrolysis in 1M NaOH solution, both PEC and PLA are clearly hydrolysed from the surface. In Fig. 3-20 (a) the surface of neat PEC became rough and eroded, and the erosion was observed heterogeneously for samples after hydrolysis for 10 h and 48 h respectively, contributing to the weight loss in Fig. 3-16. In Fig. 3-20 (b), further degradation of the neat PLA is observed, including bulk erosion across the cross-section. After hydrolysis for 20 h the surface was severely deteriorated

relative to that after for 10 h. This observation is consistent with the suggestion by Fischer *et al.*, [10] that the hydrolytic degradation of semi-crystalline PLA proceeds in for two stages which are controlled by four basic parameters: the rate constant, the amount of absorbed water, the diffusion coefficient of chain fragments within the polymer, and the solubility of degradation products [64]. The first is the random hydrolytic scission of ester bonds when the alkaline solution diffuses into the amorphous region. The polymer has a tendency to increase the degree of crystallinity as the degradation proceeds [65]. The second stage begins when most of the amorphous regions have been degraded, and the hydrolytic attack then progresses from the edge to the center of the crystalline domains.

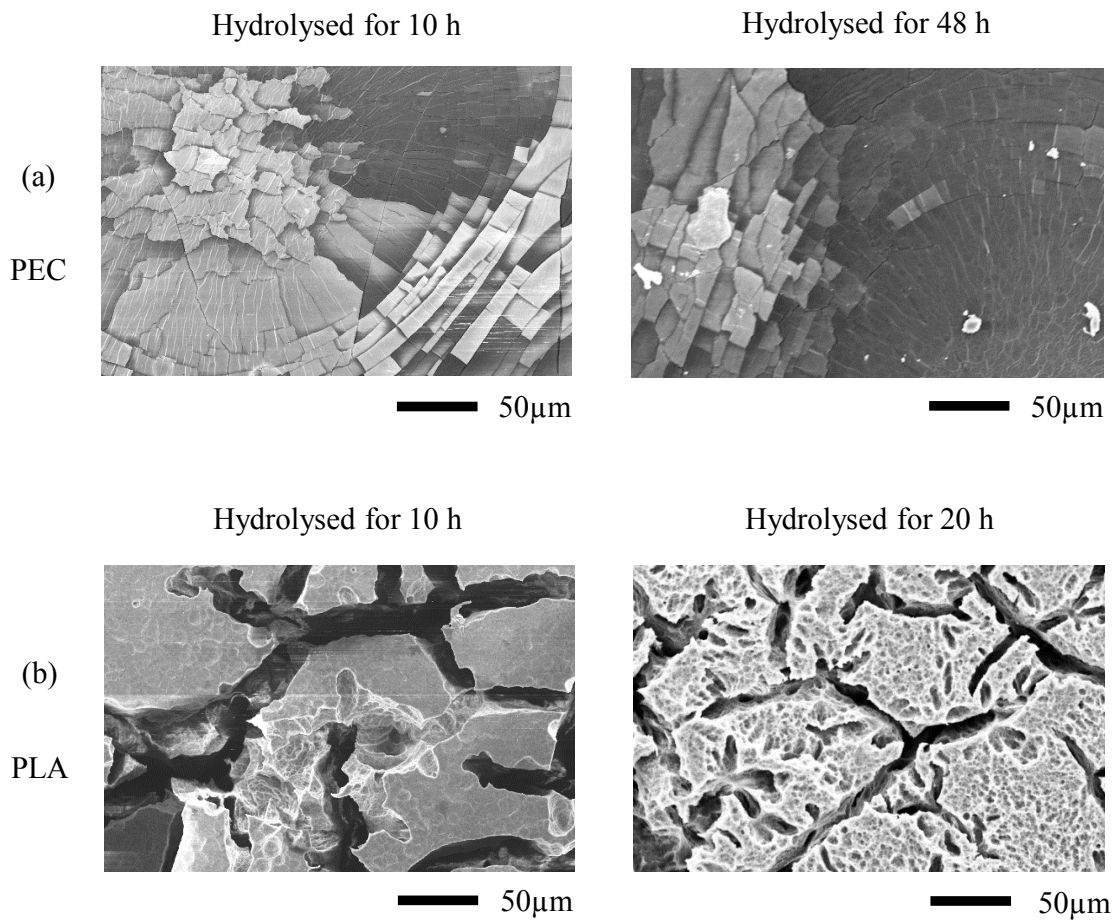


Fig. 3-20 Surface images of hydrolysed (a) PEC and (b) PLA for predetermined times in 1M NaOH at 37 ^{o}C. (Scale bar 50 µm)

For the hydrolysis of PEC/PLA blends, SEM photographs of hydrolysed PEC/PLA blends after 10 h are shown in Fig. 3-21. At the surface of all hydrolysed blends, the PLA phase clearly undergoes hydrolysis and the presence of PEC controls the overall hydrolysis process depending on the ratio of PEC and PLA. This is similar to the observation by Shirahase *et al*. [66], hydrolytic degradation of PLA/PMMA blend can be widely controlled by the PMMA content. In large-scale images of hydrolysed PEC/PLA blends (see Figs. 3-22 and 3-23), PEC and PLA were progressively hydrolysed after 10 h, and the surfaces of the PEC and PLA phases are clearly eroded. In addition, small cavities (visible in Figs. 3-21 (a) and 3-23 (a)) indicate that the surface of PLA was eroded from the blend surface of the degradation of the amorphous phase beneath the eroded area [56,57].

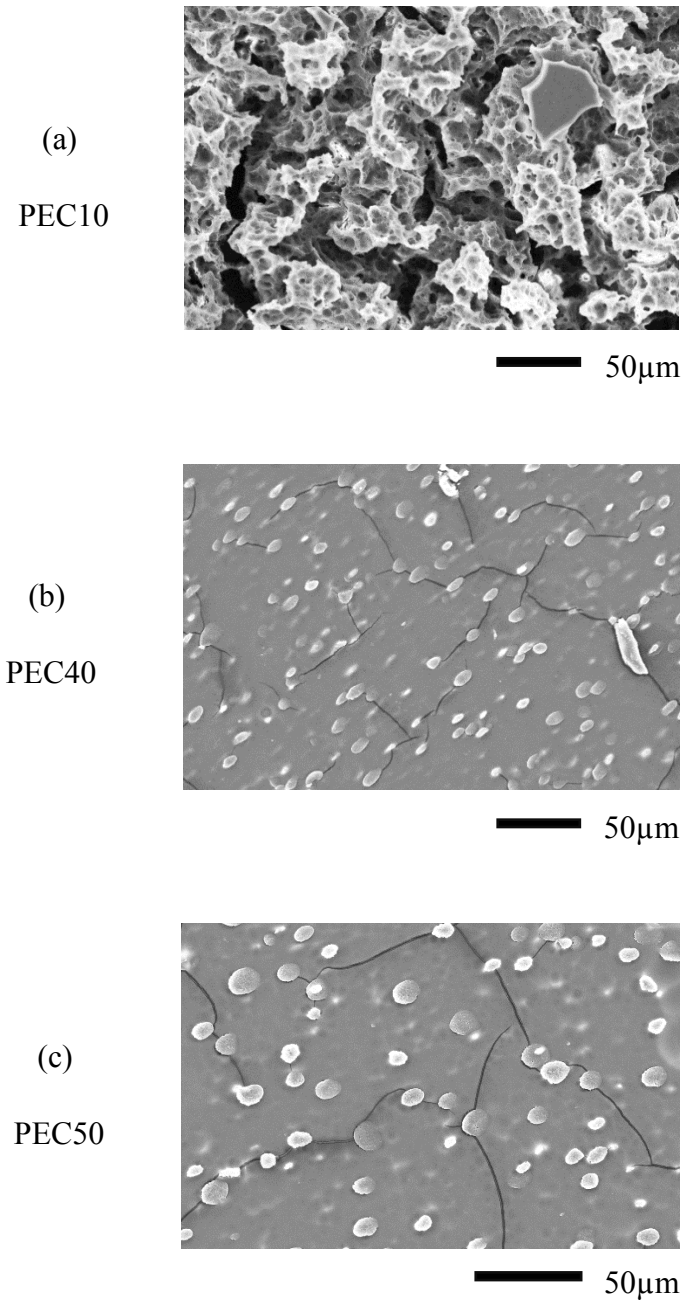
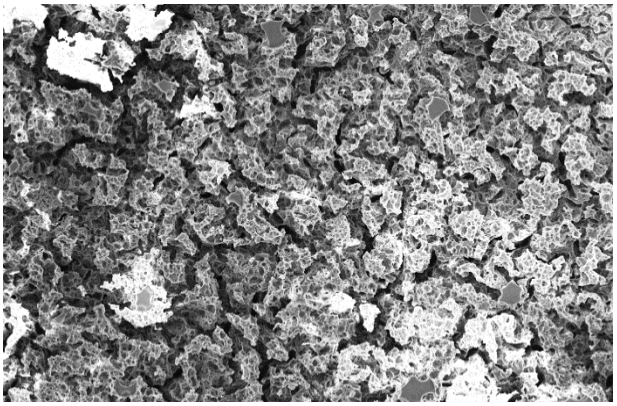


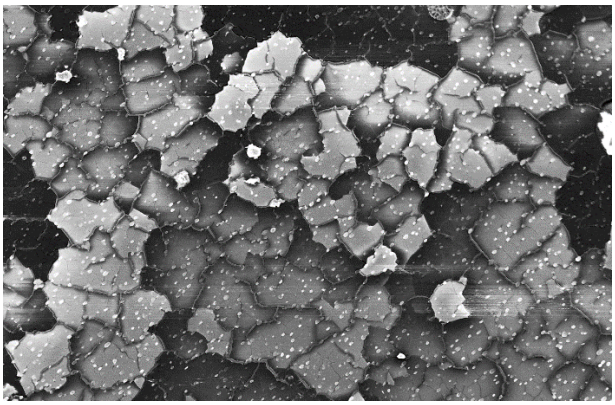
Fig. 3-21 Surface images of hydrolysed PEC/PLA blends (a) PEC10 (b) PEC40 and (c) PEC50 after 10 h hydrolysed in 1M NaOH solution at 37 ºC. (Scale bar 50 μm)

(a)
PEC10



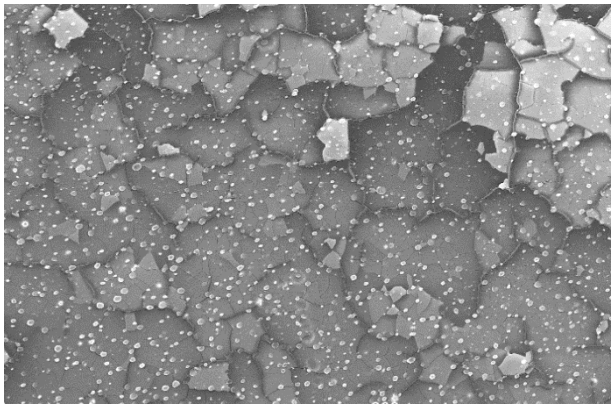
200μm

(b)
PEC40



200μm

(c)
PEC50



200μm

Fig. 3-22 Low-magnified surface images of hydrolysed PEC/PLA blends after 10 h hydrolysed in 1M NaOH solution at 37 ºC. (Scale bar 200 μm)

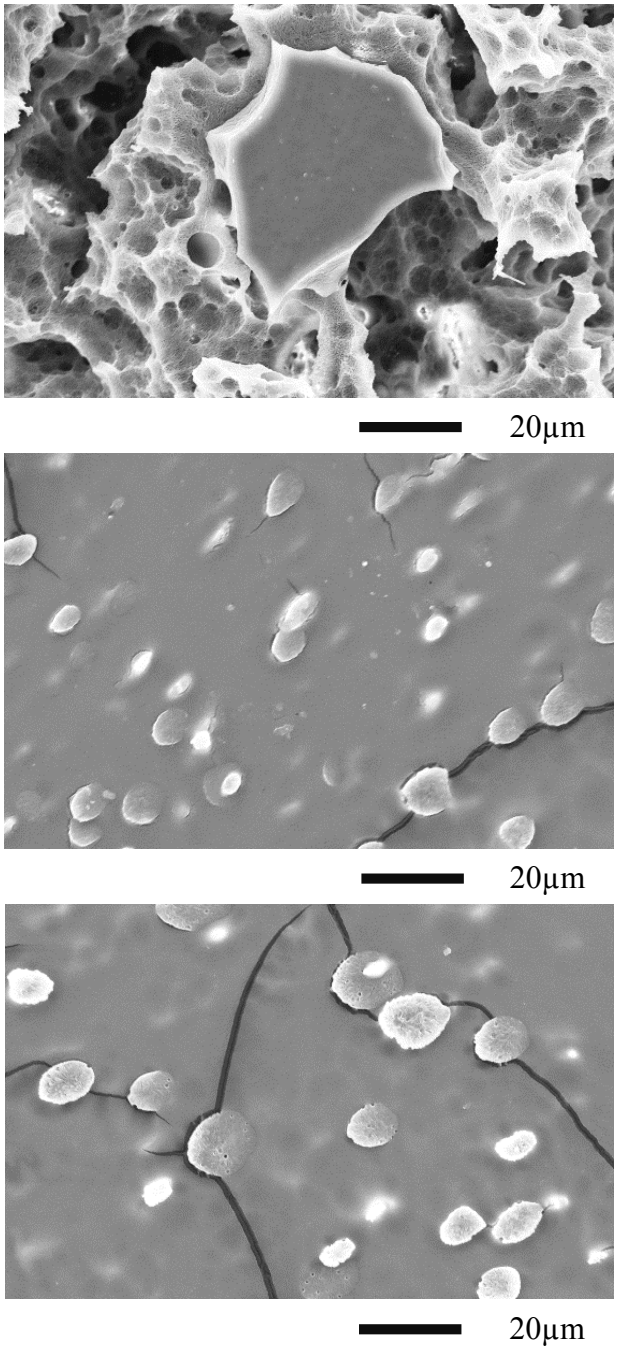


Fig. 3-23 High-magnified surface images of hydrolysed PEC/PLA blends after 10 h hydrolysed in 1M NaOH solution at 37 ºC. (Scale bar 20 μm)

This allows further degradation of the PLA phase and also contributes to the improvement of the contact area of PEC with the alkaline solution which mitigates the degradation of PEC as shown in PEC10/PLA90 blend. This might be partly why PEC in

the PEC/PLA blend system degrades much faster than the neat PEC in other blends. In contrast to PEC40/PLA60 blend, the PEC/PLA ratio and better interfacial adhesion between these polymers due to the partial interaction related to the PEC50/PLA50 blend might partly retarded the hydrolysis in agreement with the result reported strong interaction between L- and D-lactide unit sequences from the PLLA/PDLA blend having lower in vitro hydrolysis rate [67]. The combination of higher content of PEC and lower content of PLA in the PEC50/PLA50 blend may limit the alkaline solution to diffuse easily into the less amount of amorphous PLA (due to only 50 wt% of PLA). Higher amount of PEC in the PEC50/PLA50 blend undergoes erosion which the degradation is much slower in comparison with the PEC40/PLA60 blend. PEC40/PLA60 and PEC50/PLA50 blends undergo bulk and surface degradation mechanism that bound with many factors including the ratio of PEC/PLA, interfacial adhesion due to interaction between PEC and PLA phases, diffusion of alkaline solution to initiate the degradation at the amorphous phase beneath the blend surface, and change in crystallinity as the degradation progress.

3-3-4 Gel Permeation Chromatography Measurement

Fig. 3-24 shows dependences on average molecular weight by weight (M_w), by number (M_n) and polydispersity index (*PDI*) of the PEC concentration for degraded PLA, PEC and PEC/PLA blends. For the degraded neat PLA, after hydrolysis for 10 h in the alkaline solution, the value of M_w decreased slightly from 203 kDa to 198 kDa, whereas M_n increased from 92 kDa to 104 kDa. These changes might be due to a section of the chemical bonds in the main chain randomly upon hydrolysis forming large molecular fragments that result in different changes in M_w and M_n [64,68]. Relative to degraded neat PLA, the degraded PEC/PLA blends clearly have lower distribution of M_w and M_n values after the hydrolysis. According to Dadsetan *et al.* [35], the molecular weight and carbonate content are crucial parameters for biodegradability. A molecular weight of PEC greater than 100 kDa facilitates biodegradation by surface erosion [40,41]. As shown in Fig. 3-16, the PEC underwent weight loss of about 39 % after 10 h of hydrolysis in

alkaline solution. It is evident that the PEC undergoes an insignificant change in M_w even after hydrolysis for 10 h.

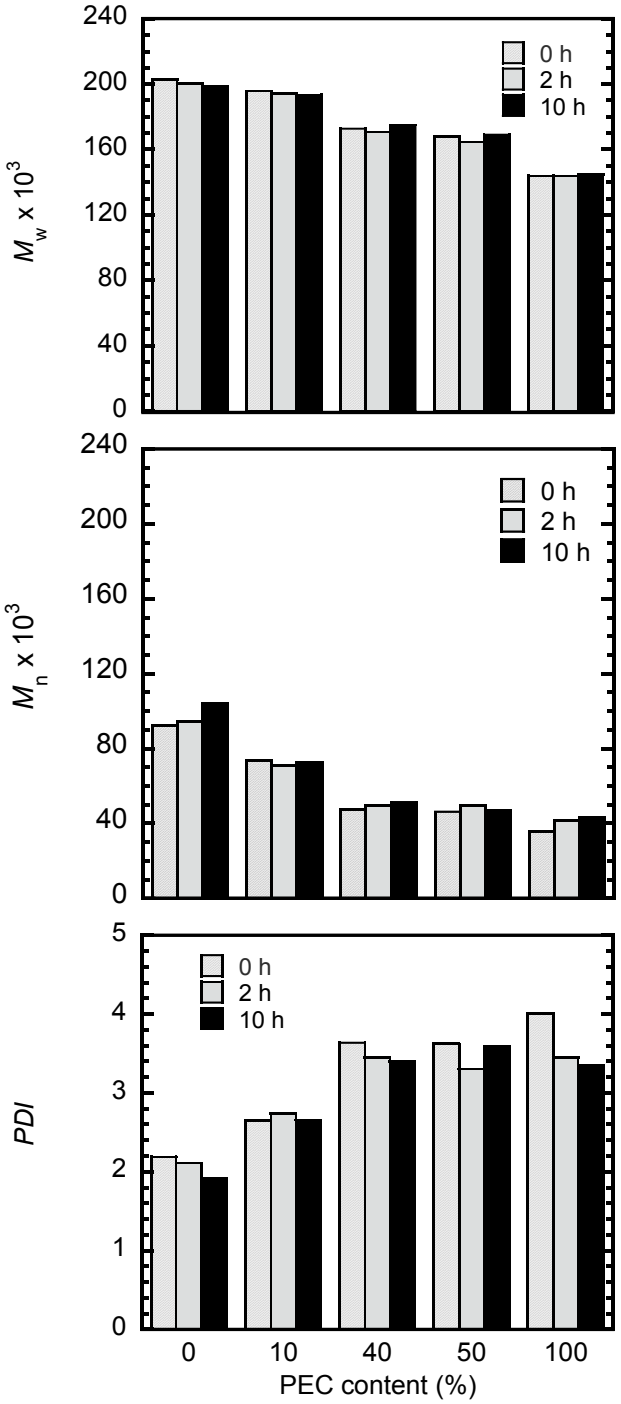


Fig. 3-24 Degradation time and PEC content dependence of M_w, M_n and *PDI* for neat PLA, neat PEC and PEC/PLA blends.

This suggests that the degradation is related to the surface erosion, consistent with previous observation. The remaining eroded PEC may however contribute to the increase in M_n that matches the heterogeneous surface erosion (as seen also in Fig. 3-20 (a)). Eroded PEC that was released into the solution facilitates further degradation at the remaining PEC surface and contributes to the weight loss. Interestingly, apart from the PEC50/PLA50 blend, there are small increases in M_n as an indication of the presence of more molecular chain fragments with low molecular weight due to the degradation of high molecular weight chain. Degradation of PEC/PLA blends are difficult to discuss in detail, because the overlay of M_w and M_n of PEC and PLA give the values between 165 kDa to 195 kDa and 46 kDa to 93 kDa, respectively. For the changes in *PDI* values, molecular weight distribution neat PLA shows uniformity which around 2.0 relative to neat PEC and blends. For degraded PEC/PLA blends, the *PDI* is in the range 2.4-3.5 which explains the broad and non-uniform molecular weight distribution caused by the change of M_w and M_n for PEC/PLA blends, as a result of surface and bulk erosion effects.

Fig. 3-25 shows the schematic illustration on the predicted hydrolytic degradation of PEC/PLA blends mechanism for a thin film. Diffusion of hydroxide ion, (OH^-) is firstly begin with the penetration of OH^- ion from the surface into inner layer, depending on the concentration of OH^-, chain mobility, crystallinity, and content of PEC in the blends particularly at the film surface. High concentration of OH^- ion, strongly accelerates the hydrolytic degradation of PLA and PEC. At the surface, heterogeneous degradation occurs following the presence of PEC domains that are degraded by the surface erosion mechanism, as characterized earlier due to the unchanged of molecular weight as the hydrolysis progressed, slowing the OH^- ion transfer further. Influence of the hydrolysis temperature which runs at 37°C, causing chain packing PEC has higher mobility, may increase the hydrolytic degradation at the hydroxyl groups following degradation temperature was elevated higher than glass transition temperature of PEC. Whereas, degradation of PLA at the surface is faster than PEC as evidence from the W_{loss} changes of PEC and PLA in Fig. 3-16, proceeds at the amorphous region and the cleavage of ester groups are reaction catalysed by the presence of the OH^- ion, resulting changes on the molecular weight and crystallinity as the hydrolysis progressed. At the PLA phases, the presence of the crystalline phase restricted the diffusion of OH^- ion to the amorphous

region, thereby, degradability decreased. At the interphases of PEC and PLA, the hydrolytic degradation is influenced by the interaction between PEC and PLA, higher interaction decreases the degradability, as a result of the interaction may disturb the diffusion of alkaline solution into the material and lowers the hydrolytic degradation rate. As the PEC content increased to 50 wt%, greater interaction between PEC/PLA has been observed giving an increase to the toughness properties for this blend as observed earlier, however, at high ratio PEC may distract the hydrolytic degradation due to slow degradation at the amorphous PEC region.

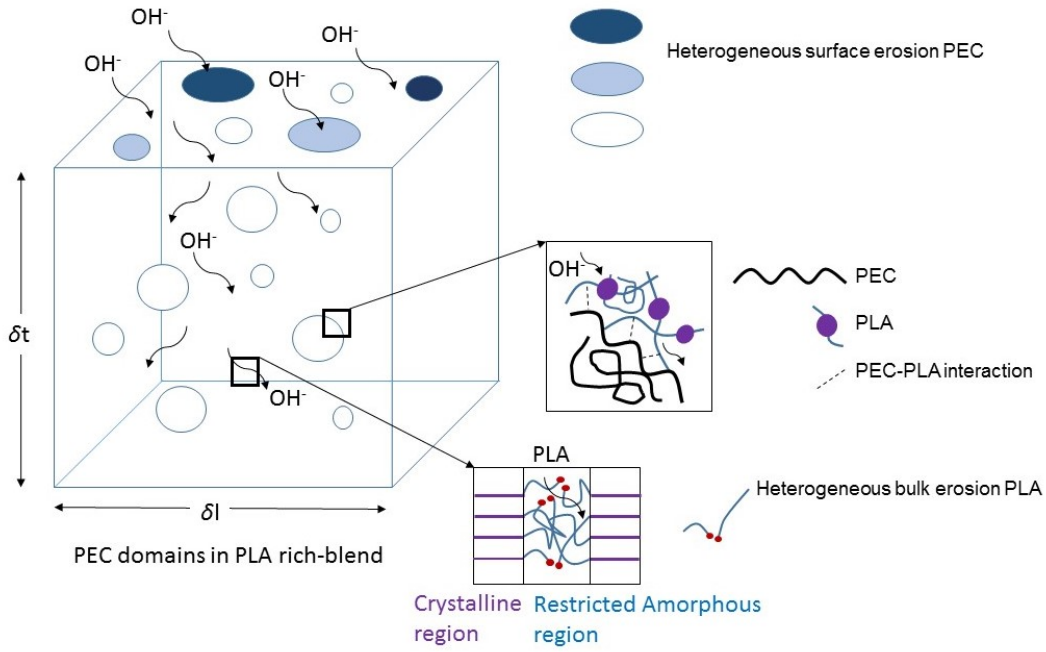


Fig. 3-25 Schematic illustration on the predicted hydrolytic degradation of PEC/PLA blends mechanism for a thin film.

3-4 Conclusion

In this chapter, a simple solution casting method provides an alternative approach to producing thin films of PEC/PLA blends having superior toughness and degradation in alkaline solution properties. Addition of at least 10 wt% of PEC caused the toughness to increase by 215% while, interestingly, the Young's modulus property is fairly comparable to PLA. The maximum toughness of PEC/PLA blends occurred in PEC50/PLA50 with a toughness of 584% relative to neat PLA. Thus, PEC is an alternative polymer to provide an acceptable toughening effect to PLA. As to the degradability performance of PEC/PLA blends in alkaline solution, the addition of more than 40 wt% PEC enhanced the degradability of PLA. The weight loss of hydrolysed PEC/PLA blends does not change linearly with the amount of PEC added. The enhancement of toughness and degradability in alkaline solution properties of PEC/PLA blends are attributable to the partial miscible characteristics observed in the shift of T_g which is positioned between the values for PEC and PLA. Degradability of PEC/PLA blends are controlled by many factors including the ratio of PEC/PLA, interfacial adhesion due to interaction between PEC and PLA phases, diffusion of alkaline solution to initiate the degradation at the amorphous phase beneath the blend surface, and change in crystallinity as the degradation progress.

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Chapter 4

Structural and physicochemical properties of melt-quenched poly(ethylene carbonate)/poly(lactic acid) blends

4-1 Introduction

Comprehensive poly(lactic acid) (PLA) study has been carried out to enhance its low toughness and crystallization rate involving procedures that include copolymerization, plasticization and polymer blend [1]. The polymer mixture is anticipated to have a higher benefit owing to its simplicity and cheapness [2], enabling the development of versatile new polymers appropriate for commercial implementation from polymer mixtures with decreased migration of the unwanted monomer or oligomer to the PLA [3]. Recently, the addition of carbon dioxide (CO_2)-synthesized biodegradable poly(ethylene carbonate) (PEC) has given a fresh strategy to PLA alteration. PEC has a higher biodegradation rate and has been considered for use in controlled drug delivery compared to other types of aliphatic carbonate such as poly(propylene carbonate) (PPC) [4]. PEC's high-stress ductile profile [5] also enhances the mechanical characteristics of semi-crystalline polymers such as PLA [6]. PEC/PLA blends have shown compatibility [8] in some studies following the preparation of PEC/PLA blends by melt extrusion [7] and solution casting methods. Associated with wet processing, the crystallinity of PLA is reported to be high, approximately 25-47% depending on PEC and PLA proportions. In addition, problems in managing solvent drying in a vacuum dryer have resulted in low reproducibility of PEC/PLA blend thin film with low surface homogeneity and uniformity, affecting overall yield. A melt-quench method is used in this present work to regulate PLA crystallization in PEC/PLA blends and enhance homogeneity.

The cooling rate of melted semi-crystalline polymer affects the structure and morphology of the final product, according to Meyer and Müller [9]. A low cooling rate enables the molecules to rearrange and form a high crystalline phase thus, decreasing the specific volume. Nevertheless, a mainly amorphous phase with elevated specific volume are demonstrated as in Fig. 4-1, due to a fast cooling rate that hinders this process. Tsuji and Ikada [10] have shown the integration of melting, quenching and two annealing procedures by which PLA films with distinct morphologies are created, which can generate a film with both the morphologies acquired by each of the single annealing procedures as shown in Fig. 4-2. The larger spherulites formed in the first annealing and were surrounded by many small spherulites formed during the second annealing.

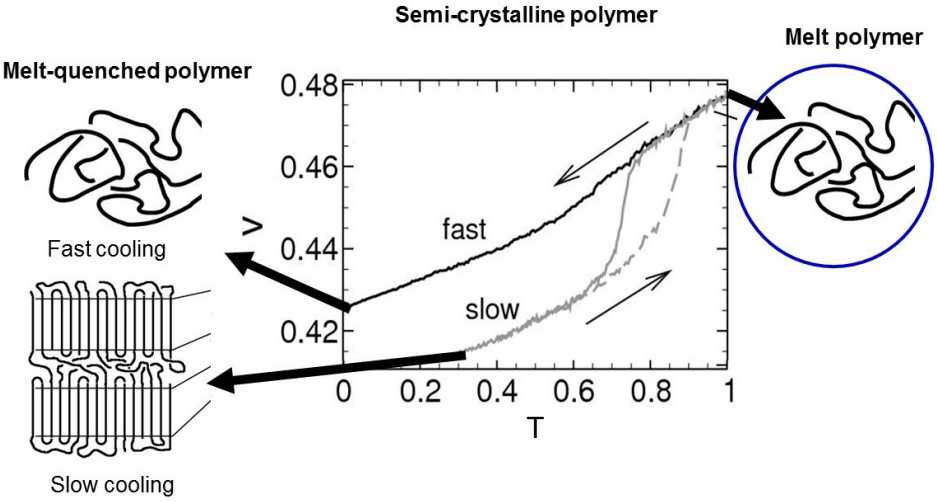

Fig. 4-1 Quenching of semi-crystalline polymer [9].

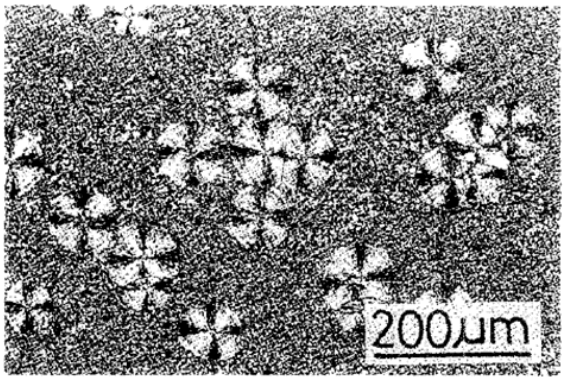

Fig. 4-2 Photomicrograph of PLA film annealed through the combined process of : melting at 200 ºC for 3 min/ annealing at 140 ºC for 20 min/ quenching at 0ºC/ annealing at 140 ºC for 580 min [10].

The melt-quench technique was used to prepare the mixture of semi-crystalline poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) [11], resulting in non-lamellar (micellar) crystallites due to polymer crystallization in the interphase area with extensive super-cooling that changes the phase morphology of the PVDF/PMMA mixture as shown in Fig. 4-3. In addition, a mixture of solution casting and melt mixing was used in past research; this mixed-method considerably encourages

the dispersion of nanotubes in the PMMA matrix and increases the homogeneity of composites as shown in Fig. 4-4.

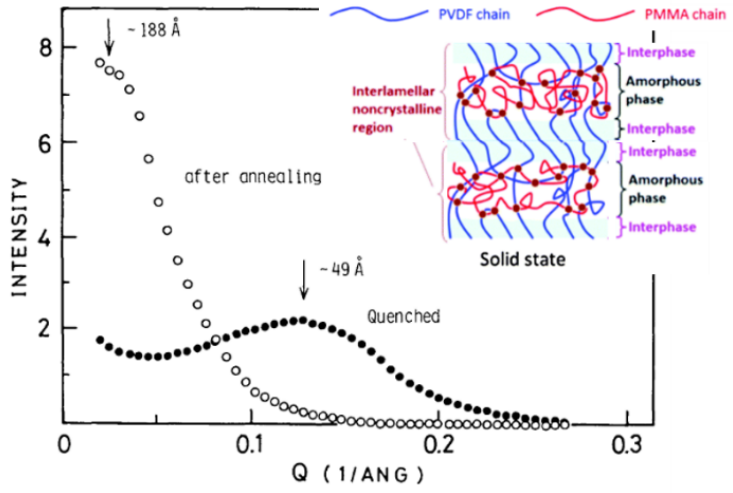

Fig. 4-3 SAXS scattering curves for quenched and annealed 60/40 PVDF/PMMA blend [11].

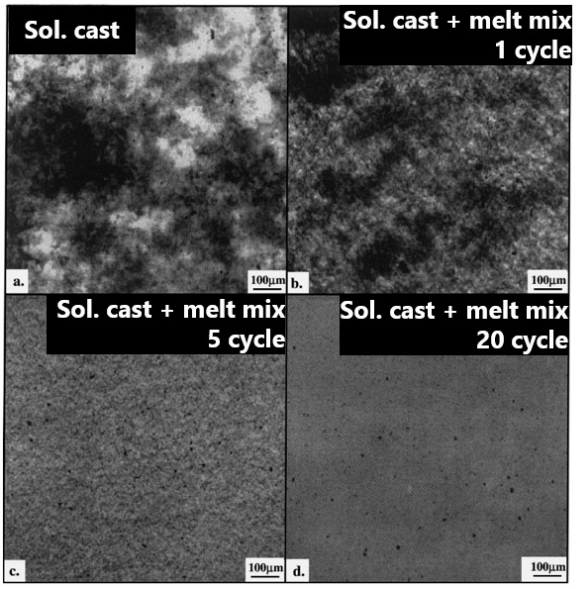

Fig. 4-4 Combination of solution casting and melt mixing promotes CNT distribution in PMMA matrix [12].

Changing the PEC/PLA composition, structural and morphologies blends with the melt-quench operation may offer rise to distinct heat and mechanical characteristics. The current research was therefore held out to further assess the impact of the melt-quench method on the structural and physicochemical characteristics of PEC/PLA blends.

4-2 Experimental Procedure

4-2-1 Materials

A commercial grade poly(L-lactic) acid (PLA, M_w = 165,000 with polydispersity index 1.7) and poly(ethylene carbonate) (PEC QPAC®25, M_w = 138,000 with polydispersity index 3.7) from Empower Materials, USA were used in this study; the chemical structures of both polymers are shown in Fig. 4-5. The PLA was first dried for 5 hours in a vacuum oven at 60 ° C to extract all moisture content. A gel permeation chromatography, TOSOH ECOSEC HLC8320 system with two columns (TSKgel GM_{HHR}-H, TOSOH CO.) was used to determine the molecular weights of PEC and PLA. HPLC grade chloroform was used as eluent at a flow rate of 1.0 mL/min, and the calibration was performed with polystyrene standards. PEC was purified by dissolving it in acetonitrile and washing it with excess methanol before drying for 24 h in a vacuum oven at 60 ° C. Before preparing the mix, PEC and PLA were both held in a glove box.

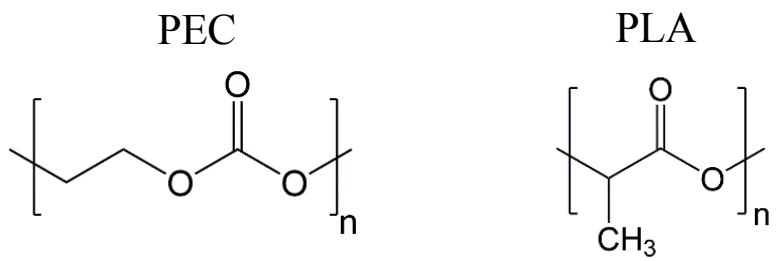

Fig. 4-5 Structure of poly(ethylene carbonate) (PEC) and poly(lactic acid) (PLA).

4-2-2 Sample Preparation

A blend of PEC/PLA was prepared by casting of a solution in which predetermined weights of both polymers were dissolved in chloroform and stirred at room temperature for 24 h. Differing blend ratios of 0, 10, 30, 40, 50, 60, 70, 90 and 100 wt% PEC content were used. The ratio of PEC to PLA is specified as the PEC/PLA blend; for example, 10/90 represents 10 wt% PEC/90 wt% PLA blend. A teflon petri dish was used to cast the PEC/PLA solution, and excess solution was removed using a vacuum evaporator. The film sample was further dried in a vacuum oven for 24 h at 60 °C. The effect of the melt-quench process on the PEC/PLA blends (as cast) was studied, as follows. The PEC/PLA blend sample as cast was sandwiched between aluminium sheets (20 μm thick) with a teflon spacer (200 μm thickness), then preheated at 180 ºC for 5 min and hot-pressed at 60 MPa for 5 min. High pressure was used to prepare a thin film for the melt-quenched PEC/PLA blends. Then, PEC/PLA were melt-quenched from fast rate at 6 ºC/s to 0 ºC. The samples were then cooled in ice water for 10 min. The melt-quenched PEC/PLA blends were analyzed so as to determine their thermal, structural and mechanical properties.

4-2-3 Characterization

Optical properties of the film samples were determined by measuring the percent transmittance using a JASCO V-650 UV-vis spectrophotometer. A rectangular sample was placed directly in the side of spectrophotometer magnetic cells, and an empty test cell was used as reference. The transparency of the films was determined by measuring the percent transmittance in the visible light range, at 660 nm, and average values of the transmittance for two samples were calculated. A DSC7020 system (Hitachi Hightec Co.) was used under dry N_2 to measure the thermal properties of all samples. The thermal properties of the melt-quenched PEC, PLA and PEC/PLA blends were quantified using non-isothermal measurement. The sample was weighed in the range 3-6 mg and sealed in an aluminum pan, and then underwent the DSC procedure. The sample was heated from -40 °C to 200 °C at a heating rate of 10 °C/min. Upon heating to 200 °C, melt-quenched

PEC/PLA blends are found to have a glass transition temperature (T_g), followed by cold-crystallization of PLA (T_{cc}); the melting temperature (T_m) of all melt-quenched PEC/PLA blends was determined as the temperature at the maximum value of the melting peak. The crystallinity of PLA (X_c), which is normalized by PLA weight fraction (X_{PLA}), was calculated using the following Eq. (4-1):

$$X_c\,(\%)=\{(\Delta H_m-\Delta H_{cc})/\Delta H^\circ_m\}\times(100/X_{PLA}) \qquad \text{Eq. (4-1)}$$

where ΔH_m (J/g) is the melting enthalpy of PLA, and ΔH°_m is the theoretical melting enthalpy of a 100 % crystalline PLA, which is reportedly 107 J/g [8,13]. The value is able to quantify the presence of α' or α crystal modifications or the influence of D-lactic acid units in the analyzed poly(lactic acid). Analysis of the effect of crystal formation occurring in the melt-quench process was then determined by XRD measurement using a Rigaku Smartlab with a Cu-Kα radiation source (λ= 0.1542 nm) and a Cu-K_β filter at room temperature. The voltage was 40 kV, and the current was 200 mA. Scanning was performed in the range of 2°-60° at a scanning speed of 4°/min. To determine the mechanical properties of the melt-quenched PEC/PLA blends, load testing took place using an IMADA Force Gauge ZTA-DPU with an elongation rate of 10 mm/min. At least five samples were measured to verify the reproducibility of the mechanical properties, and the mean values for each composition were taken as accurate. Mechanical properties, such as Young's modulus (E), tensile strength (σ), elongation at break (ε), modulus of resilience (U_R) and the modulus of toughness (U_T) of the melt-quenched PEC, PLA and PEC/PLA blends were determined from the stress-strain (S-S) curves. The modulus of resilience and modulus of toughness were calculated by integration to give the area under the S-S curves approaching the yield and fracture points respectively. A scanning electron microscope (SEM, JEOL JCM600 Plus) was used to make morphological observations of the blend samples. Prior to the SEM observation, the specimens of blends were quenched and fractured using liquid nitrogen. The degradation temperatures of the melt-quenched PEC/PLA blends were determined using a TG/DTA7200 thermogravimetric analyzer (TGA, Hitachi Hitech). The samples weighed approximately 6 mg, and were heated from 30 °C to 600 °C at a rate of 10 °C/min.

4-3 Results and Discussion

4-3-1 Sample appearances (melt-quenched)

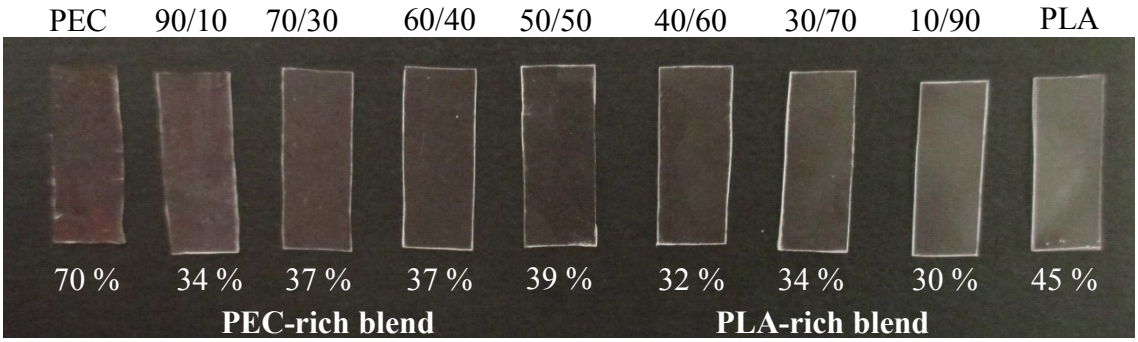

Fig. 4-6 Photographs of melt-quenched PEC, PLA and PEC/PLA blend films with their visible light percentage transmittance.

Fig. 4-6 shows photographs of the melt-quenched PEC, PLA and PEC/PLA blend films. The sample thickness was controlled in the range 100-200 μm. For PEC-rich blend films, the PEC/PLA blend films were more transparent with higher concentration of PEC. PLA-rich blend films were slightly opaque, consistent with the physical appearance of PLA film. This slight opacity might be due to small PLA crystals in the melt-quenched PEC/PLA blends. The transmittance of light at 660 nm in the visible band (400-700nm) for each blend confirms this variation in transparency; the percentage transmittance is shown in Fig. 4-6. Addition of PLA to PEC significantly reduced the optical transmittance of PEC to 30-39 %, depending on the PLA ratio. The decrease in light transmittance of the blend films is attributed to hindrance of the light passage when the ratio of PLA to PEC increases as a result of crystallinity, which can be further estimated from the Eq. (4-1) based on the heat of melting of PLA. The film surface was even and smooth for all blends as a result of the high pressure during the hot pressing in the melt-quench procedure.

4-3-2 Differential Scanning Calorimetry Measurements

This measurement aimed to determine the glass transition temperature (T_g) of PEC/PLA, the degree of crystallinity (X_c), the cold-crystallization temperature (T_{cc}) and the melting temperature (T_m) of PLA in blends, so as to clarify the effect of the melt-quench process on the thermal properties of PEC/PLA blends. DSC curves for all melt-quenched PEC, PLA and PEC/PLA blends are shown in Fig. 4-7, and the DSC data are set out in Table 4-1. For amorphous PEC, there is a significant difference in T_g, from 11 °C to -5 °C as reported previously [8], upon the introduction of the melt-quench process to PEC. This is due to the change in molecular weight of PEC as a result of the high temperature treatment during hot pressing. Several factors contribute to the value of T_g, including molecular weight, molecular symmetry, chain flexibility (or stiffness) with the presence of a side group, chain branching and intermolecular forces [14]. Since PEC is thermally weak, it is possible that, at 180 °C, PEC undergoes end chain unzipping or chain scission [15] to give slight changes in molecular weight and improved flexibility that contributes to the low T_g value.

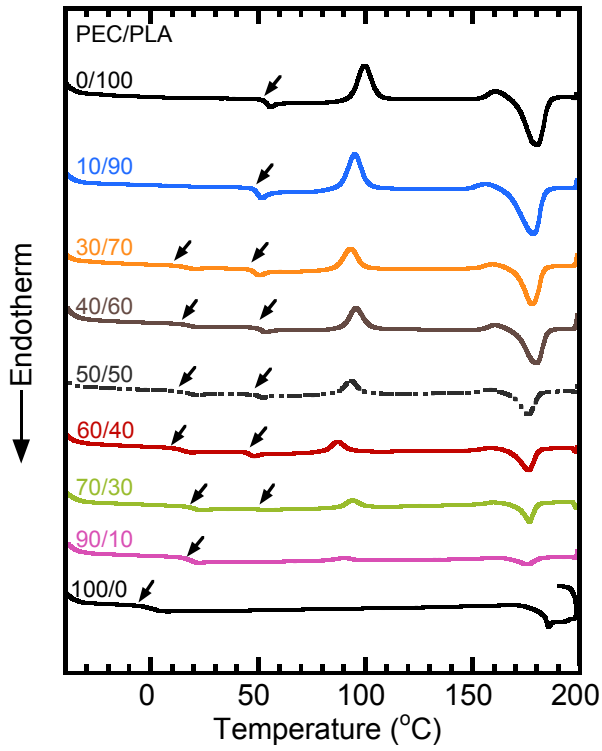

Fig. 4-7 DSC curves of melt-quenched PEC, PLA and PEC/PLA blends.

In the case of melt-quenched PLA and PEC/PLA blends, upon heating to 200 °C at a rate of 10 °C/min, melt-quenched PEC/PLA blends exhibit a glass transition temperature, around 10 °C to 50 °C, which correspond to T_g for melt-quenched PEC and PLA respectively. Then, occurs the cold-crystallization (T_{cc}) of PLA at around 98 °C, the crystal phase transformation (T_r) at around 161 °C [16], and the melting point of all PLA crystals at a melting temperature (T_m) near to 180 °C. For all blends, except for PEC90/PLA10 and PEC10/PLA90, there were two values of T_g, both positioned between the T_g values of PEC and PLA homopolymers. This shifting in the values of T_g is due to the partial miscibility feature as reported earlier [8]. For the PEC90/PLA10 and PEC10/PLA90 blends, the glass transition temperature of the minor phases is smaller and scarcely noticeable compared with the other compositions (as shown in Fig. 4-7) as these are the lowest concentrations of PEC and PLA in any blend.

Table 4-1 DSC data of melt-quenched PEC, PLA and PEC/PLA blends.

PEC/PLA	T_{gPEC} (°C)	T_{gPLA} (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_r (°C)	ΔH_r (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
0/100	-	51	98	-32	161	-5	181	40	3
10/90	15	47	93	-31	155	-4	176	43	8
30/70	12	46	91	-19	155	-4	176	29	8
40/60	14	48	93	-13	159	-2	178	23	12
50/50	13	46	93	-14	158	-3	177	21	7
60/40	10	44	86	-11	159	-2	179	18	12
70/30	16	48	91	-7	161	-2	174	11	6
90/10	15	45	88	-2	160	-1	174	4	9
100/0	-5	-	-	-	-	-	-	-	-

As a result of molecular interaction between PEC and PLA in the blend, thermal degradation of PEC is lessened with the addition of 10 wt% PLA, for which the temperature degradation of PEC rises to 229 °C [8]. It is possibly the case that, at 180 °C, the melt-quench process scarcely influences the partial miscibility interaction between

PEC and PLA. In support of this hypothesis, mobility of chains in melt-quenched PEC in the PEC/PLA blends is restricted by the appearance of small amounts of the PLA crystalline phase even at very low concentrations such as 10 wt% PLA, causing an increase in T_g of PEC of around 10-16 °C, and in other compositions depending on the concentration of PLA; this is in contrast with solely melt-quenched PEC which T_g was initially -5 °C. Melt-quenched PLA exhibited two exothermic peaks, in which the low temperature peak is around 98 °C and is due to cold-crystallization, and the peak at high temperature is due to the phase transition of the unstable crystal, such as the α' form [17–21], to a more stable form. This is due to crystal polymorphism of PLA that is a result of some defect or less stable crystals, formed during the cold-crystallization event with lower melting temperature, transforming to a more stably ordered structure. The characteristics of melt-quenched PLA are similar to the parameters reported by Ohtani *et al.*, [16] and Tsuji and Ikada [22,23]. The cold-crystallization temperature indicates that PEC added to PLA acts as a nucleating agent, which decreases the cold-crystallization temperature of PLA in the blends by more than 12 °C with the addition of 60 wt% PEC (see Fig. 4-8).

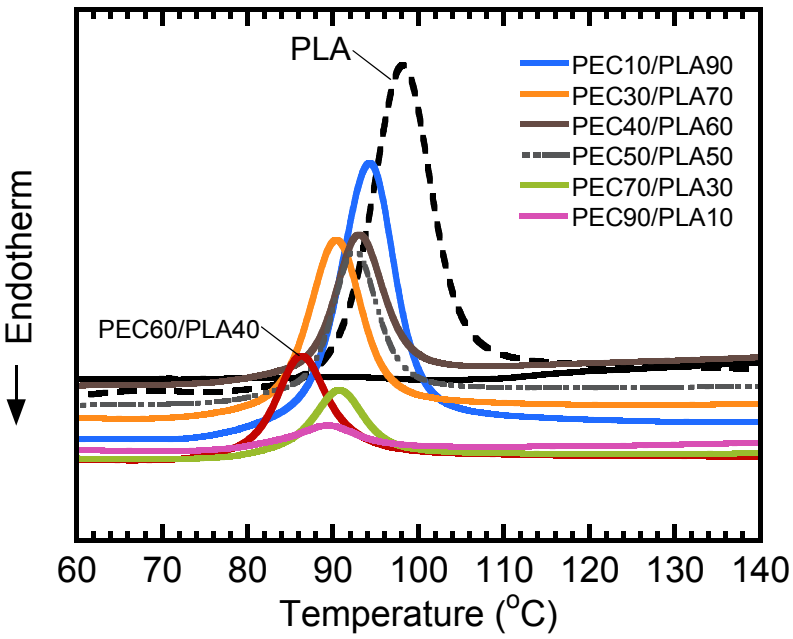

Fig. 4-8 Cold-crystallization of PLA for melt-quenched PEC, PLA and PEC/PLA blends.

Similar observations have been reported in which the addition of high flexible aliphatic carbonate such as poly(butylene carbonate) (PBC) induces nucleation leading to the PLA crystallization [24]. This is contrary to the report of Wei *et al*. that PPC limits the crystallization rate of PLA [25]. Crystallinity of PLA in melt-quenched PEC/PLA blends obviously runs at 6-12 %, depending on the PEC/PLA ratio determined by Eq. (4-1), whereas for PLA the value is initially 3 %. In the blends, it was therefore impossible to obtain completely non-crystalline PEC/PLA blends following the melt-quench treatment. Similar results have been reported for PVDF/PMMA blends, for which, upon rapid quenching, phase separation is tends to occur such that semi-crystalline PVDF crystallizes out of miscible blends [11]. The crystallinity of PEC/PLA blends (as shown in Table 4-1) increases with the addition of PEC, as shown by the PEC40/PLA60 blend; flexible PEC, added in the blend, enhances the chain mobility. Crystallinity of PEC/PLA blends also increases with the highest ratio of PLA as shown by PEC60/PLA40 blend. For melt-quenched PLA and PEC/PLA blends, the exothermic peak (H_r) related to the crystal phase transformation is small in comparison to the exothermic cold-crystallization (H_{cc}), and H_r is influenced by the ratio of PLA in the blend. H_r is relatively small in PEC-rich blends. The addition of PEC does not cause any significant deviation in the melting temperature of PLA crystals for melt-quenched PEC/PLA blends.

4-3-3 Crystal structures

Formation of crystal structures was confirmed in the case of the low crystallinity of melt-quenched PLA and PEC/PLA blends by the heat of melting PLA as measured using DSC, and further confirmed by XRD measurement. The XRD profiles for all melt-quenched PEC/PLA blends were compared with melt-quenched PEC and PLA, as shown in Fig. 4-9. The XRD curve for melt-quenched PLA was broad without any intense peak, showing reflection due to the crystalline α' and α form represented by typical semi-crystalline PLA, with the peak located between 16.7° and 19.2° attributed to (110)/(200) and (113)/(203) planes. There was no reflection due to (211) planes at 22.3°, corresponding to the characteristics of α form crystal. There are small and broad shoulder peaks around 24.0° to 25.2° that may be associated with the peak of the (213) and (116)

planes of pure PLA, as in Li *et. al* [26] reported on α and α' form crystal presents at crystallization temperature of PLA within 96 °C to 106 °C. These low intensity peaks may correspond to the 3 % PLA crystallinity inferred by DSC for the melt-quenched PLA. For all melt-quenched PEC/PLA blends, the broad peak in intensity is associated with the large amorphous phase of PEC and PLA. Large amorphous deposits of PEC and PLA have covered the PLA crystals according to the low and broad peaks around 24.0° to 25.2°, similar to PLA for the melt-quenched PEC/PLA blends.

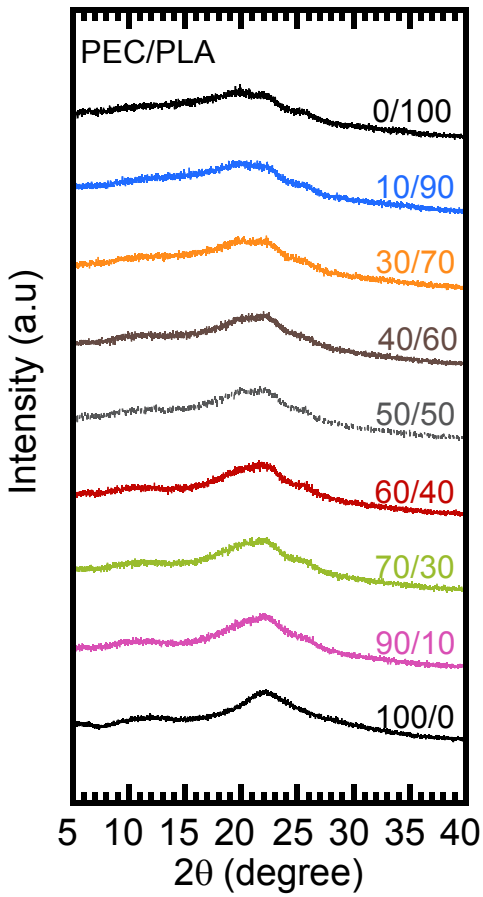

Fig. 4-9 XRD profile of melt-quenched PEC, PLA and PEC/PLA blends.

To gain further insight into crystal formation in the melt-quenched PEC/PLA blends, melt-quenched PEC/PLA blends including PEC10/PLA90, PEC40/PLA60 and PEC50/PLA50 blends were crystallized isothermally at 120 °C for 4 h. The XRD profile

clearly shows the transformation of largely amorphous melt-quenched PEC/PLA blends to crystallized PEC/PLA blends (see Fig. 4-10).

As a result of the isothermal crystallization, the XRD profile of PLA shows a few reflections due to crystal growth attributed to α' and α forms. The high intensity reflection at 16.7° and 19.2° attributed to (110)/(200) and (113)/(203) planes of PLA crystals [18] are clearly visible. Reflections due to the (011), (211) and (1010) planes correspond only to the α form crystal and are located at 14.9° [16,27,28], 22.3° [13,28] and 31.7° [18,26] respectively. In the PEC/PLA blends, formation of more α' and α is clearly observed in the PEC10/PLA90 blend, in which reflection due to the (1010) plane is greater than in the XRD profile of PLA, suggesting that addition of 10 wt% PEC to PLA induces greater crystallization and promotes PLA crystallinity, consistent with Table 4-1. For the PEC40/PLA60 and PEC50/PEC50 blends, increasing ratio of the PEC to PLA, and causing the reflection of (011), (310)/(020) located at 29.0^{o} [26], although the (1010) planes which corresponds to formation of α' and α crystals are relatively weak and virtually absent. These results show that increasing the PEC in the melt-quenched PEC/PLA blends influences the rate of crystallization and the formation of both α' and α crystals in the blends.

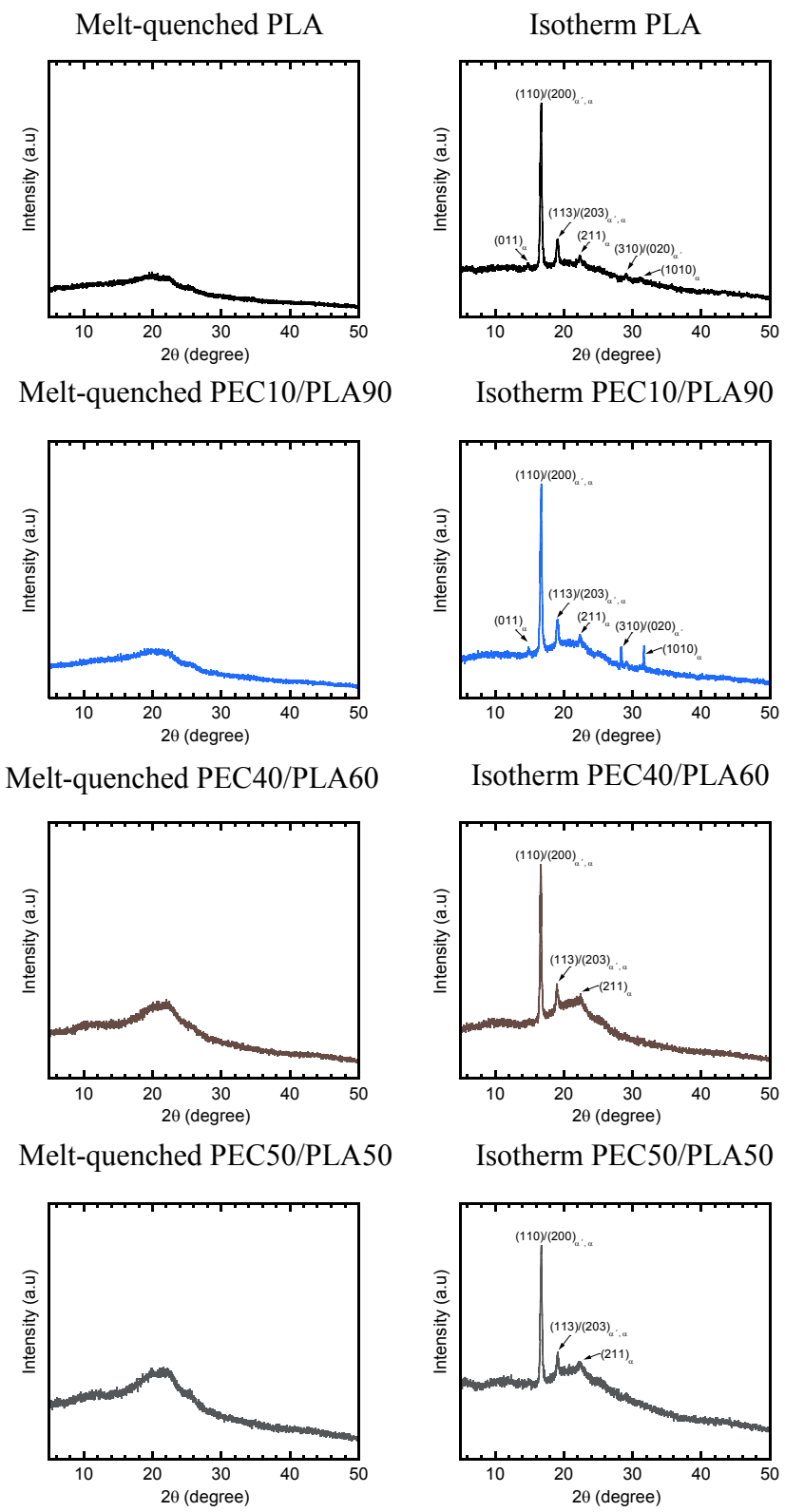

Fig. 4-10 XRD profiles of melt-quenched and isothermally crystallized PEC/PLA blend.

4-3-4 Mechanical Properties

S-S curves of melt-quenched PEC, PLA and PEC/PLA blends are shown in Fig. 4-11, and the mechanical properties of the melt-quenched PEC, PLA and PEC/PLA blends are set out in Table 4-2. The Young modulus (E) and tensile strength (σ) of melt-quenched PLA are respectively 1.9 GPa and 41.6 MPa. Elongation at breakage (ε) of melt-quenched PLA is only 15.1 %, due to the brittleness that is responsible for the low tensile toughness (U_T) of 5.1 MJ/m^3. In the melt-quenched PEC/PLA blends, PEC enhances the tensile toughness of PLA. The Young modulus and tensile strength of melt-quenched PEC/PLA blends decreases with decreasing PLA content. The elongation at breakage increased with increasing PEC fraction, because PEC has a stress-strain ductile profile in which the elongation at breakage of PEC increased by more than 600 % upon stress loading, to give a high strain hardening modulus [5]. In our previous study, the greatest improvement in PLA toughness with the addition of PEC was in the PEC50/PLA50 blend, with a peak tensile toughness of 45.8 MJ/m^3 using the solution casting method [6].

The high crystallinity of PLA, and the multiphase morphologies consisting of sea-island morphology with small domains of PEC and PLA distributed in each of the PEC and PLA phases, and the layer structure due to the intermolecular interaction between the PEC and PLA phases [8] may all contribute to the enhanced toughness of this PEC/PLA system. In contrast, the melt-quenched PEC/PLA blend has low toughness values, in the range 1.1-16.3 MJ/m^3, depending on the PEC and PLA ratios; this is due to the low values of E, σ and ε. A slight enhancement in the toughness of PLA and resistance of PEC can be seen in the PEC10/PLA90 and PEC10/PLA90 blends. The toughness of melt-quenched PLA is slightly improved, from 5.1 MJ/m^3 to 5.5 MJ/m^3, with 10 wt% PEC. For melt-quenched PEC, the modulus of toughness increased from 11.8 MJ/m^3 to 16.3 MJ/m^3 with 10 wt% PLA added. In PLA-rich blends, PEC promotes toughness, enabling ductile yield mechanisms and preventing brittle fracture. Reduced toughness is seen in other compositions of melt-quenched PEC/PLA blends. Melt-quenching significantly influences the mechanical properties, giving rise to variation in the tensile toughness. Melt-quenched PEC/PLA blends have low PLA crystallinity of around 6-12 %,

suggesting that good high chain mobility of PEC is promoted by the melt crystallization of PLA.

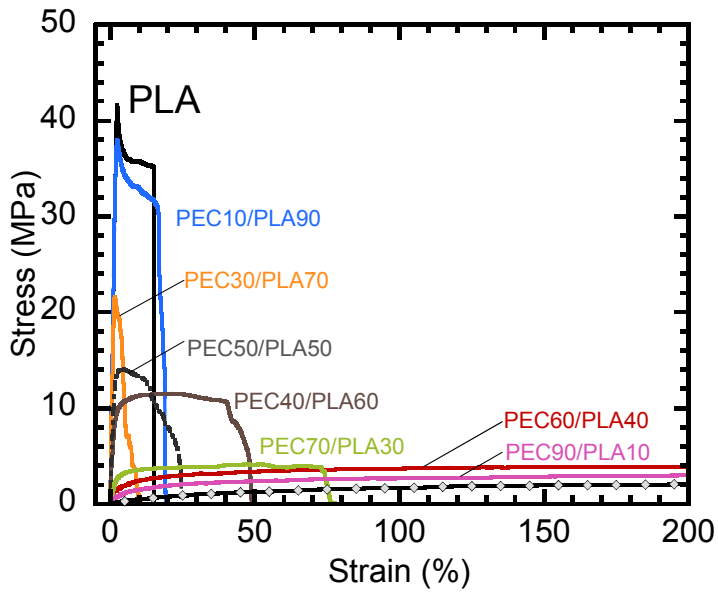

Fig. 4-11 Stress-strain curves of melt-quenched PEC, PLA and PEC/PLA blends.

Table 4-2 Mechanical properties of melt-quenched PEC, PLA and PEC/PLA blends.

PEC/PLA	Young's Modulus E (GPa)	Tensile Strength σ (MPa)	Elongation at Breakage ε (%)	Modulus of Resilience U_R (MJ/m^3)	Modulus of Toughness U_T (MJ/m^3)
0/100	1.9	41.6	15.1	0.28	5.1
10/90	1.9	37.9	19.3	0.22	5.5
30/70	1.6	21.5	10.8	0.09	1.1
40/60	0.6	11.5	48.8	0.02	4.6
50/50	0.8	14.0	24.5	0.08	2.6
60/40	0.1	3.9	216.9	0.01	7.3
70/30	0.1	4.1	76.8	0.02	2.8
90/10	0.03	3.1	569.3	0.01	16.3
100/0	0.005	2.2	607.0	0.02	11.8

Rearrangement of PEC and PLA chains during chain folding arises from the "reeling in" of chains during crystallization, leading to disentanglement of the chains from the melt and resulting in a lower entanglement density, and consequently a lower strain hardening modulus due to the rapid cooling [29]. Also, as reported in previous studies, the PLA exhibits various types of crystal modification (α, ß, and γ forms), depending on the crystallization conditions [18,19,21,30–32]. The rearrangement of amorphous PEC and PLA phases and crystal modifications with α and α' forms may have contributed to the differing PEC and PLA phase morphologies (as shown in Fig. 4-15), giving rise to low tensile toughness for melt-quenched PEC/PLA blends relative to those prepared by the solution casting method. The PEC/PLA blends (as cast) with higher crystallinity contain more dense regions, giving higher tensile strength and higher strain hardening modulus (stiffness) than an amorphous analog, based on our previous studies of PEC10/PLA90, PEC40/PLA60 and PEC50/PLA50 blends [6]. Fig. 4-12 illustrates the phase's morphology changes upon the melt quenching on the PEC/PLA blends following disentanglement of chains from the melt and cold quenched. This claim is also supported by the observation by Tsuji and Ikada [10], suggesting that ordered PLA structures formed during the solvent evaporation process in the solution casting methodology contribute to the more dense crystalline regions.

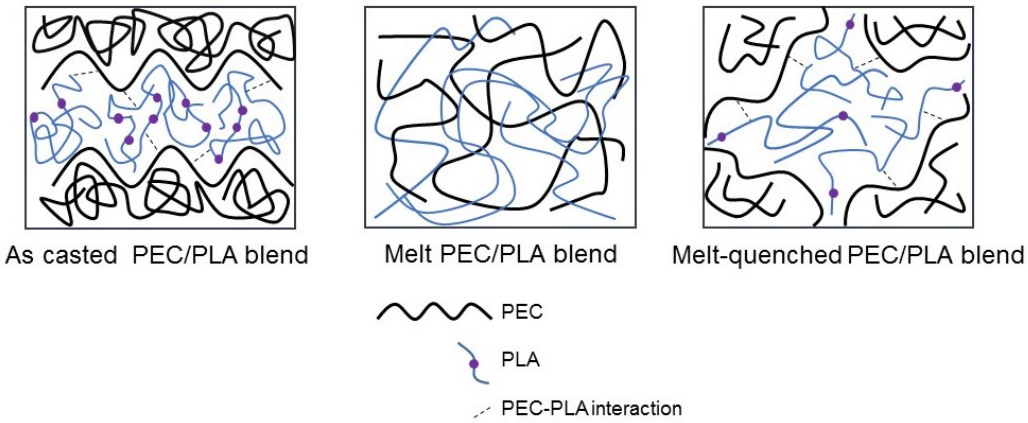

Fig. 4-12 Illustrations of entanglement rearrangement of amorphous PEC and PLA phases showing by as casted and melt-quenched PEC/PLA blends.

Based on the Pukanszky's model (as shown in Fig. 4-13), it is worth to mention that the melt-quenched PEC/PLA blends have low interfacial adhesion between PEC and PLA phases, contrary to the one prepared by the solution casting which clearly presented in chapter 3.

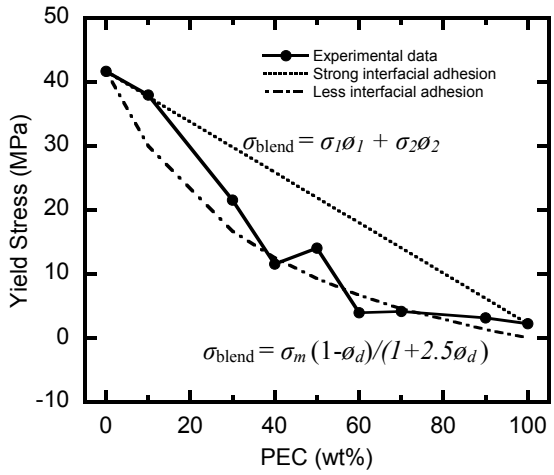

Fig. 4-13 Yield stress melt-quenched PEC/PLA blends.

4-3-5 Surface Morphology

We used a scanning electron microscope to further study the phase morphology of melt-quenched PEC/PLA blends having low toughness. Figs. 4-14 (a) and 14 (b) show SEM images of cross-section fracture following quenching with liquid nitrogen of PEC and PLA, and Fig. 4-15 shows the melt-quenched PEC/PLA blends. The surface of amorphous PEC shows smoother breakage track lines than the surface of rough PLA that corresponds to brittleness in fracturing.

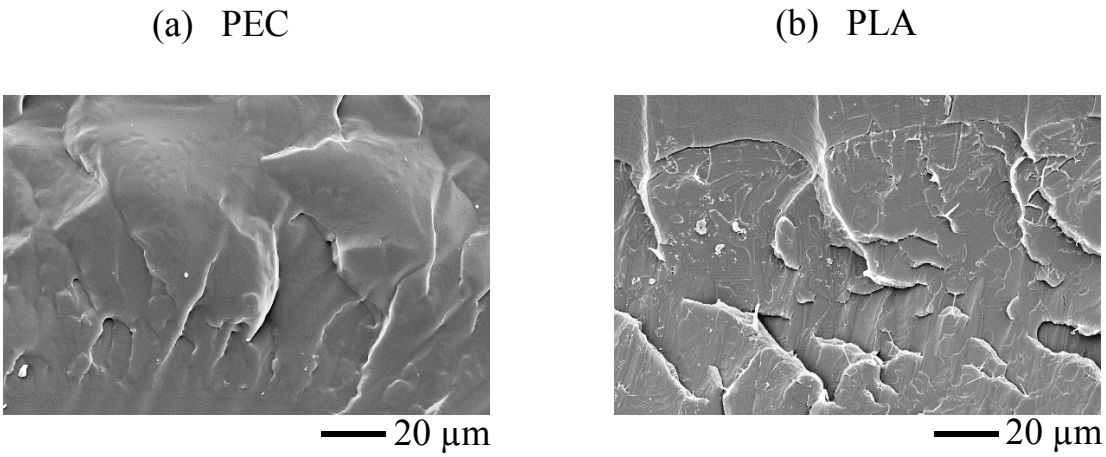

Fig. 4-14 SEM images of cross-section fracture following quenching with liquid nitrogen; (a) PEC and (b) PLA. (Scale bar 20 μm)

In the melt-quenched PEC/PLA blends, typical sea island phase morphology is observed, with the presence of small domains in the PEC-rich blends, as seen in the PEC90/PLA10 blend (see Fig. 4-15 (a)). The homogeneous distribution of the PLA domains in the PEC matrix is the result of the slight enhancement in the PEC resistance discussed earlier. In the case of PEC90/PLA10 blend, for instance, upon stress loading, more energy is dissipated in the PEC matrix and transferred to small PLA domains that are distributed homogeneously in the matrix, causing an increase in the resistance of PEC to failure; U_T = 16.3 MJ/m^3, whereas for PEC which initially U_T = 11.8 MJ/m^3. The PLA domains increased in size with increasing PLA concentration, as seen in the melt-quenched PEC70/PLA30 blend. Less interfacial adhesion between the PEC and PLA phases is noticeable in the blend, so that it fractures readily as implied by the low elongation at break, 76.8 % in comparison with 569.3 % for the melt-quenched PEC90/PLA10 blend. Furthermore, with increasing PLA content up to 60 wt%, the essentially continuous PEC phase gradually transforms into dispersed droplets, as seen in the PEC40/PLA60 blend. As the PLA content increases further, this is followed by coalescence of PLA in the PEC matrix, to form a typical sea-island morphology with domains of PEC in the PLA matrix.

The melt-quenched PEC60/PLA40 and PEC40/PLA60 blends both exhibited a rough continuous matrix, in contrast with PEC70/PEC30 and PEC30/PLA70 blends with better toughness performances. Crystallinity of melt-quenched PEC60/PLA40 and PEC40/PLA60 blends is slightly higher than that of PEC70/PEC30 and PEC30/PLA70 blends, which be the reason for the emergence of improved tensile toughness. The PEC domains are dispersed in the PLA matrix, as seen in PEC10/PLA90 and PEC30/PLA70 blends, although the domain size is larger than for PLA in the PEC-rich blend system, so that there is less interfacial adhesion between the PEC and PLA phases in the PLA continuous phase. Interfacial adhesion is relatively strong when PEC is in the continuous phase, in the PEC90/PLA10 blend. Similar results have been reported for PLA/PPC blends by Ma *et al.* [33], when phase inversion occurs in the two-phase system between 30-50 wt% PPC. The phase separation and sea-island morphology observed in melt-quenched PEC/PLA blends might be due to the effect of rapid cooling cause that triggers the spinodal decomposition (SD) mechanism [34].

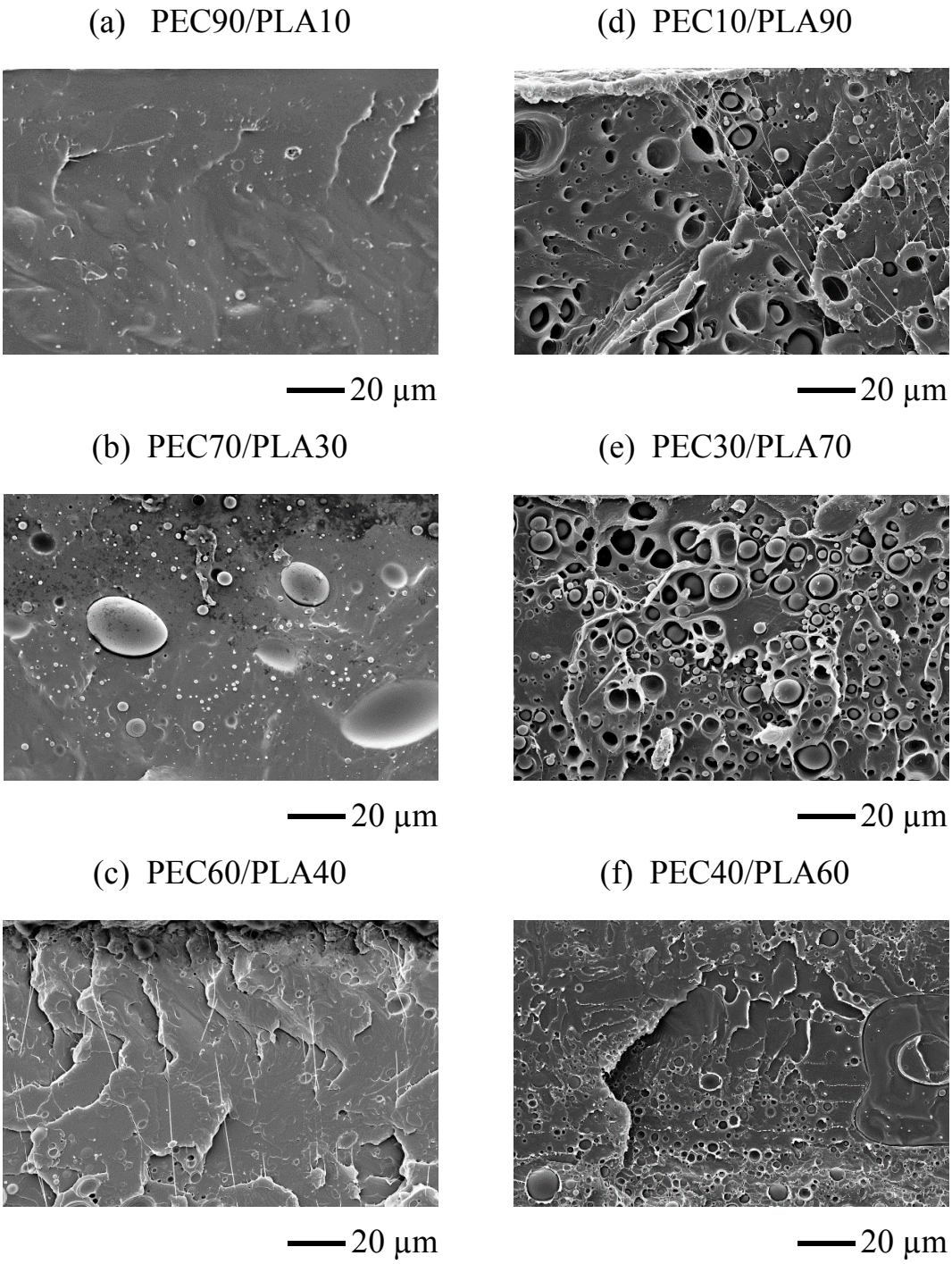

Fig. 4-15 SEM images of cross-sections obtained by freeze-fracturing with liquid nitrogen of (a) PEC90/PLA10, (b) PEC70/PLA30, (c) PEC60/PLA40, (d) PEC10/PLA90, (e) PEC30/PLA70 and (f) PEC40/PLA60 blends. (Scale bar 20 μm)

Two-phase separation of PLA/PBAT blends due to SD has also been reported during quenching [35]. At high temperatures, the supersaturated polymer blend solution with one thermodynamic phase, with a decrease in the Gibbs energy without a nucleation barrier, spontaneously forms two coexisting phases upon rapid cooling [34–36]. In addition, PEC and PLA interact favorably, upon rapid cooling, and two coexisting phases obviously promotes the tendency of PLA to crystallize out of the partially miscible PEC/PLA blends.

4-3-6 Thermogravimetric Analysis Measurements

Thermal degradation of melt-quenched PEC/PLA blends as presented in Fig. 4-16. Thermally weak characteristic of melt-quenched PEC can be seen from the T_{d5} at 175 °C, which is shown in Table 4-3. Interestingly, in melt-quenched PEC-rich blends, the presence of 10 wt% of PLA improves thermal degradation, T_{d5} of the melt-quenched PEC by more than 45 °C. Thermal degradation temperature gradually increased with increasing PLA concentration in the melt-quenched PEC/PLA blends. PEC facilitates thermal degradation of melt-quenched PEC/PLA blends to almost 50 °C as shown by T_{d5} of PEC10/PLA90 blend in comparison with the melt-quenched PLA which at 334 °C. With these results, thermal stability of PEC/PLA blends is continued to establish even with the influence of the melt-quench modification.

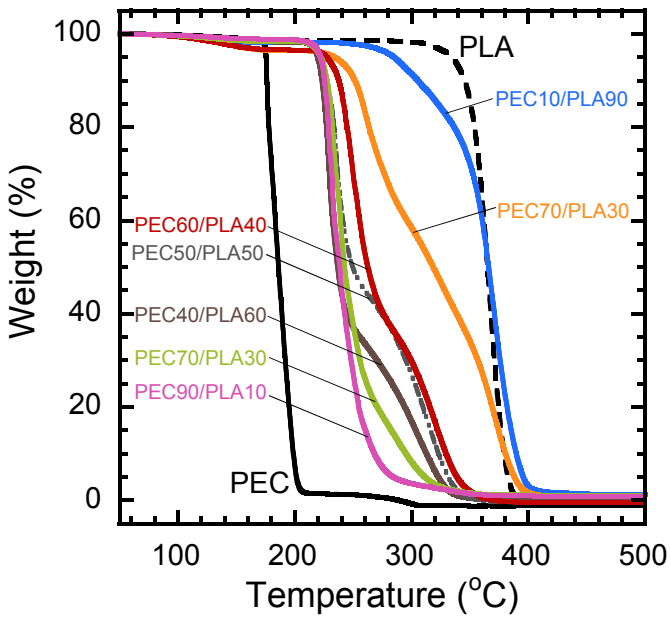

Fig. 4-16 TGA curves of melt-quenched PEC, PLA and PEC/PLA blends.

Table 4-3 Thermogravimetric data of melt-quenched PEC, PLA and PEC/PLA blends.

PEC/PLA	T_{d5} (°C)	T_{max} (°C) PEC	T_{max} (°C) PLA
0/100	334	-	370
10/90	285	291	372
30/70	234	262	373
40/60	220	230	307
50/50	222	237	315
60/40	227	251	322
70/30	222	247	303
90/10	222	233	233
100/0	175	191	-

4-4 Melt-quenched and as casted PEC/PLA blends

In the earlier chapter 2, the preparation and characterization of PEC/PLA blends by solution casting method have well-described. Additional of melt-quenching to these blends (as cast) were found to give different blend morphologies and physicochemical properties as evaluated in this present chapter. Nevertheless, to some extent, PEC/PLA blends have shown better functionality related to its degradability, depending on the PEC content upon the hydrolysis in the alkaline solution, and in more detailed the mechanism of the hydrolytic degradation have also been presented in chapter 3. The comparison between these two preparations method, considering some of the properties such as the mechanical properties, PLA crystallinity, type of crystal formation, thermal stability and the blend phases for PEC/PLA blends, are presented in the Table 4-4.

As shown by the PEC/PLA blends of 50/50 ratio, in comparison to melt-quenching technique, the preparation by solution casting results in greater of the tensile strength, elongation at break and toughness properties which the values are 27.7 MPa, 150.9% and 45.8 MJ/m^3 relative to 14.0 MPa, 24.5% and 2.6 MJ/m^3 respectively. Whereas, the low mechanical properties of melt-quenched PEC/PLA blends as a result of the highly amorphous PEC and PLA phases in the blend with the evidence of the crystallinity of PLA at 6-12 % which these values are lower than the crystallinity of as casted PEC/PLA blends at all compositions.

For as casted PEC/PLA blends, formation of α' and α crystals are characterized as a result of the high intensity for reflection planes peak at (110)/(200) and (113)/(203) that were clearly observed by XRD, while the highly amorphous phase is induced by the melt-quenching causing an insignificant appearance of these peaks in the case of melt-quenched PEC/PLA blends. Nevertheless, the low values in the crystallinity for melt-quenched PEC/PLA are corresponded to a different structure of crystal presence with the reflection plane of (213) and (116), representing α' and α crystals. From the T_{d5} values, the melt-quenched PEC/PLA blends thermal stability is continued to establish similar to one prepared by solution casting, though these blends were exposed to high

temperature at 180 ^{o}C in the melt-quenching procedure as a result of the interaction between PEC and PLA as clearly discussed in chapter 2.

Table 4-4 Comparison for melt-quenched and as casted PEC/PLA blends prepared by different methods.

Characterization	Solution casting	Melt quenching
Mechanical Properties:		
Tensile strength (MPa)	27.7	14.0
Elongation at break (%)	150.9	24.5
Toughness (MJ/m^3) (for 50/50 ratio)	45.8	2.6
PLA crystallinity:		
X_c (%)	25-47	6-12 (PLA crystallinity could further be modified)
Crystal type formed	α' and α $(110)/(200)_{\alpha',\alpha}$ $(113)/(203)_{\alpha',\alpha}$	α' and α $(213)_{\alpha}$ $(116)_{\alpha'}$
Thermal stability T_{d5} (^{o}C)	229-274	222-285
Phases PEC/PLA blend	Amorphous/semi crystalline	Highly amorphous

4-5 Conclusion

The thermal stability of partially miscible PEC/PLA blends allows for further modification by melt-quenching. The melt-quench process induced low crystallinity of PEC/PLA blends around 6-12 %, and adding PEC to PLA increased the PLA crystallization. The mechanical properties of melt-quenched PEC/PLA blends were studied and showed that the elongation at breaking increased with increasing PEC content, whereas the tensile strength decreased. Upon rapid cooling, the morphology of PEC/PLA blends leads to low toughness, especially for PEC30/70PLA and PEC70/30 blends due to large domains which cause reduced interfacial adhesion between the PEC and PLA phases. In PLA-rich blends, addition of 10 wt% PEC to PLA improved the tensile toughness slightly from 5.1 MJ/m^3 to 5.5 MJ/m^3; the ductile PEC acts to increase the toughness of PLA. SEM images of fracture cross-section surfaces of melt-quenched PEC/PLA blends confirmed that PEC and PLA gives rise to a two-phase structure in which small PLA domains distributed in the continuous PEC phase contributed to the greatest interfacial adhesion in the sea-island morphology of PEC-rich blends, giving improved resistance to failure of PEC; the tensile strength and toughness increased from 2.2 MPa and 11.8 MJ/m^3 to 3.1 MPa and 16.3 MJ/m^3 respectively. PEC/PLA blend prepared either by melt-quenching or solution casting from biodegradable PEC and PLA, gives uniqueness characteristic for PEC/PLA blend which are expected to be an alternative PLA modification, suitable as a raw material in applications including sutures, implants, biologically active controlled release devices, and also as packaging materials.

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Chapter 5

Summary and Future Perspectives

Massive attention in fulfil the environmental concerns and rapidly increasing demand for biobased/biodegradable polymers to suit in the applications such as packaging, biomedicals, textiles, and others have been highlighted, focusing on poly(lactic acid) (PLA). Interests in PLA modifications are still growing following low toughness and biodegradability due to brittleness and slow degradation upon hydrolysis, respectively. In the past years, many attempts have been made to improve PLA toughness and biodegradability with various modification approaches such as copolymerization and plasticization. Alternatively, PLA blend is foreseen a beneficial approach as a result of easy and more cost-effective and efficiency for PLA modification, but the properties of modified PLA such as mechanical strength and degradability are still limited by the miscibility, phases morphology and non-biodegradable additives. In this study, poly(ethylene carbonate) (PEC)/poly(lactic acid) (PLA) blends were developed. PEC can be synthesized by the alternating copolymerization of carbon dioxide (CO_2) with epoxides, and it contains high stress-strain hardening and possesses better degradability properties, and to some extent PEC and PLA are compatible due to the chemical structure resemblances.

In chapter 2, poly(ethylene carbonate)/poly(lactic acid) blends were successfully prepared by means of a solution film-casting method, and their physicochemical, miscibility and morphology properties were investigated. PEC/PLA blends exhibit partial miscibility and are characterized by the interaction of the ester and carbonic ester groups. One such interaction is between partial charges in –C–O– in –O–C=O of PLA and the carbonyl –C=O of PEC. Another is between –C–O– in –O–C=O of PLA and –C–O– in $–CH_2–O–$ of PEC. The interaction between PLA and PEC due to molecular structure similarities and crystallinity of PLA varies the T_g value by more than 10 ºC across the blends. PEC does not significantly influence the melting temperature of neat PLA, but non-spherical spherulites are formed in PEC-rich blends, whereas the spherulites are spherical with an average size of 30 μm in PLA-rich blends. Crystallization of PLA and the crystallinity are influenced by the addition of flexible PEC and by the proportion of PLA in the blends. Interestingly, addition of at least 10 wt% PLA increased T_g, with a crystallinity, X_c of 47 % and better thermal degradation properties, with the temperature at 5 wt% weight loss (T_{d5}) more than 30 ºC higher than for neat PEC.

In chapter 3, thin films of PEC/PLA blend exhibiting improved toughness and degradability in alkaline solutions were prepared by a simple solution casting method. With the addition of 50 wt% PEC, the toughness of PEC/PLA blend was improved to a peak value of 45.8 MJ/m^3, in contrast to 6.7 MJ/m^3 for neat PLA. Young's modulus of PEC/PLA blends at low PEC ratio were fairly similar to that of neat PLA. Addition of more than 40 wt% of PEC enhanced the degradability of PLA in alkaline solution. The weight loss of hydrolysed PEC/PLA blends changed non-linearly with the addition of PEC, and depended strongly on PLA crystallinity and the ratio of PEC to PLA. This enhancement was attributed to the high toughness and degradability of PEC/PLA blends induced by partial miscibility, as reported previously. Toughness properties shown by PEC/PLA blends particularly the blend of 10/90 ratio were greater than the one modified PLA by plasticization and also comparable to some other PLA/non-biobased and PLA/biobased blends.

In chapter 4, the effect of the melt-quench process on the thermal, structural and mechanical properties of poly(ethylene carbonate) (PEC)/poly (lactic acid) (PLA) blends was further investigated as a result of better thermal stability. A largely amorphous phase of melt-quenched PEC/PLA blends was characterized, with crystallinity in the range 6-12 %, depending on the PEC and PLA ratios. The high chain mobility of PEC reduces the cold-crystallization temperature of PLA for the melt-quenched PEC/PLA blends by more 12 °C, as in the PEC60/PLA40 blend. Upon the rapid cooling, however, the morphology of PEC/PLA blend changes to enhance the toughness, especially for the PLA-rich blend. Addition of 10 wt% PEC to PLA slightly improved the tensile toughness, from 5.1 MJ/m^3 to 5.5 MJ/m^3, in which ductile PEC improves the toughness of PLA. SEM images of the quenched fracture cross-section of melt-quenched PEC/PLA blends confirmed that PEC and PLA are compatible, with a two-phase structure in which small PLA and PEC domains are distributed in the continuous PEC and PLA phases, respectively. This structure is responsible for the high interfacial adhesion in the sea-island morphology of PLA domains in PEC-rich blends, giving improved resistance to failure of PEC. However, the mechanical properties of PEC/PLA blends were found better by the preparation of solution casting method following high crystallinity of PLA for these blends.

To conclude, partial miscible PEC/PLA blends were successfully developed, and the blends showed improvement for tensile toughness and degradability in the alkaline solution. Thermal stability of these blends allows for additional melt-quench modification, decreasing the percentage of PLA crystallinity and influenced the mechanical properties. Addition of PEC to PLA is for seen an easy strategy for the development of new PLA binary system with biodegradable polymer with well-defined physicochemical and degradation properties. PEC/PLA blends that are prepared either by melt-quenching or solution casting from biodegradable PEC and PLA, provides an alternative pathway for polymer research and industry to further extend the processibility of this new PEC/PLA blend that may capable becoming a substitute raw material suitable in the applications such as sutures, implants, biologically active controlled release devices, and also as packaging materials due to the uniqueness characteristics for each blend systems.

List of publications

Related to this PhD Thesis

[1] **N.A. Ramlee**, Y. Tominaga, Preparation and characterization of poly(ethylene carbonate)/poly(lactic acid) blends, J. Polym. Res. 25 (2018) 54–62. https://doi.org/10.1007/s10965-018-1451-4.

(Q2: Impact factor 1.434)

[2] **N.A. Ramlee**, Y. Tominaga, Mechanical and degradation properties in alkaline solution of poly(ethylene carbonate)/poly(lactic acid) blends, Polymer (Guildf). 166 (2019) 44–49. https://doi.org/10.1016/j.polymer.2019.01.043.

(Q1: Impact factor 3.483)

[3] **N.A. Ramlee**, Y. Tominaga, Structural and physicochemical properties of melt-quenched poly(ethylene carbonate)/poly(lactic acid) blends, Polym. Degrad. Stab. (2019). https://doi.org/10.1016/j.polymdegradstab.2019.02.028.

(Q1: Impact factor 3.193)

Not Related to this PhD Thesis

[1] N.N. Said, F. Hamzah, **N.A. Ramlee**, N.N. Yunus, The effect of TiO_2 particles addition on the characteristics of Polysulfone membrane, Int. J. Adv. Sci. Eng. Inf. Technol. 8 (2018).

(Q3: Impact factor 1.31)

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