Tailoring the properties of bio-based and biocompostable polymer blends

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Tailoring the properties of bio-based and biocompostable polymer blends

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 22 juni 2011 om 16.00 uur

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Tailoring the properties of bio-based and biocompostable polymer blends

Conventional oil-based synthetic polymers (plastics) have shown an almost exponential growth during the past decades and currently more than 200 million tons are produced per annum, viz. approximate 35 kg per capita in the world. In view of the uneven consumption of plastics in the world, this number is expected to grow over 1000 million tons at the end of this century which is not sustainable in view of oil depletion, and the subsequent increase in price. Alternative fossil sources for producing chemicals and plastics are already in place such as coal and gas (methane) as pioneered by Sasol (SA) but geopolitical issues promote the use of biomass for making chemicals and plastics en route towards the bio-based society.

As an alternative for fossil feedstock, a lot of attention is paid nowadays to use polymers produced by nature, the so-called biopolymers, or to derive monomers from biomass to produce new and already known polymers. A particular class of polymers is the so-called biocompostable polymers, viz. polymers which biodegrade in composting facilities within a specific time span.

Well-known examples of bio-based and biocompostable polymers are poly(β-hydroxybutyrate) (PHB), poly(lactic acid) (PLA) and starch compounds. There are also in the market nowadays biocompostable polymers which are oil-based like poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT, Ecoflex®) and poly(ε-caprolactone) (PCL).

The performance of notably bio-based and biocompostable polymers, viz. PHB, PLA and starch compounds, is rather poor. The inherent drawbacks are temperature instability, lack of processability, brittleness and high price, notably PHB, limiting their developments and applications as a substitute for oil-based plastics. The thesis focuses on tailoring the properties of PHB-based blends (Chapter 2), PLA-based blends (Chapters 3 and 4) and starch-based blends (Chapters 5 and 6).

In order to enhance the toughness of PHB and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) biopolymers, PHB(V) was melt-blended with ductile PBS in Chapter 2. Considering the poor interfacial adhesion between PHB(V) and PBS, a free-radical initiator, i.e. dicumyl peroxide (DCP), was introduced to the PHB(V)/PBS melts to induce an in-situ compatibilization. As a result, the size of PBS domains was reduced to a
sub-micro range, the interfacial adhesion between the PHB(V) and PBS was enhanced and partial crosslinking of both the PHB and PBS phases (especially of PBS) was obtained. All these effects contributed to the increased toughness of the blends. It has to be noted that despite the partial crosslinking, the blends retained melt-processability.

Two routes for improving the toughness of PLA were probed – by blending with PBS with an in-situ compatibilization (Chapter 3), and by blending with ethylene-co-vinyl acetate (EVA) (Chapter 4). The PLA/PBS blends showed a high elongation at break in the order of 200 % in comparison with ~ 5 % of pure PLA. However, the notched impact toughness of the PLA/PBS blends was still low and comparable to pure PLA (~ 3 kJ/m²). To improve the impact toughness, a similar approach as used in Chapter 2 was carried out in the PLA/PBS blends, viz. in-situ compatibilization in the presence of DCP. Consequently, the size of the PBS domains was reduced by a factor of 4, accompanied by an increase in the interfacial adhesion between the PLA and PBS phases. The notched impact toughness of the PLA/PBS blends was improved by a factor of 10 after addition of 0.1 wt% DCP. The main toughening mechanism involved interfacial debonding and matrix yielding. In addition, the optical clarity of the PLA/PBS blends was improved due to a decrease in the size and crystallinity of the PBS domains.

A further improvement on the toughness of PLA was obtained by blending with EVA which is a commercially available commodity copolymer (Chapter 4). The compatibility and phase morphology of the PLA/EVA blends were tuned by the ratio of vinyl acetate and ethylene in the EVA random copolymers. The highest impact toughness (increased by a factor of 30) of the PLA/EVA (80/20) blends was achieved at a vinyl acetate content of approximately 50 wt%. The dominant toughening mechanism revealed by scanning electron microscope (SEM), transmission electron microscope (TEM) and small-angle X-ray scattering (SAXS) is internal rubber cavitation in combination with matrix yielding.

Since PLA/EVA (or EVA) can be biocompostable in the presence of starch (Patent WO2010043648), attempts were made, Chapters 5 and 6, to prepare PLA/EVA/starch blends with fine dispersion of starch and attractive properties by reactive blending in the presence of maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol (Chapter 5). The following procedure was used, EVA chains were grafted onto the starch molecules forming EVA-g-starch copolymers which acted as a compatibilizer and enabled a very fine dispersion of starch particles in the EVA matrix.

Subsequently, PLA was melt-blended with the pre-compatibilized EVA/starch compounds (Chapter 6). The fine dispersion of the starch phase (0.5 - 2.0 μm) was retained also in the
PLA/EVA/starch ternary blends in which EVA with starch has core-shell-like (or starch-in-EVA) morphology. The ternary compatibilized blends showed good and stable mechanical properties (during storage), e.g. elongation at break up to 150 % and notched impact toughness of 12 kJ/m².

The thesis provides possible routes for tailoring the properties of bio-based and biocompostable polymer blends. The relatively simple approach of (reactive) melt blending of selected materials, addressed here, could be of direct use for industrial processing and production of bio-based and biocompostable plastics with good properties, and broaden the range of their applications.
Chapter 1

Introduction

1.1. Petro- vs. bio-based plastics

Plastics are widely used in society due to the follows: low cost, ease of fabrication into complex shapes, light weight and excellent performance, from soft rubbers to fibers stronger and stiffer than steel\(^1\). Synthetic polymers/plastics have shown an almost exponential growth during the past decades. Currently, over 200 million tons/annum are produced world-wide, about 35 kg per capita in the world. The forecast is that in view of the uneven distribution of the plastics production and consumption in the world, viz. > 100 kg/capita in Western Europe vs. < 10 kg/capita in India, the world production of plastics could grow to more than 1 billion tons/annum at the end of this century\(^2\). Currently, approximately 5 % of oil is used to produce plastics, but in view of the forecast more than 25 % of the current oil production is needed to make plastics by the end of this century. This is not sustainable.

Alternative feedstock to produce plastics are already in place such as coal and gas to provide monomers via Fischer-Tropsch catalysis, the so-called C-1 Chemistry, and pioneered by Sasol (South Africa)\(^3\) and currently in operation by companies such as Sasol, Shell and BP.

In conclusion, fossil sources will be available to produce plastics for the coming decades, and maybe centuries, but there are drivers to get away from fossil sources such as geopolitical and economic issues, while another issue is the environment and notably recently the debate about the so-called “plastic soup”. In the oceans gigantic gyres have been discovered containing plastic debris (Charles Moore)\(^4\). These plastic particles can be very small, < 0.3 mm, and up to 5 kg/km\(^2\). It is not possible to fish out these micro-sized plastic particles by small mesh nets because organic living matter will be fished out as well resulting in dead oceans. Another even more important issue is that so-called POP’s (persistent organic pollutants) such as dichloro-diphenyl-trichloroethane (DDT) and poly(chlorinated biphenyls) (PCBs) adhere to these plastic particles\(^5,6\).

All polymers, man-made or made in nature, are biodegradable but it can take a long time, sometimes many decades. Moreover, in practice, plastics are made by compounding synthetic polymers with numerous additives such as colourants, stabilizers and processing aids.
Additives such as anti-oxidants will prolong the service-life of plastic products, e.g. poly(propylene).

Consequently, the plastic islands will remain in the oceans for many decades to come and additives within the fragmented plastics or POP’s adhered to the fragmented plastics will pose a future danger to the environment. The so-called “cradle-to-cradle” concept, as coined by Michael Braungart\(^7\), might at least render less harmful additives for the plastics industry, but since there is no technology available to cure human lack of discipline better alternatives are looked for and biocompostable plastics or in general bio-based plastics might provide the solution for an environmentally friendly new class of polymeric materials.

Nature provides us with many polymeric materials such as cellulose (in plants and trees), starch (in cassava, maize, potatoes), natural rubber (poly-cis-isoprene), proteins and last but not least DNA, our heritage carrier. The level of sophistication of nature to make polymers is far beyond man, e.g. the programmed polymerization of amino acids into proteins at ambient temperature and pressure. But, nature does not produce polymers to serve mankind with engineering materials but for its own purposes such as energy reserve materials.

The main advantage of synthetic polymers/plastics is that their chemical structure is relatively simple and more heat stable than the natural counterparts. Synthetic polymers/plastics are usually processed via the molten state (melt), the so-called thermoplastics. Natural polymers such as proteins, cellulose and starch can not be heated into the molten state due to thermal degradation/decomposition. Wood with the main constituents, i.e. cellulose, lignin and hemi-cellulose, is a classical construction material but has to be machined into useful parts and is not compatible with the current nano-Era with a high demand on dimensional stability.

In the discussions about a bio-based economy and the use of bio-based materials (plastics) one has to distinguish between:

1) biopolymers or polymers produced by nature (cellulose, starch, natural rubbers, proteins and poly(hydroxyalkanoates));

2) monomers derived from biomass to make polymers by industry, e.g. poly(lactic acid) (PLA).

**Bio-plastics** are biopolymers or bio-based polymers which can be processed as conventional plastics. **Biocompostable polymers/plastics** are polymers/plastics which can be converted by micro-organisms into CO\(_2\) and H\(_2\)O in industrial composting plants and comply with standards, e.g. EN-13432 in Europe, ASTM-D-6400-04, ISO-17088, and DIN-V-54900.
Only a few bio-plastics are biocompostable but also some synthetic petro-based plastics are biocompostable which is a confusing issue. To make it more confusing, master batches are sold on the market making standard oil-based plastics biodegradable, the so-called oxo-degradables. Oxo-degradables [master batches containing Co and/or Mn compounds as catalysts added to poly(ethylene) (PE), poly(propylene) (PP) and poly(styrene) (PS)] are very popular in many countries, e.g. Brazil, sold as biodegradable supermarket bags. Oxo-degradables do not comply with the biocompostable standards because the oxidation process takes longer than the 180-day-period required by the standards. Summarizing, one can distinguish nowadays between 4 different classes of (bio-)plastics, see Table 1.1.

Table 1.1: Classification of (bio-)plastics.

<table>
<thead>
<tr>
<th>Bio-based</th>
<th>Petro-based</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biocompostable</strong></td>
<td><strong>Aliphatic/Aromatic polyesters</strong></td>
</tr>
<tr>
<td>Starch-based polymers (TPS)</td>
<td>(PBAT)</td>
</tr>
<tr>
<td>Poly(hydroxy alkanoates) (PHA)</td>
<td>Poly(butylene succinate) (PBS)</td>
</tr>
<tr>
<td>Poly(lactic acid) (PLA)</td>
<td>Poly(caprolactone) (PCL)</td>
</tr>
<tr>
<td><strong>Non-biocompostable</strong></td>
<td></td>
</tr>
<tr>
<td>Stereo-complex (sc) PLA</td>
<td>Poly(ethylene) (PE)</td>
</tr>
<tr>
<td>Poly(trimethyl terephthalate) (PTT)</td>
<td>Poly(propylene) (PP)</td>
</tr>
<tr>
<td>Poly(urethane) (PU)</td>
<td>Poly(styrene) (PS)</td>
</tr>
<tr>
<td>Nylon 11</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PE, PP from bio-ethanol</td>
<td>(PET)</td>
</tr>
</tbody>
</table>

The interest in biocompostable plastics is mainly in the huge packaging market. Approximately 40% of all plastics produced are used for packaging such as films, bottles and containers. The volume of biocompostable plastics is still very limited, << 1% of the oil-based plastics, notably due to a high price, poor performance and/or processing problems, to be discussed below.

The petrochemical industry is nowadays focused not so much on biocompostable plastics but on durable, bio-based plastics in engineering application such as automotive applications (green image). In this respect we have to distinguish between replacing existing plastics with bio-based plastics such as bio-poly(ethylene), viz. PE made from ethylene derived from bio-ethanol (Braskem, Brazil) or “look-alikes”, e.g. nylon 11 derived from castor oil vs. new polymer structures, e.g. Furan copolymers (Avantium, NL) and stereo-complex PLA (sc-PLA).
1.2 Biocompostable plastics (properties, pros and cons, of current biocompostable plastics)

At present, only six biocompostable plastics made an inroad in the market: bio-based and biocompostable plastics such as poly(hydroxybutyrate) (PHB), PLA and TPS vs. oil-based but biocompostable plastics such as poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL) and poly(butylene adipate-co-terephthalate) (PBAT).

1.2.1 Poly(hydroxyalkanoates)

Poly(hydroxyalkanoates), PHAs, refer to hydroxyalkanoates polyesters, which are synthesized and accumulated intracellularly by a number of micro-organisms. The best-known and the best characterized PHA is PHB discovered in Bacillus megaterium by Lemoigne in 1926. The morphology of PHB in bacteria cells is shown in Figure 1.1. The weight-average molecular weight of PHAs can be up to 3 MDa which is the standard way for nature to avoid build-up of osmotic pressure. PHB is produced through fermentation of sugar and starch with the help of bacteria. Crystallization does not occur within the cell due to the lack of heterogeneous nuclei.

Figure 1.1: PHB in bacterium cells. The size of the amorphous PHB granules is 0.2 - 0.7 μm.

The mechanical and thermal properties of PHB are similar to those of poly(propylene) (PP). However, PP can not be replaced by PHB yet, since there are many technical drawbacks which limit the applications of PHB. One major drawback is the low rate of crystallization related to the low heterogeneous nucleation density, relatively stiff chain, short chain segment, and, consequently a high $T_g$, viz. approximately 10 °C. Upon molding PHB homopolymers, e.g. injection-molding, the molded parts have not completed crystallization yet resulting in
pronounced after-molding ageing effects, viz. secondary crystallization resulting in brittle products\textsuperscript{14}. The $T_g$ can be lowered by incorporation of specific co-monomers such as 4-hydroxybutyrate (Metabolix, USA), hydroxyvalerate (Tianan, China) and hydroxyhexanoate (Kaneka, Japan), but then the rate of crystallization is even lower. Furthermore, synthesis of PHB copolymers could improve the toughness of PHB, but also leads to lower strength and modulus of the materials. At high co-monomer content, rubbery materials will be obtained. Another drawback of PHB is its thermal instability resulting in very narrow processing window. Serious degradation due to random chain scission occurs during melt processing.

PHB and its copolymers are bio-based plastics and have good biocompatibility. Furthermore, PHB is fast in biocomposting and can bio-compost both aerobically and anaerobically into CO$_2$ and H$_2$O (or CH$_4$). Therefore, PHB and its (co-)polymers could have specific niche applications due to the above characteristics\textsuperscript{12,15}. Main PHB (co)polymer producers are Tianan, Metabolix, Kaneka, Tianjin Green Bioscience (China) and PHB industrial (Brazil).

1.2.2 Poly(lactic acid)

Poly(lactic acid) (PLA) is an aliphatic polyester. It can be synthesized either via direct polycondensation of lactic acid monomers or via ring opening polymerization of the cyclic lactide dimers using a metal catalyst\textsuperscript{16}. However, high molecular weight PLA is not feasible via a direct polymerization of lactic acid monomers, because in this equilibrium reaction water is formed, which is difficult to remove when the viscosity rises during the course of the polymerization reaction. The commercially adopted route is ring opening polymerization (ROP) of the cyclic lactide dimer. The lactic acid (LA) monomers can be obtained through fermentation of corn or sugar. Depending on the bacterial strain, predominantly left-handed L-LA or right-handed D-LA can be obtained. Consequently, a family of PLAs can be obtained with a variety of stereo chemical purity, from pure P(L)LA and pure P(D)LA (Figure 1.2) to P(D/L)LA copolymers.

![Molecular structure of P(L)LA (left) and P(D)LA (right).](image_url)
Commercial grades of PLA produced by Natureworks (USA) are (L)LA and (D)LA copolymers with few percent of (D)LA monomers. Purac (the Netherlands) has ample experience with producing P(D/L)LA grades for medical applications such as bone screws. Purac also has the technology for producing high quality stereo-chemically pure (L)LA and (D)LA grades. Currently, the leading PLA producers over the world are Natureworks, Synbra (the Netherlands), Teijin (Japan), Futerro (Belgium), Hisun biomaterials (Zhejiang, China), and Jiuding (Jiangsu, China).

Although PLA is biocompostable, it is not suitable for hot-packaging applications, e.g. coffee cup, due to its low \( T_g \) (around 55 °C) and low crystallization rate. When the temperature approaches its \( T_g \), PLA becomes soft and its E-modulus cannot be backed up by crystallinity because PLA generally is amorphous after processing. One concept developed recently to make high (temperature) performance PLA materials is the use of stereo-complex PLA (sc-PLA) obtained by mixing the standard P(L)LA and its stereo-isomer P(D)LA. The melting temperature of sc-PLA is up to 210 - 230 °C, depending on the stereo-chemical purity of the P(L)LA and P(D)LA and their molecular weight. Successful application of sc-PLA is carried out by Mazda (automotive application)\(^{17}\) and Teijin (durable application). But it has to be noted that sc-PLA is not biocompostable like standard PLA, and the melt processing of sc-PLA is still a challenge. In addition, pure PLA is a brittle and notch sensitive material at ambient temperature, which restricts its applications to a certain extent. However, PLA is regarded as one of the most promising plastics thanks to its bio-based origin, biocompostability, reasonable strength, transparency, and biocompatibility\(^{15}\).

1.2.3 Starch

Starch is produced abundantly in nature with a special chemical structure, i.e. poly-glucose molecules. Native starch is semi-crystalline (crystallinity \( X_c = 20 - 45\% \)) consisting of two types of macromolecules: amylose and amylopectin (Figure 1.3). Amylose, with a weight-average molecular weight in the order of 0.5 \( \times \) 10\(^6\) g/mol, is a linear polymer with D-glucose as repeat units which are connected by \( \alpha \)-1, 4 linkage (Figure 1.3). Amylopectin is a highly branched polymer and has a weight-average molecular weight of 10 - 500 \( \times \) 10\(^6\) g/mol. In amylopectin, the D-glucoses are linked at positions \( \alpha \)-1, 4 and \( \alpha \)-1, 6, as illustrated in Figure 1.3. The \( \alpha \)-1, 6 linkage is the position for branches. The weight ratio between these two macromolecules very depends on the source of starch. For example, potato starch generally
Introduction

consists of 80 wt% amylpectin, while waxy corn starch contains nearly 100 %
amylpectin\textsuperscript{19}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{amylose_amylpectin.png}
\caption{Structures of amylose (left) and amylpectin (right) molecules.}
\end{figure}

Considering that starch is a rather cheap material compared with oil (albeit that currently
the price is up to \(~ 700 \) Euro’s/ton, April 2011), it would be an ideal polymer for applications
such as packaging. However, starch cannot be processed by conventional techniques, e.g.
extrusion and injection-molding in view of its high molecular weight and the low thermal
decomposition temperature of starch which is lower than its melting point\textsuperscript{20}. However, starch
is able to swell in the presence of water or suitable plasticizer or under the influence of
certain energy such as heat or shear. An important step of processing starch is gelatinization.
It is not easy to define gelatinization accurately. The most common definition for starch
gelatinization is the collapse (disruption) of molecular order within the starch granule
manifested in irreversible changes such as granular swelling, native starch crystalline melting,
lose of birefringence, and starch solubilization. To process starch, it has to be gelatinized and
mixed with additional additives, e.g. glycerol\textsuperscript{21}. This combination of gelatinized starch and
additives is referred to as thermoplastic starch, viz. TPS. After processing, retrogradation of
starch may happen, which is a process that takes place in gelatinized starch when the amylose
and linear parts of amylpectin reorganize themselves into an ordered structure, even a
crystalline structure upon storage, a kind of ageing. Furthermore, some issues of TPS such as
moisture sensitivity, plasticizer migration and starch retrogradation lead to embrittlement\textsuperscript{22}.
These issues can be partly circumvented by dispersing the TPS into a hydrophobic polymer
matrix. In that case the starch is locked up in the matrix and if finely dispersed the starch will
not affect the overall mechanical properties, dominated by the matrix, too much. The role of
starch in that case is just a cheap filler.
Chapter 1

The leading starch (or TPS) manufacturers are Novamont (Italy), Cardia Bioplastics (China), BIOP (Germany), Biotec (Germany), Biome (UK), Rodenburg (the Netherlands), Plantic (Australia) and Wuhan Huali (China).

1.2.4 Poly(butylene succinate)

Poly(butylene succinate) (PBS), an aliphatic polyester with a $T_g$ around -30 °C and $T_m$ approximately 112 °C\textsuperscript{23, 24}, is manufactured through traditional chemistry based on fossil sources. Meanwhile, the monomers (succinic acid and butanediol) for PBS polymerization can also be obtained from renewable resources through fermentation\textsuperscript{25, 26}. PBS is biodegradable and biocompostable and it can be considered as bio-based in the near future, at least partly bio-based. PBS has acceptable mechanical properties and processability\textsuperscript{23}, and it can be easily utilized to manufacture mulch film, packaging bags and hygiene products. However, the notched impact strength and transparency of the films of PBS are still needed to be improved and the price of PBS (currently approximately 4 Euro/kg) needs to be reduced for wider applications.

The main producers of PBS are Mitsubishi Gas Chemicals (Japan), Showa Highpolymers (Japan), Ire Chemical (Korea), Hexing Chemical (China) and Xinfu (China).

1.2.5 Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate) (PBAT), which is well known as Ecoflex® produced by BASF via conventional chemistry, is a well-established biocompostable but oil-based aromatic-aliphatic copolymer. PBAT ($T_g$ of around -30 °C and $T_m$ of around 120 °C\textsuperscript{27}) is a flexible thermoplastic and is used in mixing with starch (Novamont) and PHBV (Tianan) to produce trash bags and disposable films/bags. PBAT is also considered to be a good candidate to modify other brittle biocompostable materials such as PLA\textsuperscript{27} (an example is Ecovio®), due to its high flexibility and biocompostability. However, the price competitiveness (> 4 Euro/kg) and production capacity of PBAT still need to be enhanced to meet the market’s requirements. In 2011 BASF expanded the production capacity to 70 ktonnes/annum.
1.2.6 Poly(ε-caprolactone)

Poly(ε-caprolactone) (PCL) is obtained by ring opening polymerization of ε-caprolactone in the presence of aluminum isopropoxide\textsuperscript{28}. The most common use of poly(ε-caprolactone) is in the manufacture of polyurethanes. It finds also some bio-medical applications based on its biocompatible character, mostly in controlled release of drugs, and some packaging applications thanks to its biocompostable character. PCL can be used as a solid plasticizer for PVC as well. Different commercial grades are produced by Solvay (CAPA®) or by Union Carbide (Tone®). PCL shows a very low $T_g$ (-60 °C) and a low melting point (60 °C), which could be a handicap in some applications. The biocompostability can be clearly claimed but the homopolymer hydrolysis rate is very low\textsuperscript{29}. The presence of starch can significantly increase the biodegradation rate of PCL\textsuperscript{30}. Therefore, PCL is generally blended or modified (e.g. copolymerization or crosslinking) for further applications\textsuperscript{31,32}.

1.3 (Partly) bio-based and biocompostable polymer blends

1.3.1 Advantages of blending technology

As discussed in the previous sections, the price of most of the biocompostable plastics is rather high, 4 - 6 Euro/kg, whereas the properties, notably toughness, are inferior to standard oil-based plastics. Blending is an option to compensate for deficiencies in properties and, when TPS is used as filler, lowering the price and enhancing the overall biodegradation rate.

In the case of biocompostability, the constituents of the blends should be in principal biocompostable and well-known examples are Ecovio®, which is a PLA/PBAT blend developed by BASF, suitable for injection-molding and film-blowing and TPS based grades from Novamont, Mater-Bi®, typically TPS in PBAT. However, it was claimed recently that the presence of starch (TPS) could also render some conventional copolymers biocompostable with as prime examples: ethylene-co-vinyl acetate (EVA) with starch and with starch and PLA\textsuperscript{33}. 
1.3.2 Classification of (partly) bio-based and biocompostable polymer blends

Based on their miscibility, polymer blends in general can be divided into miscible, partly miscible and immiscible polymer blends, which can be distinguished by their phase morphology and changes in glass transition temperatures.

For miscible polymer blends, homogeneity is obtained at a molecular level (no phase separation). Typical miscible blends in the area of (partly) bio-based and biocompostable plastics are PHB/poly(vinyl acetate) (PVAc)\textsuperscript{34},\textsuperscript{35}, PLA/PVAc\textsuperscript{36}, PHB/poly(methyl methacrylate) (PMMA)\textsuperscript{37,38}, PHB/poly(vinyl phenol) (PVPh)\textsuperscript{39,40}, PHB/poly(epichlorohydrin) (PEC)\textsuperscript{41,42}, PHB/poly(ethylene oxide) (PEO)\textsuperscript{43,44}, PHB/cellulose-acetate-butryate (CAB) and PHB/cellulose-acetate-propionate (CAP)\textsuperscript{45,46}, PHBV/CAB and PHBV/CAP\textsuperscript{47}, PLA/PMMA\textsuperscript{48} and PLA/poly(ethylene glycol) (PEG)\textsuperscript{49}.

In immiscible blends, heterogeneity is observed due to a poor affinity between the constituents and these blends generally have a coarse morphology (complete phase separation). To obtain a finer, less coarse, morphology, a so-called compatibilizer is usually applied. Compatibilizer has a good affinity with each blend component. By using compatibilizer, an immiscible polymer blend can be changed into a compatible blend. To understand the role of compatibilizer, the morphology development of a polymer blend during melting blending has to be discussed first.

An elementary step in the mixing process is the deformation of dispersed droplets in the flow field, yielding an increase in the interfacial area accompanied by a decrease in local dimensions perpendicular to the flow direction, viz. the diameter of threads. The final morphology is a consequence of a dynamic equilibrium between break-up and coalescence of droplets. The morphology development during (melt-)blending is schematically demonstrated in Figure 1.4 (left). Deformation of the droplets is promoted by the shear stress ($\tau$) exerted on the droplets by the flow field and counteracted by the interfacial stress $\Gamma/R$ (with the interfacial tension, $\Gamma$, and the local radius, $R$) minimizing the surface to volume ratio, thus tending to a spherical shape. The ratio between the two stresses is called the capillary number $Ca$:

$$Ca = \frac{\tau \cdot R}{\Gamma}$$  \hspace{1cm} (1-1)

A critical $Ca$ value ($Ca_{crit}$) is present for each immiscible polymer blend, which is dependent on the flow types and viscosity ratio of the dispersed phase to the matrix ($\eta_d/\eta_m$)\textsuperscript{50,51}. When the $Ca$ is $> Ca_{crit}$, the stretched big droplets (threads) finally breaks up into
smaller ellipsoid domains because the shear stress overrules the interfacial stress; on the contrary, if $Ca$ is $< Ca_{crit}$, slight deformation but no break-up of droplets occurs since the shear stress is insufficient to overcome the interfacial stress.

The interfacial tension ($\Gamma$) between blend components can be significantly reduced when compatibilizer is used in an immiscible polymer blend, increasing the $Ca$ value and postponing Rayleigh disturbance (Figure 1.4 left), which is beneficial for the break-up of droplets into finer ones. Then, the compatibilizer preferably locates at the surface of the new (finer) droplets. To a large extent, the coalescence process of the finer droplets is prevented and the finer morphology is stabilized by the compatibilizer during the subsequent mixing process, as schematically illustrated in Figure 1.4 (right).

![Figure 1.4: Schematic illustrations of morphology development during polymer melt-blending (left, drawing based on reference^{52}) and the stabilization effect of compatibilizer in morphology development (right).](image)

A review on compatibilization of polymer blends was given by Koning et al^{52}. They summarized the compatibilization strategies which can be roughly classified into (i) physical approach by addition of a premade compatibilizer which has good affinity with both blend components and (ii) chemical approach by introduction of chemical reaction or specific interaction between the blend components. A specific strategy in (ii) is so-called in-situ compatibilization or reactive compatibilization, during which compatibilizer is produced in-situ.

Most polymer blends are immiscible and usually form two types of morphology, i.e. matrix-droplet and co-continuous. A number of immiscible (partly) bio-based and biocompostable polymer blends have been reported such as PHB/poly(methylene oxide)
(POM)\(^{53}\), PHB/PE\(^{54}\), PHB/PCL\(^{55}\), PHB/poly(glutamate)\(^{56}\), PHB(V)/PBS\(^{57,58}\), PHB/poly(butylene succinate-co-butylene adipate) (PBSA) and PHB/poly(butylene succinate-co-ε-caprolactone) (PBSC)\(^{59,60}\), PLA/PHAs\(^{61,62}\), PLA/PCL\(^{63-65}\), PLA/PBS\(^{66}\), PLA/PBAT, PLA/poly(urethane) (PU)\(^{67}\), PLA/PE\(^{68}\), PLA/poly(ethylene-co-glycidyl methacrylate) (EGMA)\(^{69}\), PLA/poly(soybean oil) (PSO)\(^{70}\), PLA/poly(L-lactide-co-caprolactone) rubber\(^{71,72}\) and PLA/thermoplastic polyolefin elastomer (TPO)\(^{73}\), PHAs/starch\(^{74-76}\) and PLA/starch\(^{77-79}\). Compared with miscible and immiscible polymer blends, rather less partially miscible blends such as PHB/PHBV\(^{80}\) and PHB/low-Mw-PLA\(^{81,82}\) blends have been reported.

### 1.3.3 Toughening of (partly) bio-based and biocompostable polymer blends

The interplay between strain localization and delocalization, to a large extent, determines the toughness of a material. The strain localization could initiate crazes and subsequently the failure of a polymer material. If the strain can be delocalized effectively during deformation, the material will be tough, otherwise brittle.

To delocalize the strain, a polymer material should be designed heterogeneously\(^{83,84}\), which can be carried out, e.g. by addition of another (flexible) polymer, notably a rubber. Localization of strain is induced by severe intrinsic strain softening whereas the evolution of this plastic zone depends on the stabilizing effect of the strain hardening which is determined by the entanglement density\(^{85}\). For pure PS, severe strain softening causes the strain to localize which can not be stabilized by low strain hardening modulus due to low entanglement density, thus brittle. Pure poly(carbonate) (PC) has a limited strain softening and a more pronounced strain hardening, resulting in ductile behavior.

In order to circumvent the notch sensitivity of a ductile polymer such as PC and brittle polymer such as PS, a dispersed rubber phase is needed, and for PS a pre-cavitated rubber is necessary\(^{84}\).

Good mechanical properties, especially toughness, of such polymer blends could be obtained by controlling the extent of phase separation, the particle size, the inter-particle distance and the interfacial adhesion\(^{86,87}\). Cavitation of rubber particles or partial interfacial debonding is an essential way to release tri-axial stress and to induce massive plastic deformation of the matrix, resulting in toughness of the materials\(^{83}\). It was found that maximum toughness of rubber-toughened plastics is achieved when the particles are large enough to cavitate a long way ahead of a notch or crack tip, but not so large to initiate
unstable crazes and thus to reduce fracture resistance\(^{87}\). Apparently, the particle size is very important in determining the toughness of the blends. Immiscible polymer blends usually have course morphology with large particle size (several to tens \(\mu\)m) and weak interfacial adhesion\(^{67-70,73,88-90}\). As mentioned above, the morphology and interfacial properties of polymer blends can be improved by compatibilization.

The improved morphology and interfacial properties via compatibilization are beneficial for the toughness of a rubber-toughened thermoplastic. Good mechanical properties of (partly) bio-based and biocompostable polymer blends have been obtained via compatibilization. In PLA/PCL\(^{65}\) and PLA/PBS\(^{24}\) systems, a free radical initiator, i.e. dicumyl peroxide (DCP), was introduced into the melt to induce \textit{in-situ} compatibilization. As a consequence, the particle size of dispersed PCL and PBS reduced significantly accompanied by an increase in interfacial adhesion, resulting in an improved toughness of the PLA/PCL and PLA/PBS blends. Oyama\(^{69}\) blended PLA with EGMA random copolymer (containing 30 wt% of methacrylate and 3 wt% of glycidyl methacrylate) to induce a reaction between epoxide groups of the EGMA and acid groups of the PLA to achieve \textit{in-situ} compatibilization. Super-tough PLA/EGMA blends (notched impact toughness of 70 kJ/m\(^2\)) were finally obtained after an extra annealing process where PLA crystallized. PLA is incompatible with poly(ethylene-co-octene). Anderson et al.\(^{68}\) and Ho et al.\(^{73}\) used pre-made PLA-b-PE copolymer and TPO-g-PLA copolymer respectively to improve the compatibility between PLA and poly(ethylene-co-octene). As a result, a fine morphology and a very high toughness of the PLA/poly(ethylene-co-octene) blends were obtained (notched impact toughness up to 700 J/m). The toughness of PHB was improved by 440\% by addition of epoxy natural rubber due to a reactive compatibilization\(^{89}\). Yoon et al.\(^{90}\) found that the morphology and the toughness of PHB/poly(cis-isoprene) (PIP) blends were also improved by using PIP-g-PVAc to enhance the compatibility between PHB and PIP.

1.4 Scope and outline of the thesis

Bio-based and biocompostable plastics enjoy more and more attention, but the application of these plastics is limited due to their unsatisfying price/performance. In the case of PHB and PLA, due to their brittleness and relatively high price, both polymers still cannot meet the requirements for wide applications. Blending is chosen as an approach to improve the properties of these materials in this thesis. It is known that the morphology in terms of particle size and the interfacial properties is of extreme importance in tailoring the
Chapter 1

mechanical properties of polymer blends, e.g. toughness. Due to the fact that most polymer blends are immiscible and usually coarse morphology of polymer blends is obtained, in this thesis different compatibilization strategies are applied on different bio-based and biocompostable polymer blends. The compatibilization effect and its influence on the mechanical properties of the blends are studied in detail and, a correlation is made between the morphology and the mechanical properties. The prime objective of the thesis is to provide possible routes for tailoring the properties, notably the toughness, of bio-based and biocompostable polymer blends. The advantages and disadvantages of the technology described in the thesis are also evaluated. The thesis is structured as follows:

In **Chapter 2**, reactive compatibilization in the presence of dicumyl peroxide (DCP) is applied to improve the mechanical properties of PHB(V)/PBS blends. The morphology, mechanical properties and toughening mechanisms of the *in-situ* compatibilized PHB(V)/PBS blends are studied.

In **Chapter 3**, PLA/PBS blends are prepared via reactive compatibilization with DCP. The crystallization behavior, rheology, mechanical properties, and toughening mechanisms of the *in-situ* compatibilized PLA/PBS blends are discussed.

In **Chapter 4**, PLA is highly toughened by ethylene-co-vinyl acetate copolymer (EVA) with different vinyl acetate (VA) contents. The effect of VA content in the copolymer and the effect of EVA content in the blends on toughening of the PLA/EVA blends are studied. The toughening mechanism is investigated based on the analysis of local deformation.

In **Chapter 5**, reactive compatibilization is performed on EVA/starch blends in the presence of maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol. The *in-situ* reaction and its compatibilization effect are studied.

In **Chapter 6**, PLA is blended with the EVA/starch compounds that are prepared in Chapter 5. The effect of *in-situ* compatibilization on the morphology and the mechanical properties of the PLA/EVA/starch blends is investigated.

The **technology assessment** evaluates the feasibility of the modification methods addressed in this thesis for industry production. The advantages and disadvantages of these technologies are discussed. Some potential problems in production are pointed out and the possible solutions were given.

### 1.5 References

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Chapter 2

*In-situ* compatibilization of PHBV/PBS and PHB/PBS blends

Poly(β-hydroxybutyrate) (PHB) and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) with low hydroxyvalerate (HV) content are very brittle materials. In order to make PHB or PHBV tough(er), PHBV/poly(butylene succinate) (PHBV/PBS) blends and PHB/PBS blends were prepared with *in-situ* compatibilization using dicumyl peroxide (DCP) as a free radical grafting initiator. A considerable reduction in PBS particle size and a significant increase in the interfacial adhesion between the PHB(V) and PBS phases were observed after the compatibilization. As a consequence, the elongation at break of the PHBV/PBS blends was considerably improved, however, the notched Izod impact toughness was only slightly enhanced. The local deformation mechanism, studied by using SEM and TEM, indicates that matrix yielding together with dilatation, deformation and fibrillation of the PBS particles are responsible for the improved tensile toughness of the compatibilized PHBV/PBS blends. The tensile strength, impact toughness and elongation at break of injection-molded PHB/PBS blends were increased as well after the *in-situ* compatibilization with a decrease in the flexural modulus. In addition, the *in-situ* compatibilization addressed in this chapter could be useful for different grades of PHB-based materials.
2.1 Introduction

Poly(β-hydroxybutyrate) (PHB) and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV), synthesized by bacteria, are semi-crystalline thermoplastics that have attracted considerable attention not only because of their biocompostability and biocompatibility, but also due to their renewable nature. Up to now, the application of PHB based materials is limited due to their severe brittleness, narrow processing window in view of poor thermal stability and a low rate of crystallization resulting in ageing after molding\(^1\).

The toughness and processability of PHB can be improved by incorporation of the hydroxyvalerate (HV) monomers in the bacterial fermentation process. PHBV with a high HV content has high flexibility, low crystallinity and low crystallization rate. Increasing HV content compromises on the yield strength and E-Modulus of PHB, which can result in rubbery materials, meanwhile, increases the cost of materials. Consequently, it is of interest to find a more useful way to modify the properties of PHB and PHBV with low HV content.

Blending PHB-based materials with other polymers is an effective and economic way to tune their properties. Polymers, such as poly(ethylene oxide)\(^2\)\(^-\)\(^3\), poly(vinyl alcohol)\(^4\), poly(lactic acid) (PLA)\(^5\)\(^-\)\(^6\), cellulose fiber\(^7\), poly(ε-caprolactone) (PCL)\(^8\)\(^-\)\(^9\), poly(propylene carbonate) (PPC)\(^10\)\(^-\)\(^11\), poly(butylene succinate) (PBS)\(^12\)\(^-\)\(^13\), poly(ethylene succinate) (PES)\(^14\) and poly(butylene adipate-co-terephthalate) (PBAT)\(^15\), have been blended with PHB or PHBV to produce even biocompostable materials based on various standards (e.g. EN 13432).

However, the toughness of PHB or PHBV in the above mentioned blends was not significantly improved, probably due to a complete phase separation and a poor interfacial adhesion between PHB (or PHBV) and the other polymers. Moreover, no efficient compatibilizer and compatibilization technique have been reported yet to improve the interfacial adhesion of PHB-based blends. In another study, the ductility of PHBV (HV content = 12 mol\%) was considerably enhanced by incorporation of 20 wt\% bisphenol-A (BPA) ascribed to a formation of hydrogen bond network between the two components\(^16\). The yield strength and elongation at break of the PHBV/BPA (80/20) blend were reported to be 16 MPa and 370 % respectively.
In-situ compatibilization of PHBV/PBS and PHB/PBS blends

BPA can improve the tensile toughness of PHBV, but it is not biocompostable and its impact on the environment is not clear yet. Compared with BPA, PBS may be an ideal alternative. PBS is a condensation polymer of succinic acid and 1, 4-butanediol\textsuperscript{17}, and the two monomers can be derived from renewable resources via fermentation\textsuperscript{18,19}. Thus, PHBV/PBS and PHB/PBS blends can retain both compostable and renewable characteristics. PBS is a type of ductile polyester, but is not miscible with PHBV and PHB, except in the solution-casted PHB/PBS (20/80) blend which showed some limited miscibility\textsuperscript{12,13}. Compatibilization could be a critical factor in optimizing the mechanical properties of PHBV/PBS and PHB/PBS blends, since the mechanical properties of a multiphase system are usually driven by the ability of the interface to transmit stress from one phase to the other\textsuperscript{20}.

Although considerable work has been devoted to the miscibility and crystallization behavior of PHBV/PBS and PHB/PBS blends, rather less attention has been paid to their mechanical properties and interfacial modification. Additionally, most PHB-based blends in previous studies were prepared via a solvent-casting technique\textsuperscript{2-14}, which is not very feasible in the industry and not environmentally friendly.

The primary objective of this work is to provide a toughening method for PHB-based materials by reactive compatibilization during melt blending with PBS in the presence of dicumyl peroxide (DCP). This method would enable creation of materials with novel performance and could possibly broaden the application range of PHB and PHBV. In the first part of this chapter, PHBV (copolymer)/PBS blends with varying amount of DCP were prepared in a Haake mixer to study the toughening effect and mechanisms. In the second part, PHB homopolymer/PBS/DCP blends with varying PBS content were prepared via extrusion to demonstrate that the toughening method is also effective on the PHB homopolymer and to evaluate the feasibility of continuous production.

2.2 Experimental

2.2.1 Materials

PHBV copolymer with a HV content of 12.7 mol\%, measured by \textsuperscript{1}H-NMR spectroscopy,
was provided by Tianan Biologic Material Co., Ltd., Ningbo, China. Its molar mass was measured based on viscosity in chloroform at 30 °C and yielded $M_n = 250$ KDa according to the equation \[ \eta = 1.18 \times 10^{-4} \cdot M_n^{0.78} \], where $\eta$ is the intrinsic viscosity. PHB (containing ~1 mol% HV) was provided by the same company with $M_n = 200$ KDa. Due to the very low HV content this sample is considered to be a homopolymer and is referred to as PHB in the text. PBS was supplied by Zhejiang Hangzhou Xinfu Pharmaceutical Co., Ltd. China with a melt-flow index (MFI) of 7.8 g/10 min (150 °C × 2.16 kg). DCP (purity ≥ 99.5 %) with typical half-life time about 1 min at 171 °C was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

### 2.2.2 Blend preparation

PHBV and PBS were dried in a vacuum oven at 50 °C for 12 hours before use. PHBV/PBS blends with weight ratios of 100/0, 90/10, 80/20, 70/30 and 0/100, and PHBV/PBS (80/20, wt/wt) blends with DCP contents of 0, 0.2, 0.5 and 1.0 wt% were melt-blended in a mixing chamber of a Rheocord 90 Haake Rheometer (Mess-Technic GmbH, Germany) at 170 °C and 40 rpm (rotation speed) for 4 min. After preheating, the samples were compression molded at 170 °C for 3 min into sheets using a compression-molding machine. The compression-molded samples were used for further testing and characterization.

In order to evaluate the feasibility of continuous production and the effectiveness of the \textit{in-situ} compatibilization in PHB homopolymer/PBS blends, the PHB/PBS blends were prepared using a twin-screw extruder (L/D = 41, D = 25 mm) with a water-bath cooling system. The setting temperatures along the extruder (from feeder to die) were 40, 160, 160, 160, 160, 160, 165 and 160 °C respectively. The screw rotation speed was fixed at 160 rpm. Before feeding, dried PHB and PBS were pre-mixed with DCP in a high-speed mixer at ambient temperature. The extruded pellets were dried before injection molding. The tensile and Izod impact specimen (ASTM standard) were prepared using an injection-molding machine (L/D = 28, D = 25 mm). The barrel temperatures were 160, 170, 170, 170 and 165 °C respectively from hopper to nozzle. The mold temperature was kept at 85 °C to obtain a
fast crystallization rate of PHB during holding and cooling. A holding time of 5 s and a cooling time of 15 s were used. The injection pressure was controlled approximately at 30 MPa.

2.2.3 Characterization

**Extraction:** Chloroform is a good solvent for PHB, PHBV and PBS but not for the crosslinked network. Therefore, chloroform was used for the extraction experiment. The amount of gel from the PHB(V)/PBS/DCP blends was obtained by extraction in boiling chloroform for 3 days using a Soxhlet extractor. The gel fraction (gel wt%) was calculated via equation (2 - 1):

\[ \text{gel wt\%} = \frac{m_1}{m_0} \times 100\% \]  

(2 - 1)

where \( m_0 \) is the original weight of samples and \( m_1 \) is the weight of dry residues obtained after extraction.

**Thermogravimetric analysis (TGA):** TGA (Perkin Elmer, Inc., USA) was used to analyze the gel composition of the PHBV/PBS/DCP blends. PHBV, PBS, PHBV/PBS blends and the extracted residues were heated from room temperature to 700 °C in nitrogen atmosphere (40 ml/min) at a heating rate of 20 °C/min.

**Mechanical properties:** For the PHBV/PBS system, the tensile properties were measured using an Instron 4465 tester (Instron Co., UK) at a crosshead speed of 10 mm/min. The dimensions of the dumbbell-shaped tensile bar were 75 mm in length, 0.8 mm in thickness and 4 mm in width. Notched Izod impact toughness was tested using an impact analyzer (Ray-Ran Test Equipment Ltd., UK) according to ASTM D256. Flexural properties were measured using the Instron 4465 tester according to ASTM D790. The dimensions of the specimen for impact and flexural testing were 63.5×12.7×3.2 mm³. The testing was done at ambient temperature.

The injection-molded dumbbell-shaped tensile bar was 135 mm in length, 3.2 mm in thickness and 12.7 mm in width. For injection-molded PHB/PBS blends, the mechanical properties were measured using the same equipments and under the same testing conditions.
except that a crosshead (tensile) speed of 50 mm/min was used.

**Scanning electron microscope (SEM):** SEM (S-2150 Hitachi Co., Japan) was used to characterize the phase morphology of PHBV/PBS/DCP blends. The samples were first fractured in liquid nitrogen and the cryo-fractured surface was observed after sputter-coating with a thin gold layer.

**Transmission electron microscope (TEM):** TEM was used to evaluate the phase morphology of PHB(V)/PBS blends. The transmission electron microscopy was performed using a Tecnai 20 microscope, operated at 200 KV. Ultrathin sections (70 nm) were obtained at -40 °C using a Leica Ultracut S/FCS microtome. Considering that the PHB(V) and PBS have enough electron density contrast, no extra staining was applied.

**2.3 Results and discussion**

**2.3.1 In-situ compatibilization of the PHBV/PBS blends**

**2.3.1.1 Gel analysis of the PHBV/PBS blends**

Both PHB(V) and PBS can form branched and/or crosslinked structures with peroxide as pure materials\(^{22, 23}\). At the interface of the PHBV/PBS blends, grafting can occur via a combination of PHBV and PBS free radicals. The formation of PHBV-g-PBS copolymer at the interface is schematically illustrated in Figure 2.1. It has to be noted that the combination reaction of free radicals not only occurs at the interface, but can also occur in the PBS domains and in the PHBV matrix. As a consequence, complex reaction products could be obtained, including branched/crosslinked PHBV, branched/crosslinked PBS, PHBV-g-PBS copolymers and PHBV-crosslinked-PBS network. Furthermore, the melt blending was accompanied by chain scissions due to the thermal instability of PHBV and the instability of free radicals, resulting in even more complicated products.
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Figure 2.1: Schematic illustration of the formation of graft copolymers and crosslinked network between the PHBV and PBS components. The possible reactions occurred in the PBS phase or in the PHBV matrix are not present in this scheme.

The gel fraction of PHBV/DCP, PBS/DCP and PHBV/PBS/DCP blends were calculated based on the extraction experiments. Figure 2.2 shows the gel fraction of these materials as a function of DCP content. Obviously, the gel fraction of the PHBV/PBS blends steadily increased with the DCP content. This is reasonable since more DCP provides more free radicals. It was also found that the gel fraction of pure PBS was much higher than that of pure PHBV at the same DCP content (0.5 wt%).

Figure 2.2: Gel fraction of the PHBV/PBS/DCP (80/20/x), PHBV/DCP and PBS/DCP blends as a function of DCP content.

Figure 2.3: TGA curves of (a) PHBV, (b) PBS, (c) the PHBV/PBS/DCP (80/20/0.5) blend and (d) gel of the PHBV/PBS/DCP (80/20/0.5) blend.

The content of PHBV and PBS in the gel (or blends) can be easily measured via TGA because of the large difference between the decomposition temperatures of PHBV (ca. 280 °C) and PBS (ca. 420 °C), and the sharp decomposition temperature sensitivity of the two
polymers, as shown in Figure 2.3. The content of PBS in the initial blends (no DCP) is 20 wt\% (Fig. 2.3 c), however, it is much higher (ca. 50 wt\%) in the gel of PHBV/PBS/DCP blend (Fig. 2.3 d). This feature is very important regarding the processability of the compatibilized blends because PBS is the dispersed phase in this study, see below.

2.3.1.2 Phase morphology of the PHBV/PBS blends

The morphology of the PHBV/PBS blends was studied by SEM. Figure 2.4 shows the SEM images of cryo-fractured surface of the physical and compatibilized PHBV/PBS (80/20) blends. PBS particles and dark holes left by them during fracture were observed on the surface of the physical blend (Fig. 2.4 a). The surface of these particles is smooth with clear borders, suggesting a poor compatibility and weak interfacial adhesion between the PHBV and PBS phases\(^{24}\). In contrast, no PBS traces were observed on the surface of the compatibilized blend (Fig. 2.4 b) probably due to a considerable decrease in particle size. Hence, little information about the morphology of the PBS in the compatibilized blend can be obtained from SEM.

![SEM images of PHBV/PBS (80/20) blends with DCP content: (a) 0 and (b) 0.5 wt\%.](image)

Figure 2.4: SEM images of the PHBV/PBS (80/20) blends with DCP content: (a) 0 and (b) 0.5 wt\%.

The morphology of the PHBV/PBS blends with different DCP contents was studied by TEM. The TEM images are shown in Figure 2.5. Being consistent with the SEM results, the physical PHBV/PBS blend (Fig. 2.5 a) shows a typical matrix-droplet morphology with clear domain borders. After addition of DCP to the PHBV/PBS melts, *in-situ* formed PHBV-g-PBS
In-situ compatibilization of PHBV/PBS and PHB/PBS blends

copolymers which acted as compatibilizer between PHBV and PBS, crosslinked PHBV, crosslinked PBS and a network consisting of both PHBV and PBS were formed. Low concentration of DCP (0.2 wt%) made the dispersion of PBS non-uniform (Fig. 2.5 b), but when the DCP content is ≥ 0.5 wt%, much finer and more uniform dispersion of the PBS was obtained. These results indicate that an emulsifying effect occurred after addition of a sufficient amount of DCP due to the formation of PHBV-g-PBS copolymer and PHBV-crosslinked-PBS network at the interface of PBS and PHBV phases. Meanwhile, the interface between the PBS domains and the PHBV matrix became less clear after the addition of DCP, which indirectly indicated an improved compatibility between the PHBV and PBS.

Figure 2.5: TEM images of the PHBV/PBS (80/20) blends with DCP content of (a) 0, (b) 0.2, (c) 0.5 and (d) 1.0 wt%.

2.3.1.3 Mechanical properties of the PHBV/PBS blends

The tensile properties of the PHBV/PBS blends (in the absence of DCP) with different weight ratios are shown in Figure 2.6. The PHBV used in this study is brittle with a low
elongation at break (4.5%), while PBS is ductile with an elongation at break of 260% and yield strength of 35 MPa. The tensile yield strength and the elongation at break of PHBV were only slightly improved by the incorporation of PBS, as shown in Figure 2.6.

![Figure 2.6: Tensile properties of the PHBV/PBS blends as a function of PBS content.](image)

The effect of adding DCP on the mechanical properties of the PHBV/PBS (80/20) blends is shown in Table 2.1. Compared with other mechanical properties, the elongation at break ($\varepsilon_b$) and impact toughness ($\sigma_i$) are more sensitive to the compatibilization effect in incompatible binary blends. The physical PHBV/PBS (80/20) blend in the absence of DCP is brittle with low $\varepsilon_b$ and $\sigma_i$. With 0.2 wt% DCP, the elongation at break of the blend increased to 200%, indicating a ductile behavior. This could be ascribed to the enhanced interfacial adhesion and the crosslinked network in the blend since the average PBS particle size did not change significantly. In the presence of 0.5 wt% DCP, the $\varepsilon_b$ of the blend was increased by a factor of 50, thus, the tensile toughness of PHBV/PBS blends was improved. However, the notched Izod impact toughness of the PHBV/PBS blends was only slightly improved after applying the compatibilization, i.e. from 2.8 to 5.5 kJ/m². It means the blend after compatibilization is still sensitive to notch, which might limit the range of its (potential) applications. The compatibilized PHBV/PBS blends show high tensile toughness but low notched impact toughness probably may due to the strain rate dependence of toughness and the notch sensitivity of the blends. Meanwhile, the flexural modulus ($\sigma_{f-yield}$) of the blends decreased with the DCP content. The crystallinity of PHBV and PBS for the physical PHBV/PBS
In-situ compatibilization of PHBV/PBS and PHB/PBS blends

(80/20) blends is around 27 and 36 % respectively according to DSC heating curves (not shown here). After addition of 0.5 wt% DCP, the crystallinity of PHBV did not change much, while the crystallinity of PBS reduced to 25 %. The reduction in crystallinity of PBS may account for the decrease in modulus after the in-situ compatibilization.

Table 2.1: Mechanical properties of the PHBV/PBS/DCP (80/20/x) blends.

<table>
<thead>
<tr>
<th>DCP content (x) (wt%)</th>
<th>(D_r) (μm)</th>
<th>(\varepsilon_b) (%)</th>
<th>(\sigma_i) (kJ/m²)</th>
<th>(\sigma_{yield}) (MPa)</th>
<th>(\sigma_{f-yield}) (MPa)</th>
<th>(M_f) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.55</td>
<td>8</td>
<td>2.8</td>
<td>25</td>
<td>39</td>
<td>1.2</td>
</tr>
<tr>
<td>0.2</td>
<td>0.50</td>
<td>200</td>
<td>3.0</td>
<td>29</td>
<td>43</td>
<td>1.4</td>
</tr>
<tr>
<td>0.5</td>
<td>0.24</td>
<td>400</td>
<td>5.0</td>
<td>28</td>
<td>32</td>
<td>0.7</td>
</tr>
<tr>
<td>1.0</td>
<td>0.24</td>
<td>350</td>
<td>5.5</td>
<td>27</td>
<td>30</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Typical error bar for the data in Table 2.1 is 5% to 10%; \(D_r\), Number-average particle size of PBS; \(\varepsilon_b\), elongation at break; \(\sigma_i\), notched Izod impact toughness; \(\sigma_{yield}\), yield tensile strength; \(\sigma_{f-yield}\), yield flexural strength; \(M_f\), flexural modulus.

2.3.1.4 Toughening mechanisms under tensile conditions

The PHBV/PBS blends without DCP failed immediately after yielding. On the contrary, all compatibilized samples showed neck formation and neck growth indicating a tough behavior. The local deformation of a plastic/elastomer blend is usually used to investigate the toughening mechanism of the blend\(^{25,26}\). In order to study the toughening mechanism of the compatibilized PHBV/PBS blends, microscopic deformation of the morphology after drawing was characterized by SEM and TEM. The tensile bars after drawing were longitudinally cryo-fractured for SEM observations and cryo-microtomed for TEM characterization, as shown in Figures 2.7 and 2.8 respectively.

In Figure 2.7 a the PBS particles in the physical blend were only slightly stretched because of low elongation at break. Due to the poor interfacial adhesion between the PBS and PHBV, the applied stress in the PHBV matrix could not be effectively transferred to the dispersed PBS phase via the interface\(^{26}\). It causes the matrix to bear most of the stress, resulting in brittle behavior. In contrast, the compatibilized blends (Fig. 2.7 b) showed ductile behavior.
during drawing with $\varepsilon_b$ up to 400%. Also in Figure 2.8, it is shown that the dispersed PBS particles were largely elongated in the PHBV matrix. Due to the difference of Poisson ratio and bulk modulus between the PHBV and PBS, the stress concentration was positioned around the PBS particles, causing volume dilatation in the interior of the PBS particles. This type of microscopic deformation occurs when the interfacial adhesion is stronger than the stress concentrated at the interface between the PBS and PHBV, otherwise, interfacial debonding occurs. In rubber-toughened plastics systems, such dilatation could further result in internal rubber cavitation if the rubber particles are larger than a critical size and the shear modulus of the rubber is low$^{27,28}$. However, the SEM (Fig. 2.7 b) and TEM (Fig. 2.8) images did not show traces of internal cavitation of the PBS particles, probably due to the partial crosslinking and crystallization of the PBS phase which could increase the energy needed for creation of new surface$^{27}$. Furthermore, no multiple crazing was observed in the PHBV/PBS/DCP blends after drawing (Fig. 2.8). Consequently, the dilated PBS particles were highly deformed and oriented together with the PHBV matrix (Fig. 2.8) upon drawing. Somewhat fibrillized debonding was also observed (but was not general), as shown in the inset in Figure 2.7 b. This kind of debonding indicates a high interfacial adhesion and absorbs a certain amount of energy$^{29-31}$. In addition, the PBS phase is partially crosslinked and possesses a lower crystallinity and a higher elasticity$^{23}$, which in combination with slightly crosslinked PHBV could also contribute to the toughness of the compatibilized blends.

![Figure 2.7: SEM images of the stretched PHBV/PBS (80/20) blends with DCP content of (a) 0 and (b) 0.5 wt%](image)
2.3.2 In-situ compatibilization of the PHB/PBS blends

PHB homopolymer is more brittle than PHBV but shows a higher stiffness and strength. Meanwhile, it is more available on the market at lower cost. In order to broaden the application range of the toughening method, in-situ compatibilized PHB/PBS blends were compounded via melt extrusion and subsequently injection molded. Considering that DCP 0.5 wt% showed an optimum effect on properties of the PHBV/PBS system, a DCP content of 0.5 wt% was used for the PHB/PBS blends with PBS contents from 20 to 50 wt%.
2.3.2.1 Gel fraction of the PHB/PBS blends

The PHB/PBS/DCP blends were extracted by chloroform after reactive extrusion. The gel fraction is shown in Figure 2.9. At the same DCP content, the gel fraction of the PHB/PBS blend is nearly proportional to the PBS content. This is consistent with the former argument that PBS is more reactive in forming a network with peroxide. However, the overall gel fraction is lower than 25 wt% when the PBS content is lower than 50 wt%.

![Figure 2.9: Gel fraction of the PHB/PBS/DCP blends as a function of PBS content.](image)

Compared with the gel fraction of PHBV/PBS blends (Fig. 2.2), at the same composition (i.e. 80/20+0.5 wt% DCP), PHB/PBS has a lower gel fraction. Since thermal degradation of PHB is present during melt blending and the shear force in the extruder is stronger than that in the haake mixer, more serious thermal degradation of PHB may occur in the extruder. This could be a reason for the lower gel fraction of PHB/PBS blends from extruder. Another reason may be due to the different molecular structures between PHB homopolymer and PHBV copolymer, which may result in differences between PHB and PHBV in the thermal stability and the reactivity with free radicals.

2.3.2.2 Effect of compatibilization on the morphology of PHB/PBS blends

Figure 2.10 shows the differences in morphology between the physical and the
compatibilized PHB/PBS blends. The final morphology of a polymer blend is a consequence of a dynamic equilibrium between break-up and coalescence of the droplets during melt-blending. Compatibilization is helpful for break-up and preventing coalescence of droplets. As expected, a significant reduction in average particle size ($\bar{D}_p$) of the PBS domains was observed after the *in-situ* compatibilization. For example, the average diameter of PBS particles ($\bar{D}_p$) in the PHB/PBS (80/20) blend is around 1 $\mu$m which decreased by a factor of 3 after compatibilization.

![Figure 2.10: TEM images of the PHB/PBS blends: (a) PHB/PBS(80/20), (a') PHB/PBS/DCP(80/20/0.5), (b) PHB/PBS(70/30), (b') PHB/PBS/DCP(70/30/0.5), (c) PHB/PBS(50/50) and (c') PHB/PBS/DCP(50/50/0.5).](image)

The PHB/PBS (50/50) blend has co-continuous morphology which, after the compatibilization, shows matrix-droplet morphology with a fine dispersion of PBS domains. The change in phase morphology of the PHB/PBS (50/50) blend is caused by the fact that the viscosity of both PHB and PBS phases was changed after addition of DCP, which affected the (critical) capillary number of the blend and enhanced the break-up of the PBS phase. Therefore, PBS tended to be a dispersed phase after addition of DCP. Meanwhile, the
in-situ formed compatibilizer, PHB-g-PBS copolymers, additionally restricted the coalescence of the PBS domains.

2.3.2.3 Mechanical properties and processability of the PHB/PBS blends

The mechanical properties of the PHB/PBS blends were improved after the in-situ compatibilization, as shown in Table 2.2. The yield tensile strength ($\sigma_{\text{yield}}$), the yield flexural strength ($\sigma_{f,\text{yield}}$), the elongation at break ($\varepsilon_b$), the notched Izod impact toughness ($\sigma_i$) and the un-notched Izod impact toughness (Unnotched-$\sigma_i$) increased after the use of DCP. All specimen of the physical PHB/PBS blends were easily fractured during un-notched Izod impact testing, while the specimen of the compatibilized PHB/PBS (70/30) and PHB/PBS (50/50) blends were only partially fractured or even not fractured under the same testing conditions. These results indicate a high un-notched impact toughness of the in-situ compatibilized PHB/PBS blends.

Table 2.2: Mechanical properties of the PHB/PBS/DCP blends.

<table>
<thead>
<tr>
<th>PHB/PBS/DCP (wt/wt)</th>
<th>Unnotched-$\sigma_i$ (KJ/m²)</th>
<th>$\sigma_i$ (kJ/m²)</th>
<th>$\sigma_{\text{yield}}$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$\sigma_{f,\text{yield}}$ (MPa)</th>
<th>$M_f$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0(^a)</td>
<td>/</td>
<td>0.6</td>
<td>25</td>
<td>1</td>
<td>40</td>
<td>3.6</td>
</tr>
<tr>
<td>0/100/0(^a)</td>
<td>/</td>
<td>6.5</td>
<td>35</td>
<td>260</td>
<td>34</td>
<td>0.6</td>
</tr>
<tr>
<td>80/20/0</td>
<td>6</td>
<td>1.5</td>
<td>37</td>
<td>2</td>
<td>52</td>
<td>3.2</td>
</tr>
<tr>
<td>80/20/0.5</td>
<td>17</td>
<td>3.5</td>
<td>39</td>
<td>4</td>
<td>60</td>
<td>2.3</td>
</tr>
<tr>
<td>70/30/0</td>
<td>9</td>
<td>3.0</td>
<td>33</td>
<td>2</td>
<td>55</td>
<td>2.5</td>
</tr>
<tr>
<td>70/30/0.5</td>
<td>54</td>
<td>4.0</td>
<td>38</td>
<td>11</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>50/50/0</td>
<td>23</td>
<td>3.0</td>
<td>34</td>
<td>4</td>
<td>45</td>
<td>1.7</td>
</tr>
<tr>
<td>50/50/0.5</td>
<td>82</td>
<td>5.5</td>
<td>37</td>
<td>15</td>
<td>54</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Typical error bar for the data in Table 2.2 is 5% to 10%.
\(^a\), obtained from compression-molded samples; Unnotched-$\sigma_i$, un-notched Izod impact toughness; $\sigma_i$, notched Izod impact toughness; $\sigma_{\text{yield}}$, yield tensile stress; $\varepsilon_b$, elongation at break; $\sigma_{f,\text{yield}}$, yield flexural strength; $M_f$, flexural modulus.
However, the notched Izod impact toughness of these samples is still very low, e.g. lower than that of a commercial high-impact poly(styrene) (HIPS, Styron A-Tech™ 1300) which was reported to be 136 J/m\(^3\) (i.e. ~ 13.6 kJ/m\(^2\)). For injection-molded samples, orientation of polymer molecules may exist along the flow direction. Since all the tested bars were prepared under the same conditions and the tests were performed on the same direction, the effect of orientation is not discussed in this study. However, it has to be noted that the particle size and the viscosity of the blend components are changed by the \textit{in-situ} compatibilization, which changed the rheology of the materials as well\textsuperscript{35} and, thus, the extent of orientation may also be influenced. Because of the poor processability of PHB (very low melt viscosity, serious thermal degradation and low crystallization rate), pure PHB and PHB/DCP specimen could not be successfully injection molded. This indicates that the melt processability of PHB could be obviously improved by addition of PBS.

After addition of DCP, the blends are still processable – can be extruded and injection molded using conventional devices. The gel formation did not sacrifice the processability of the PHB/PBS blends probably due to (i) the overall gel fraction of the blends is not too high (< 25 wt%), (ii) the matrix (i.e., PHB) which dominates the processability is not seriously crosslinked, and (iii) the melt-processing is accompanied by a thermal degradation of the matrix.

### 2.4 Conclusions

The compatibility between PHBV (or PHB) and PBS is poor, resulting in a relatively large particle size and a weak interfacial adhesion in their blends. To enhance their compatibility, an \textit{in-situ} compatibilization was performed on PHB(V)/PBS blends in the presence of dicumyl peroxide (DCP). During processing, DCP initiated a free-radical reaction between PHB(V) and PBS forming PHB(V)-g-PBS copolymers which subsequently acted as compatibilizer in the blends and partially crosslinked networks in the blends. SEM and TEM images showed that the size of PBS particles in the PHB or PHBV matrix decreased significantly after the \textit{in-situ} compatibilization, accompanied by an improvement of the interfacial adhesion. Consequently, the mechanical properties of the PHB(V)/PBS blends
were improved. After addition of 0.5 wt% DCP, the elongation at break from < 10 % to 400 % for the PHBV/PBS (80/20) blend and the un-notched Izod impact toughness from 10 kJ/m² to 50 kJ/m² for the PHB/PBS (70/30) blend were observed.

However, the notched impact toughness of the PHBV/PBS or PHB/PBS blends was very low even after the in-situ compatibilization, which means the notch sensitivity of the blends was not improved significantly. The local deformation mechanism of the PHBV/PBS/DCP blends under tensile conditions was studied using SEM and TEM, and the results indicated that matrix yielding together with dilatation, deformation and fibrillation of the PBS particles, and partially crosslinking of the blends contributed to the enhanced toughness of the compatibilized blends. It is mainly the dispersed PBS phase in the blends that was crosslinked after addition of DCP, while the less crosslinked PHB or PHBV matrix retained the melt processability of the blends. The in-situ compatibilization is effective in both PHBV(copolymer)/PBS and PHB(homopolymer)/PBS blends, demonstrating that this method could be useful for different PHB grades.

In addition, crosslinked pure PHBV and pure PBS were reported to be fully biocompostable based according to non-standard testing\(^{22,23}\). Therefore, the biocompostability of the crosslinked PHB(V)/PBS blends is expected to remain.

### 2.5 References

In-situ compatibilization of PHBV/PBS and PHB/PBS blends

20 Díaz, M. F.; Barbosa, S. E.; Capiati, N. J. Polymer 2007, 48, 1058.
32 Wu, S. Polymer 1985, 26, 1855.
Chapter 3

Toughening of poly(lactic acid)/poly(butylene succinate) blends via *in-situ* compatibilization

Biocompostable poly(lactic acid)/poly(butylene succinate) (PLA/PBS) blends were prepared in the presence of dicumyl peroxide (DCP). The toughness of PLA was improved by PBS in combination of an *in-situ* compatibilization initiated by DCP. The effects of DCP on the mechanical properties, rheological behavior, crystallization and melting behavior, phase morphology and the toughening mechanisms of the blends were investigated. The notched Izod impact toughness of PLA/PBS (80/20) blend increased significantly after the addition of 0.05 - 0.2 wt% DCP, while the tensile strength and modulus decreased monotonically with increasing DCP content. The addition of DCP induced an increase in viscosity of the blends, a finer dispersion of PBS particles and a better interfacial adhesion between the PLA and the PBS phases. These phenomena indicate that *in-situ* compatibilization occurs between the matrix and the dispersed phases with DCP. The cold crystallization temperature of PLA was decreased by addition of PBS, but the cold crystallization of PLA in the blends was restricted to a certain extent after addition of DCP. Interfacial debonding-initiated matrix yielding is considered as the main toughening mechanism for the *in-situ* compatibilized PLA/PBS blends via studying the microscopic deformation. In addition, the optical clarity of the PLA/PBS blends was improved after the addition of DCP due to a reduction in size and crystallinity of the PBS particles.
3.1 Introduction

In recent years, biodegradable polymers such as poly (ε-caprolactone) (PCL)\textsuperscript{1,2}, poly(lactic acid) (PLA)\textsuperscript{3-6}, poly(hydroxyalkanoate)s (PHAs)\textsuperscript{7}, poly(butylene succinate) (PBS)\textsuperscript{8,9} and poly(butylene adipate-co-terephthalate) (PBAT)\textsuperscript{10} have been extensively investigated due to their attractive biomedical and practical applications. PLA is a renewable material with good biocompatibility, excellent transparency, and high strength and modulus. However, its brittleness, low-melt viscosity and low-heat distortion temperature have restricted PLA’s applications\textsuperscript{11-13}.

Literature reports show that blending can improve the properties of PLA-based materials. PLA has been blended with other biodegradable polymers such as PCL\textsuperscript{14}, PBS\textsuperscript{15-17}, polymerized soybean oil (PSO)\textsuperscript{18}, PBAT\textsuperscript{10}, and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx)\textsuperscript{19,20} to improve its toughness. The elongation at break of PLA was increased to 200% by addition of 20 wt% PBAT, however the notched Izod impact toughness of the PLA/PBAT blends was still lower than 5 kJ/m\textsuperscript{2}. Generally, these blends were prepared by simple mixing and suffered from poor impact resistance due to complete phase separation and poor interfacial adhesion between the different components\textsuperscript{10}. It is thus crucial to enhance the interfacial adhesion or improve the compatibility between different components in a PLA blend to improve its toughness\textsuperscript{21-27}. In-situ compatibilization is one of the methods to be applied. In PLA/PCL systems\textsuperscript{28}, a free radical initiator, i.e. dicumyl peroxide (DCP), was introduced into the melt to induce an in-situ compatibilization. As a consequence, the size of dispersed PCL particles reduced significantly with increasing the interfacial adhesion, resulting in an improved toughness of the PLA/PCL blends.

PBS is a condensation polyester of succinic acid and 1,4-butandiol. Both monomers can be derived from renewable resources\textsuperscript{29-31}. Thus, PLA/PBS blends could retain both biodegradable and renewable characteristics. Furthermore, it reported that the tensile fracture behavior could change from a brittle fracture of PLA to a ductile fracture of PLA/PBS blends, suggesting an effective modification of PLA by adding PBS\textsuperscript{15-17,26}. However, the notched impact toughness of PLA/PBS blends is still very low due to the poor compatibility between PLA and PBS.

In Chapter 2, we have addressed an effective approach, i.e. in-situ compatibilization, to improve the compatibility and interfacial adhesion between poly(β-hydroxybutyrate) and PBS. In this chapter, the same compatibilization method by addition of DCP was used for PLA/PBS blends. The prime goal is to prepare PLA/PBS blends with increased toughness.
while retaining biodegradability. The specific objectives of this chapter are to assess the crystallization, miscibility, phase morphology, rheology, and mechanical properties of the in-situ compatibilized PLA/PBS blends.

3.2 Experimental

3.2.1 Materials

PLA (3051D) was supplied by Natureworks LLC., USA, with a melt-flow index (MFI) (190 °C, 2.16 kg) of 10 g/10 min and a specific density of 1.25 g/cm³. PBS was supplied by HKH National Engineering Research Center of Plastic Co., Ltd., China, with a MFI (190 °C, 2.16 kg) of 25 g/10 min and a specific density of 1.25 g/cm³. DCP (purity ≥ 99.5 %) was supplied by Sinopharm Chemical Reagent Co., Ltd., China.

3.2.2 Blend preparation

PLA and PBS were dried in a vacuum oven at 60 °C for 12 hours before use. All the samples were prepared in the mixing chamber of a Haake Rheometer RC90 at 170 °C and 50 rpm for 4 min. Afterwards, the blends were preheated at 170 °C and then compression molded for 2 min into sheets with a thickness of 1 mm and 3 mm respectively for further characterization. The compositions of the PLA/PBS/DCP blends were as follows: 80/20/0, 80/20/0.05, 80/20/0.1, 80/20/0.15, 80/20/0.2 (weight ratio).

3.2.3 Characterization

**Mechanical properties:** The tensile properties of the blends were measured using an Instron 4465 machine (Instron Co., UK) at a crosshead speed of 20 mm/min. The dumbbell-shaped samples with a dimension of 75 × 4 × 1 mm³ for tensile testing were cut from the compression-molded sheets. Notched Izod impact toughness was tested using a Ray-Ran Universal Pendulum Impact Tester according to ASTM D256. Flexural properties were measured using the Instron 4465 machine with a speed of 2 mm/min according to ASTM D790. The dimension of the samples for impact and flexural testing was 63.5 × 12.7 × 3.0 mm³.

**Differential scanning calorimetry (DSC):** DSC measurements were performed on a
Perkin-Elmer DSC (Pyris 1, USA) in nitrogen atmosphere. All specimen were first heated to 180 °C at a heating rate of 20 °C/min and maintained at this temperature for 3 min to erase previous thermal history, then cooled to 0 °C at a rate of 100 °C/min. After that, the second heating scans were monitored at a heating rate of 10 °C/min for determining glass transition temperature \( T_g \), cold crystallization temperature \( T_{cc} \) and melting temperature \( T_m \).

**Wide-angle X-ray diffraction (WAXD):** WAXD experiments were carried out using an X-ray diffractometer (SA-HF3, Rigaku, Japan) equipped with a Ni-filtered Cu Kα radiation source with a wavelength of 1.54 Å. The measurements were operated at 40 kV and 40 mA with a scan angle from 5 to 40 ° at a scan rate of 4 °/min.

**Rheology:** The rheological behavior was measured on a stress-controlled rheometer (Gemini 200 rheometer, Bohlin Co., UK) using a parallel-plate geometry (25 mm in diameter and 1 mm in thickness). Dynamic oscillation frequency sweeps from 100 to 0.1 rad/s were performed at 170 °C under nitrogen atmosphere with a strain of 5 %, which is in the linear viscoelastic region of the blends.

**Scanning electron microscope (SEM):** SEM (HITACHI-S-2150, Japan) was used to study the morphology and the impact fracture surface of specimen. The fracture surface was coated with a thin gold-layer before observation.

**Transmission electron microscope (TEM):** TEM (HITACHI H-800-1, Japan) was used to characterize the dispersion of PBS in the PLA matrix. TEM ultrathin sections with a thickness of around 100 nm were prepared by a cryo-ultramicrotome (Reichert-UltracutE, Germany). Considering that there was enough electron density contrast between PLA and PBS, no staining was used.

**Transmittance:** Spherical Hazemeter (BS 2782, Diffusion Systems Ltd., UK) was used to investigate the optical clarity of the specimen according to ASTM D1003. The specimen were compression molded into discs of around 1 mm in thickness and then mounted in the hazemeter to measure the amount of visible light being able to transmit through the samples.

### 3.3 Results and discussion

PLA and PBS with the weight ratio of 80/20 were melt-blended with DCP. The effect of DCP on the mechanical properties, thermal behavior, rheology, morphology and transparency of the PLA/PBS/DCP blends were investigated respectively. The toughening mechanisms were studied based on the local deformation after impact tests.
3.3.1 Mechanical properties of the *in-situ* compatibilized PLA/PBS blends

The objective of this chapter is to improve the toughness of the PLA/PBS blend by addition DCP. Therefore, the effect of DCP on the mechanical properties such as tensile, impact and flexural properties of the blends were studied first. The mechanical properties of PLA and PLA/PBS/DCP blends are shown in Table 3.1. Neat PLA was rigid and brittle with an elongation at break ($\varepsilon_b$) of 4%. The $\varepsilon_b$ of PLA was improved dramatically to 250% after the addition of 20 wt% PBS, indicating that the fracture behavior in the tensile test changed from a brittle fracture of neat PLA to a ductile fracture of the blend. However, the tensile yield strength ($\sigma_{yield}$), flexural yield strength ($\sigma_{f\text{-}yield}$) and the flexural modulus ($M_f$) of the PLA/PBS blend decreased in comparison to pure PLA. In addition, the notched Izod impact toughness of the PLA/PBS blend was still too low (4 kJ/m$^2$) to meet certain applications. This is due to a poor compatibility between the PLA and PBS phases. To improve the compatibility, DCP was used to initiate an *in-situ* compatibilization during melt blending. Table 3.1 shows that with increasing the amount of DCP from 0.05 to 0.2 wt%, the strength and the flexural modulus of PLA/PBS blends decrease monotonically, while the elongation at break remains constant. Contrarily, the notched Izod impact toughness ($\sigma_i$) of the blends is improved significantly (Table 3.1). The highest $\sigma_i$ of 30 kJ/m$^2$ is found for the sample with 0.1 wt% DCP, which is ca. 10 times higher than that of neat PLA. Thus, it can be concluded that the PLA/PBS blend had been successfully toughened by the addition of a small amount of DCP.

Table 3.1: Mechanical properties of PLA and the PLA/PBS/DCP blends.

<table>
<thead>
<tr>
<th>PLA/PBS/DCP</th>
<th>$\sigma_i$ (kJ/m$^2$)</th>
<th>$\sigma_{yield}$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$\sigma_{f\text{-}yield}$ (MPa)</th>
<th>$M_f$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
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<td>56</td>
<td>250</td>
<td>80</td>
<td>2.9</td>
</tr>
<tr>
<td>80/20/0.05</td>
<td>12</td>
<td>50</td>
<td>280</td>
<td>70</td>
<td>2.7</td>
</tr>
<tr>
<td>80/20/0.1</td>
<td>30</td>
<td>50</td>
<td>250</td>
<td>65</td>
<td>2.5</td>
</tr>
<tr>
<td>80/20/0.15</td>
<td>20</td>
<td>45</td>
<td>250</td>
<td>63</td>
<td>2.4</td>
</tr>
<tr>
<td>80/20/0.2</td>
<td>15</td>
<td>45</td>
<td>250</td>
<td>60</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The typical error bar for $\varepsilon_b$ is around 20%, while for the other data is within 10%; $\sigma_i$, notched Izod impact toughness; $\sigma_{yield}$, tensile yield strength; $\varepsilon_b$, elongation at break; $\sigma_{f\text{-}yield}$, flexural yield strength; $M_f$, flexural modulus.
3.3.2 Thermal behavior of the in-situ compatibilized PLA/PBS blends

PLA is a semi-crystalline polymer, but has a very slow crystallization rate during cooling from melt. Therefore, usually amorphous PLA materials are obtained after melt processing. This behavior limits its application such as coffee-cups, due to no crystallinity backing up the modulus (stiffness) reduction above its $T_g$ (around 55 °C). However, PLA can easily crystallize in a heating process which is referred to as cold crystallization. Therefore, crystallization of PLA is of great technological importance. The crystallization behavior can be monitored by DSC. The second DSC heating curves of PLA and PLA/PBS/DCP blends after quenched from the melt are shown in Figure 3.1, which show three transitions, i.e. glass transition temperature, cold crystallization exothermic peaks and melting endothermic peaks. The corresponding data are summarized in Table 3.2.

![Figure 3.1: The second DSC heating curves of PLA and the PLA/PBS/DCP blends.](image)

Figure 3.1 shows that $T_g$s of PLA in the blends remain constant with DCP content, indicating an immiscible behavior between PLA and PBS ($T_g$ of neat PBS is around -30 °C) even after addition of DCP. Neat PLA displays a broad cold crystallization exothermic peak ($T_{cc}$) around 122 °C, implying a low cold crystallization capability. The cold crystallization temperature of PLA shifts to a lower temperature after the addition of PBS, indicating that the PBS accelerates the starting of cold crystallization of the PLA component. Compared with the pure PLA, PLA in the PLA/PBS (80/20) blend shows a melting peak at 148 °C with a shoulder-melting peak at 153 °C. PLA has three different crystallographic forms, $\alpha$, $\beta$, and $\gamma$. Generally, the $\beta$ and $\gamma$ crystal forms only appear under some special conditions such as hot drawing and epitaxial crystallization. Therefore, the appearance of bimodal melting peaks
may be ascribed to the fact that during the DSC heating scan, the less-perfect crystals (with $T_m$ around 148 °C) had enough time to melt and reorganize into crystals with a higher structural perfection, which have a higher melting temperature of 153 °C\textsuperscript{18,32,35}.

**Table 3.2: Thermal parameters of PLA and PBS in the PLA/PBS/DCP blends.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>PLA</th>
<th>PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ ($^\circ$C)</td>
<td>$T_{cc}$ ($^\circ$C)</td>
</tr>
<tr>
<td>PLLA/PBS/DCP</td>
<td>55</td>
<td>122</td>
</tr>
<tr>
<td>100/0/0</td>
<td>52</td>
<td>116</td>
</tr>
<tr>
<td>80/20/0.05</td>
<td>51</td>
<td>115</td>
</tr>
<tr>
<td>80/20/0.1</td>
<td>52</td>
<td>120</td>
</tr>
<tr>
<td>80/20/0.15</td>
<td>52</td>
<td>123</td>
</tr>
<tr>
<td>80/20/0.2</td>
<td>51</td>
<td>124</td>
</tr>
</tbody>
</table>

$T_g$, glass transition temperature; $T_{cc}$, cold crystallization peak temperature; $T_m$, melting temperature; $\Delta H_c$, cold crystallization enthalpy; $\Delta H_m$, melting enthalpy.

Figure 3.1 and Table 3.2 point out that the addition of DCP significantly changes the thermal behavior of the PLA/PBS blends. Firstly, the melting peak of PBS (at 113 °C) gradually disappears with increasing DCP content, indicating that the PBS domains become amorphous when the DCP content $\geq 0.1$ wt%. Secondly, the cold crystallization temperature of PLA increases with increasing DCP content indicating a decreased cold crystallization ability of the PLA, which was further confirmed by the gradual decrease in the cold crystallization enthalpy ($\Delta H_c$) and the melting enthalpy ($\Delta H_m$) of the PLA component in the blends (Table 3.2). The similar $\Delta H_c$ and $\Delta H_m$ values for the blends reveal that the PLA component is primarily amorphous when it is cooled from the melt. It has to be noted that the $\Delta H_c$ of PLA can not be measured for the PLA/PBS blends with 0 – 0.05 wt% DCP because of the overlap of the melting peak of PBS and the cold crystallization peak of PLA (Fig. 3.1).

The 1-dimensional WAXD (1D-WAXD) patterns of PLA, PBS, and PLA/PBS/DCP blends were investigated to obtain further insight into the crystallization behavior of these materials, as shown in Figure 3.2. A single broad diffraction peak was observed for neat PLA, suggesting that the specimen under the processing conditions is amorphous or the amount of crystallinity is too low to be traced. Diffraction peaks at $2\theta = 19.5, 21.5$ and 22.5° are clearly observed in the 1D-WAXD pattern of pure PBS (Figure 3.2). The crystal unit cell of PBS is
monoclinic. These three peaks are regarding to the diffraction from [020], [021] and [110] lattice planes respectively. PLA/PBS/DCP blends also show these peaks when the DCP content is ≤ 0.05 wt%, indicating that the PBS crystalline structure is retained in the blends. When the DCP content is ≥ 0.1 wt%, no such peaks are detected, signifying an amorphous structure of the PBS phase. This is in accordance with the DSC results. The changes of the crystallization behavior of the PBS component might be related to the decrease in the strength and modulus of the blends.

Figure 3.2: 1D-WAXD patterns of PLA, PBS and the PLA/PBS/DCP blends.

3.3.3 Rheology of the in-situ compatibilized PLA/PBS blends

In the presence of DCP, PLA and PBS could form polymer radicals (i.e. PLA• and PBS•) via a hydrogen abstraction mechanism. Consequently, PLA and PBS can form branched and/or crosslinked structures with DCP as pure materials. In the PLA/PBS blends, such branching/crosslinking reactions could occur between the PLA• and PBS• radicals forming PLA-g-PBS copolymers. Meanwhile, branching and crosslinking may also occur in the PBS domains and/or in the PLA matrix. The in-situ generated PLA-g-PBS copolymers, subsequently, act as compatibilizer in the PLA/PBS blends. These reactions initiated by DCP are proposed in Figure 3.3.

The viscoelastic response of polymer blends in the melt has been widely used to investigate the structures of the polymer blends. In this study, the dynamic rheological behavior of the PLA/PBS blends was studied at the processing temperature, as shown in Figure 3.4. For linear polymers, the slope of storage modulus ($G'$) versus frequency ($\omega$) at low frequency region is equal to 2. The $G'$ versus $\omega$ for the PLA/PBS blends with DCP (Fig.
3.4 a) shows deviations from the slope of 2. This could be attributed to the reactions proposed in Figure 3.3, or due to the compatibilization effect between PLA and PBS, which has been already reported in literatures 38-41. The viscosity of PLA/PBS (80/20) blend increases after the addition of DCP and the non-Newtonian behavior is more pronounced in the low frequency region (Fig. 3.4 b). At high frequencies, the viscosity of the compatibilized PLA/PBS blends is similar to that of the physical PLA/PBS blend. This indicates that the processability of PLA/PBS blends retains after compatibilization, since processing such as injection molding is generally performed at high shear rates.

Figure 3.3: Schematic illustration of the chemical reactions in the PLA/PBS blends initiated by DCP (P represents PLA and PBS chains).

Figure 3.4: Frequency dependence of (a) storage modulus $G'$ and (b) complex viscosity of the PLA/PBS blends with different contents of DCP at 170 °C and 5% strain.
3.3.4 Morphology of the *in-situ* compatibilized PLA/PBS blends

To confirm the previous discussion about the *in-situ* compatibilization, the morphology of the blends was studied. Moderate interfacial adhesion between the matrix and the dispersed phase in polymer blends is beneficial to the improvement of mechanical properties, especially toughness, since very strong interfacial adhesion does not allow the stress to be relieved via interface debonding while weak interfacial adhesion cold not effectively transfer stress from the matrix to the dispersed phase\(^\text{10,42}\).

Figure 3.5: SEM images of the cryo-fractured surface of PLA/PBS/DCP blends (a) 80/20/0, (b) 80/20/0.05, (c) 80/20/0.1, (d) 80/20/0.1 (with a higher magnification).

It was reported that PLA and PBS were not miscible\(^\text{15,16}\). The SEM image (Figure 3.5 a) of the PLA/PBS (80/20) blend shows that large PBS particles with a diameter of 1-3 μm are embedded in the PLA matrix. The adhesion between PLA and PBS is poor as evidenced by the large number of oval cavities left after the cryogenically fracture (Figure 3.5 a). After the addition of DCP, the morphology of the blends becomes uniform. Few cavities and dispersed PBS particles are observed when the DCP content is 0.05 wt% (Figure 3.5 b). The image for the blend after the addition of 0.1 wt% DCP displays a much more uniform morphology (Figure 3.5 c). In the higher magnification image (Figure 3.5 d), it can be clearly seen that the PBS domain size is significantly reduced to 0.2 - 1.0 μm, which is demonstrated more clearly in the TEM images (Figure 3.6). Furthermore, no obvious debonding was observed for the
samples with DCP after the cryogenically fracture (Fig. 3.5), suggesting a dramatic increase in the interfacial adhesion between PLA and PBS after addition of DCP. This phenomenon is very similar to that we observed for the PHBV/PBS/DCP system (Chapter 2).

The improvement on the interfacial adhesion can be regarded as an indirect evidence of the formation of a compatibilizer in the PLA/PBS blends after addition of DCP. The effect of the in-situ compatibilization on the morphology of the PLA/PBS blends is schematically illustrated in Figure 3.7. PLA-g-PBS copolymers are formed in-situ upon blending with DCP. The PLA-g-PBS copolymers reduce the interfacial tension which results in a fine morphology. Meanwhile, the in-situ formed copolymers, which are located at interface between the PLA and PBS, stabilize the fine PBS particles in the subsequent processing. As a result, PLA/PBS blends with a fine dispersion of PBS domains and an improved interfacial adhesion can be obtained via the in-situ compatibilization, as schematically shown in Figure 3.7 b.
3.3.5 Toughening mechanisms

It was reported in recent studies that crystallization of the PLA matrix plays a role in the mechanical properties. Oyama\textsuperscript{44} and Afrifah et al.\textsuperscript{45} reported that a certain extent of crystallinity in PLA matrix was beneficial to the toughness of PLA/rubber blends. As indicated by the WAXD (Figure 3.2) and DSC (Table 3.2) results, the PLA matrix in our samples is amorphous. Consequently, the effect of crystallization of the PLA matrix on the toughening behavior in these samples can be ruled out. The PBS phase crystallized in the PLA/PBS blend in the absence of DCP. However, the PBS phase changed into amorphous when the DCP content is > 0.1 wt\% (Table 3.2 and Figure 3.2), which may contribute to the increased toughness of the PLA/PBS blends since amorphous PBS is a rubbery material at ambient temperature ($T_g$ of PBS is about -30 °C).

To understand the toughening mechanism of the studied system, the impact fracture surface of the specimen was characterized. In a rubber-toughened plastic system, two types of cavitational processes can be induced under impact (or tensile) conditions, i.e. (1) internal rubber cavitation when there is a strong interfacial adhesion between the components in combination with a low shear modulus of rubber itself and (2) interfacial debonding when the impact (or tensile) stress is higher than the bonding strength at the interface\textsuperscript{10, 42}. As the elasticity and Poison ratio of PBS are different from those of PLA, the PBS particles could act as stress concentrators in the PLA matrix resulting in a tri-axial stress state during deformation. This tri-axial stress could be released via interfacial debonding (i.e. void formation) where the strain in the matrix would be delocalized. Simultaneously, the stress state in the thin ligaments of the PLA matrix between the voids is converted from a tri-axial to a uni-axial stress state. The new stress state is favorable for the initiation of shear bands leading to shear yielding of the matrix\textsuperscript{46}. To delocalize such tri-axial stress state, a material should be designed heterogeneously\textsuperscript{47, 48}.

As shown in Figure 3.8, the brittle-to-ductile transition under impact testing after the addition of DCP is observed. PLA shows a very smooth surface (Figure 3.8 a), indicating a typical brittle fracture behavior. In the PLA/PBS blend (Figure 3.8 b), interfacial debonding between PLA and PBS after impact is clearly observed, but no plastic deformation of the PLA matrix occurred, which is in accordance with the poor interfacial adhesion between the PLA and PBS. The fracture surface of the PLA/PBS/DCP (80/20/0.05) blend becomes rough, and some elongated fibrils and cavities were observed (Figure 3.8 c). The fibrillation of rubber particles is regarded as an important energy absorption process in a previous study\textsuperscript{45}. 
For the PLA/PBS/DCP (80/20/0.1) blend, not only fibrils and cavities but also matrix deformation (i.e. matrix yielding) is clearly observed (Figure 3.8 d). This indicates that a moderate interfacial adhesion between the PLA and PBS was obtained via the in-situ compatibilization. Thus, interfacial debonding-initiated matrix yielding is proposed to be the dominant toughening mechanism for the in-situ compatibilized PLA/PBS blends.

3.3.6 Optical clarity of the in-situ compatibilized PLA/PBS blends

Transparency is a great advantage of the PLA material, which makes it attractive in package applications. Therefore, the optical clarity of modified PLA/PBS blends was studied. Figure 3.9 shows visible light transmittance of PLA and PLA/PBS/DCP blends.

Neat PLA exhibited excellent light transparency with a high transmittance of 90%. After the addition of 20 wt% PBS, the transmittance significantly decreased to around 50 %. The reduction in light transmittance could be due to the light scattering effect of (1) large PBS domains which have different refractive index from the PLA matrix and (2) spherulites of PBS. Pure PLA showed high transparency because it is a homogeneous amorphous material. After addition of 20 wt% PBS, the visible light was scattered to a certain extent by the PBS domains (d = 1- 3 µm) with spherulites, resulting in opaque materials. After the addition of
DCP, the domain size of PBS reduced to 0.2 - 0.9 µm in the case of DCP 0.1 wt% (Fig. 3.5), which is comparable to the wavelength of visible light (390 - 780 nm). Meanwhile, the dispersed PBS phase became amorphous. Therefore, the light scattering effect of PBS domains and spherulites became weak after the addition of DCP, resulting in an increased light transmittance of the PLA/PBS (80/20) blends. The optical clarity of these samples is demonstrated in Figure 3.10 by optical photographs. The macroscopic clarity of these samples is, apparently, in consistent with the light transmittance results (Fig. 3.9).

![Figure 3.9: Light transmittance of PLA and the PLA/PBS/DCP blends.](image)

3.4 Conclusions

Biodegradable PLA/PBS blends with good toughness have been successfully prepared via reactive compatibilization by addition of DCP. The PLA/PBS (80/20) blend had much higher elongation at break than PLA, and further addition of 0.05 - 0.2 wt% DCP significantly
increased the impact toughness of the blends. The effect of \textit{in-situ} compatibilization on the rheological behavior of the PLA/PBS blends was studied. An increase in the melt viscosity of PLA/PBS blends at low frequencies indicates interactions between the PLA matrix and the dispersed PBS particles and even a formation of network after adding DCP. The crystallization behavior of these blends was studied by DSC and WAXD. Without DCP, PBS increased the starting cold crystallization temperature of the PLA matrix, meanwhile itself crystallized. After addition of DCP, PBS in the PLA/PBS blends gradually became amorphous. The decrease in PBS crystallinity might account for the reduction in strength and modulus of the PLA/PBS blends. SEM and TEM images show that the addition of DCP induced a reduction in the particle size of PBS, and a stronger interfacial adhesion between the PLA and PBS phases. The toughening mechanism was investigated by studying the microscopic deformation of morphology on the impact fracture surface. A debonding-initiated shear yielding mechanism was used to explain the improvement on the toughness of the reactively compatibilized blends. In addition, the reduction in the size and the crystallinity of PBS particles increases the light clarity of the PLA/PBS blends.

3.5 References

42, 764.
Toughening of poly(lactic acid) by ethylene-\textit{co}-vinyl acetate with different vinyl acetate contents

The well-known bio-based and biocompostable poly(lactic acid), PLA, suffers from brittleness and a low heat distortion temperature. In this chapter, we address a possible route to make PLA tough(er) by blending with ethylene-\textit{co}-vinyl acetate (EVA) with different vinyl acetate contents. The compatibility and phase morphology of PLA/EVA blends could be tuned by the ratio of vinyl acetate and ethylene in the random copolymers. Tough PLA/EVA blends with an increased impact toughness, up to a factor of 30, were obtained with a maximum toughness at a vinyl acetate content of approximately 50 wt%. The local deformation mechanism was studied by TEM, SAXS and SEM. It revealed that internal rubber cavitation in combination with matrix yielding is the dominant toughening mechanism for the PLA/EVA blends under both impact and tensile conditions.
Chapter 4

4.1 Introduction

Polymeric materials derived from biomass have drawn considerable attention in recent years because of the environmental concerns and sustainability issues associated with petroleum-based polymers\(^1,2\). Poly(lactic acid) (PLA) is one of the most extensively studied renewable materials. PLA is bio-based and biocompostable which make it one of the most promising materials as a substitute for conventional petroleum-based polymers. However, there are also some limitations for PLA, notably brittleness and a low heat distortion temperature due to the low \(T_g\) of PLA and a low crystallization rate which can not back-up the E-modulus above the \(T_g\) of PLA\(^3-5\).

In order to overcome the brittleness of PLA, many approaches have been explored, such as copolymerization\(^6,7\), plasticization\(^8,9\) and blending with other polymers\(^10-23\). Among these approaches, blending with other polymers is the most effective and convenient to modify PLA. A number of reports appeared on blends with PLA to improve its performances, including poly(hydroxyalkanoate)s (PHAs)\(^10\), poly(caprolactone) (PCL)\(^11-13\), poly(butylene succinate) (PBS)\(^14,15\), poly(butylene adipate-co-terephthalate) (PBAT)\(^16,17\), poly(urethane) (PU)\(^18\), poly(ethylene) (PE)\(^19\), poly(ethylene-co-glycidyl methacrylate) (EGMA)\(^20\), polymerized soybean oil (PSO)\(^21\), poly(ethylene-co-acrylate)\(^22\) and poly(ethylene-co-octene) (TPO)\(^23\). PLA was reported to be immiscible with these polymers, leading to a limited improvement on the impact toughness by physical blending.

To obtain a high toughness of PLA blends, compatibilization is essential. Compatibilization can be performed by either addition of pre-made copolymers or by an *in-situ* reaction between the polymers during blending that forms copolymers at the interface. In PLA/PCL\(^13\) and PLA/PBS\(^14\) blends, a free radical initiator, i.e. dicumyl peroxide (DCP), was introduced into the melt to induce *in-situ* compatibilization. As a consequence, the particle size of dispersed PCL and PBS reduced significantly accompanied by an increase in interfacial adhesion, resulting in an improved toughness of the PLA/PCL and PLA/PBS blends. Oyama introduced 3 wt\% of glycidyl methacrylate into the EGMA random copolymer to induce a reaction between the epoxide groups of the EGMA and the acid groups of PLA to achieve *in-situ* compatibilization\(^20\). In his study, super-tough PLA/EGMA blends were finally obtained after an extra annealing process upon which PLA crystallized. The PLA block of the PLA-\(b\)-EGMA copolymers that formed at the interface by reactive blending was trapped in the crystallized PLA matrix, which resulted in an increase in the interfacial adhesion. The improvement on toughness was attributed to the increased
interfacial adhesion. Considerable work has been devoted to blending PLA with ethylene copolymers, e.g. ethylene-octene copolymer and ethylene-acrylate copolymer. PLA is incompatible with ethylene-octene copolymers. Anderson et al.\textsuperscript{19} and Ho et al.\textsuperscript{23} used pre-made PLA-\textit{b}-PE copolymers and TPO-g-PLA copolymers respectively to improve the compatibility of PLA and ethylene-octene copolymers. As a result, a finer morphology and a very high toughness of the PLA/poly(ethylene-\textit{co}-octene) blends were obtained.

In the foregoing blends, additional compatibilization was needed to obtain promising mechanical properties. It would thus be of interest to use a commercially cost-effective impact modifier which is compatible with PLA. Afrifah et al.\textsuperscript{22} blended PLA with a commercial impact modifier (Biomax\textsuperscript{®} Strong 100, DuPont), which is a petroleum-based ethylene-acrylate copolymer (EAC) and is claimed to be compatible with PLA. The toughness of the PLA was improved to a certain extent, e.g. by a factor of 4 – 6 after incorporation of 30 wt\% EAC. In their study, the effect of crystallization on the toughness and the toughening mechanisms were discussed as well.

Although considerable work has been devoted to blending PLA with ethylene copolymers, rather limited attention has been paid to PLA/poly(ethylene-\textit{co}-vinyl acetate) (PLA/EVA) blends. Moreover, to the authors’ knowledge, no detailed investigation on the toughening of PLA by EVA has been reported yet.

EVA is a widely applied ethylene copolymer. With increasing vinyl acetate (VA) content, EVA copolymers change from a semi-crystalline thermoplastic material (LDPE) into a rubber and again into an amorphous thermoplastic material (PVAc). It is known that PLA is miscible with poly(vinyl acetate) (PVAc)\textsuperscript{24,25} and immiscible with PE\textsuperscript{19}. Therefore, the compatibility between PLA and EVA can be achieved by tuning the VA content of the EVA copolymer without the need for additional compatibilization.

The prime objective of this chapter is to provide a simple but effective and economic route to prepare tough PLA materials based on physical (melt-)blending of PLA with EVA copolymers. The effect of both the VA content in the EVA copolymer and the EVA content in the blends on the toughening was examined. The toughening mechanism was studied based on the analysis of the local deformation mechanism by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

The authors hasten to remark that one of the prime advantages of PLA in single-use packaging applications is the biocompostability, whereas EVA copolymers are not biocompostable according to various standards such as EN13432. Interestingly, PLA/EVA blends in combination with starch can pass the standard tests on biocompostability\textsuperscript{26}.
Consequently, to design a tough PLA/EVA blend to serve as the future matrix material in PLA/EVA/starch blends is beyond pure academic interest.

### 4.2 Experimental

#### 4.2.1 Materials

PLA, 2002D, was obtained from Natureworks LLC., USA, with $M_w = 180$ KDa and $M_w/M_n = 1.7$. The content of L-lactide is approximately 96%. EVA rubbers (Levapren®), with VA contents from 40 to 90 wt% were kindly supplied by Lanxess Chemical Co., Ltd.. The data of different grades of EVA are shown in Table 4.1. The structure of PLA and EVA copolymers are shown in Figure 4.1. LDPE (Lupolen 3020K), in this chapter coded as EVA0, with a MFI (190 °C, 2.16 kg) of 4 g/10min was supplied by LyondellBasell, the Netherlands.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>VA content (wt%)</th>
<th>Mooney viscosity $^a$ ML (1+4) 100 °C (MU)</th>
<th>Density (kg/m$^3$)</th>
<th>$T_g^b$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA40</td>
<td>40 ± 1.5</td>
<td>20 ± 4</td>
<td>980</td>
<td>-32</td>
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<tr>
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</tr>
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<td>EVA90</td>
<td>90 ± 2.0</td>
<td>38 ± 6</td>
<td>1150</td>
<td>14</td>
</tr>
</tbody>
</table>

$^a$ Tested according to IS289/ASTM D1646.

$^b$ Measured by DSC at a heating rate of 10 °C/min.

![Figure 4.1: The structures of (a) PLA and (b) EVA copolymers.](image-url)
4.2.2 Blend preparation

Both PLA and EVA were dried in a vacuum oven at 50 °C for 12 hours before use. PLA/EVA blends were melt-blended in a mixing chamber of a Rheocord 90 HAAKE Rheometer (Mess-Technic GmbH, Germany) at 170 °C and 40 rpm for 4 min.

Two series of blends were studied:
- PLA/EVA (80/20) blends, a fixed ratio, but with varying the VA content in EVA copolymers from 0 to 90 wt%;
- PLA/EVA50, a fixed VA content of 50 wt%, and blend compositions of 100/0, 95/05, 90/10, 85/15, 80/20 and 70/30.

After preheating, the melt-blended samples were compression molded at 170 °C for 3 min. The molded samples were used for further testing and characterization.

4.2.3 Characterization

**Mechanical properties:** The tensile properties were measured using a Zwick Z100 tensile tester at a crosshead speed of 10 mm/min. The dimensions of the narrow parallel-sided portion of dumbbell-shaped tensile bars were 12 mm in length, 0.8 mm in thickness and 2 mm in width. The notched Izod impact toughness was tested using an impact analyzer (Zwick 5102, Germany) according to ASTM D256. The flexural properties were measured according to ASTM D790. The dimensions of the specimen for impact and flexural measurements were 63.5×12.7×3.6 mm³. All the tests were performed at ambient temperature.

**Differential scanning calorimetry (DSC):** Glass transition temperature ($T_g$) and the melting behavior of PLA/EVA blends were investigated by DSC (TA Instruments, USA). The samples were first heated to 170 °C in a nitrogen atmosphere and held for 3 min. Then, the samples were cooled to -50 °C and reheated to 170 °C at a scanning rate of 10 °C/min. The second heating scans were analyzed.

**Transparency measurements:** Transmittance of PLA and PLA/EVA (80/20) samples with a thickness of approximately 0.6 mm was measured on a Shimadzu UV-3102PC UV–VIS–NIR scanning spectrophotometer in the wavelength range of 350 ~ 750 nm. The averaged transmittance (T %) was used.

**Transmission electron microscope (TEM):** TEM was used to evaluate the phase morphology of PLA/EVA blends. Transmission electron microscopy was performed using a Tecnai 20 microscope, operated at 200 kV. Ultrathin sections (70 nm) were obtained at -
100°C using a Leica Ultracut S/FCS microtome. The ImageJ analysis software was used to analyze the average particle size from the TEM images. The area of each particle ($A_i$) was calculated and then converted to an equivalent diameter ($d_i$) of a sphere by $d_i = 2 \cdot \sqrt{\frac{A_i}{\pi}}$. The number average diameter ($d_n$) of EVA particle is then obtained from $d_n = \frac{\sum N d_i}{N}$.

**Wide-angle X-ray diffraction (WAXD):** X-ray diffraction measurements were performed on a Bruker D8 discover with GADDS, a two-dimensional (2D) detector, and parallel beam optics. The 2D-WAXD patterns were obtained with the Bruker system using Cu radiation, wavelength 1.54 Å, at 40 kV and 40 mA, and an exposure time of 2.5 min. One-dimensional (1D) WAXD patterns were integrated from the 2D patterns.

**Small-angle X-ray scattering (SAXS):** The mode of microscopic deformation was studied by performing small-angle X-ray scattering (SAXS) measurements after tensile testing. The samples were stretched using the Zwick Z100 tensile test machine at a strain rate of 10 mm/min. Measurements were performed on the DUBBLE beamline (BM 26B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The data were collected on a gas-filled multiwire 2-D detector positioned at approximately 6 m from the sample using a wavelength of 1.55 Å. To calibrate the SAXS detector, oriented dry collagen from a rat-tail tendon was used. The experimental data were divided by the detector response to correct for intrinsic errors of the detector. Subsequently, the data were corrected for background scattering by subtraction of the scattering of a direct beam, i.e. without sample.

**Scanning electron microscope (SEM):** SEM (Quanta 3D, FEI, the Netherlands) was used to characterize the morphology of the PLA/EVA50 blends after deformation. The samples were measured after sputter-coating with a thin gold layer.

**Single-edge notched three-point bending experiments (SEN3PB):** The same specimen as for notched Izod impact testing were used also for SEN3PB measurement. Sharp notches with different depths were made with a fresh razor blade. Then, three-point bending experiments were performed on these “single-edge notched” samples. The geometry of the specimen will be discussed below. The ligament length ($\ell$) was measured from the initial crack tip to the beginning of the hinge and the total fracture energy was calculated from the area under load - displacement curves.
4.3 Results and discussion

4.3.1 Effect of VA content on the miscibility of the PLA/EVA blends

A first approach towards the miscibility and phase separation of two polymers is comparing their solubility parameters ($\delta$). The solubility parameters ($\delta$) which can be calculated via equation 4-1:

$$\delta = \frac{\sum F}{V}$$

where $F$ is the molar attraction constant of each group in a repeat unit of a polymer chain, $V$ is the molar volume of the polymer. Two polymers usually show a miscible behavior when their solubility parameters are close to each other. An example is PVAc and PLA whose solubility parameters are 9.6 and 9.7 (cal/cm$^3$)$^{1/2}$ respectively$^{27}$. The solubility parameter of the EVA copolymers varies between the $\delta$ of LDPE (8.3 (cal/cm$^3$)$^{1/2}$)$^{27}$ and the $\delta$ of PVAc depending on the composition of the EVA. Thus, it is possible to tune the compatibility between PLA and EVA by controlling the solubility parameter (i.e. composition) of the EVA copolymers.

Figure 4.2 shows the heating DSC curves of PLA and PLA/EVA (80/20) blends with varied VA content in EVA copolymer. The PLA/EVA90 (80/20) blend shows a single glass transition temperature ($T_g = 48$ °C) between the $T_g$ of PLA (57 °C) and the $T_g$ of EVA90 (14 °C). However, the other PLA/EVA blends show two separate glass transition temperatures corresponding to the respective constituent polymers. These results indicated that EVA is miscible with PLA when VA content is 90 wt%, while the EVA with VA $\leq$ 70 wt% are not miscible with PLA. These results are consistent with a previous study$^{25}$.

Although PLA is immiscible with EVA at VA content lower than 70 wt%, the compatibility between the PLA and EVA increases with an increase in VA content, which results in a monotonically enhanced transparency of the blends, as shown in Figure 4.3. Data in Figure 4.3 show that PLA can remain good transparency after blending with EVA copolymer which is beneficial for the packaging application.
Figure 4.2: DSC second heating curves of PLA and PLA/EVA (80/20) blends with different VA content in EVA copolymer showing the $T_g$'s of PLA and EVA copolymers.

Figure 4.3: Transmittance of PLA and PLA/EVA(80/20) blends as a function of VA content in EVA copolymer.

Figure 4.4: TEM images (scale bar = 2 μm) of the PLA/EVA (80/20) blends with VA content in EVA copolymers: (a) 0 wt%, (b) 40 wt%, (c) 50 wt%, (d) 70 wt% and (e) 90 wt%. The dark domains are dispersed EVA particles while the bright matrix is PLA. The slight orientation of the EVA particles in these images was most probably resulted from section-preparation (70 nm in thickness).

Figure 4.4 shows the phase morphology of PLA/EVA (80/20) blends. When the VA content in the EVA copolymer is lower than 70 wt%, phase separation is observed between
PLA and EVA. Since PLA is miscible with PVAc, the vinyl acetate segments in the EVA copolymers have a good affinity with PLA matrix. Therefore, the interfacial properties are improved with an increase in VA content. At low VA content (≤ 40 wt%), the particle size of the EVA is large which can be ascribed to a high interfacial tension. Moreover, voids due to interfacial debonding between the PLA matrix and the EVA0 particles (LDPE) are observed (Fig. 4.4 a), indicating a weak interfacial adhesion. On the contrary, hardly any phase separation occurs in the PLA/EVA90 blend (Fig. 4.4 e), which is miscible as evidenced by a single glass transition ($T_g = 48 \, ^\circ C$) of the blend (Fig. 4.2). Phase morphology and interfacial properties of a polymer blend are important to its mechanical properties. Thus, the mechanical properties of the PLA/EVA (80/20) blends would be affected by the VA content which influences the morphology and interfacial properties of the blends.

### 4.3.2 Effect of VA content on the mechanical properties of the PLA/EVA blends

The random copolymerized EVA used in this study are fully amorphous. The success of rubber toughening can be achieved by controlling the extent of phase separation, the interfacial adhesion, the particle size and the rubber content\(^{28-32}\).

Figure 4.5 shows the impact toughness of the PLA/EVA (80/20) blends as a function of VA content in the EVA copolymers. For low VA contents, EVA has a poor compatibility with PLA, resulting in a weak interfacial adhesion and large particle sizes. As a consequence, the PLA/EVA (80/20) blends with low VA content have brittle behaviors.

![Figure 4.5: Impact toughness of the PLA/EVA (80/20) blends as a function of VA content in the EVA copolymers.](image1)

![Figure 4.6: Tensile properties of the PLA/EVA (80/20) blends as a function of VA content in the EVA copolymers.](image2)
The toughness of the blends goes through a maximum with increasing the VA content in the EVA copolymers. The maximum is found at VA content between 50 and 60 wt%. In this range, the compatibility between EVA and PLA is such that sufficient phase separation is obtained with a moderate interfacial adhesion required for effective rubber toughening\cite{28,32-34}. However, very good compatibility usually leads to a too small rubber particle size. If the particle size reduces below a critical value, no internal rubber cavitation occurs\cite{35,36}, which is not beneficial for rubber toughening. Concomitantly, the impact toughness of the PLA/EVA (80/20) blends reduced with increasing VA content further in the EVA copolymers.

Figure 4.6 shows the tensile properties of the PLA/EVA (80/20) blends. The toughness of the PLA was only improved to a certain extent by 20 wt% EVA\textsubscript{0}, having an elongation at break (\(\varepsilon_b\)) of 28 %. After incorporation of 20 wt% of EVA copolymer (with VA content between 40 and 70 wt\%), the \(\varepsilon_b\) of PLA increased to more than 300 %, meanwhile the yield strength (\(\sigma_y\)) dropped in comparison with that of the pure PLA (75 MPa, Table 4.2). Upon drawing, extensive stress-whitening throughout the specimen was observed accompanied by neck formation and stable neck growth. The mechanism of this ductile behavior will be discussed later. Since PLA is miscible with EVA\textsubscript{90} (no phase separation), the PLA/EVA\textsubscript{90} (80/20) blend exhibits similar tensile behavior to pure PLA, viz. low \(\varepsilon_b\) and high \(\sigma_y\).

4.3.3 Phase morphology of the PLA/EVA\textsubscript{50} blends

In the above examined EVA grades, EVA\textsubscript{50} showed an optimum toughening effect to PLA. Consequently, EVA\textsubscript{50} was chosen for further study. The phase morphology of the PLA/EVA\textsubscript{50} blends as a function of EVA\textsubscript{50} content is shown in Figure 4.7. The EVA\textsubscript{50} copolymer comprises 50 wt% vinyl acetate which generates a good compatibility between the PLA and the EVA\textsubscript{50}. The number-average particle size of EVA\textsubscript{50} in the PLA matrix increased from 0.2 to 0.6 \(\mu\text{m}\) with increasing the EVA\textsubscript{50} content from 5 to 30 wt\%. The morphology of a polymer blend, e.g. the particle size of the dispersed phase, is determined by a complex interplay among the viscosity of the components, the interfacial properties, the composition and the processing conditions\cite{37}. The final morphology is a consequence of the dynamic equilibrium between break-up and coalescence of droplets. The increase in EVA\textsubscript{50} particle size with EVA\textsubscript{50} content can be attributed to a larger coalescence effect during melt-blending, since more droplets are expected at a higher EVA\textsubscript{50} content.
4.3.4 Mechanical properties of the PLA/EVA50 blends

The mechanical properties of the PLA/EVA50 blends are presented in Table 4.2. As a consequence of the elastomeric nature of EVA50, the tensile yield strength, modulus and hardness of the blends decrease gradually with increasing EVA50 content. On the contrary, the impact toughness and the elongation at break increase steeply after adding a certain amount of the EVA50. The notched Izod impact toughness of the PLA/EVA50 blends is still low when EVA50 content is lower than 10 wt%, probably because the small EVA50 particles are difficult to cavitate under the impact condition (high strain rate)\textsuperscript{36, 38}. However, a significant increase in the impact toughness is found at 15 wt% of EVA50. Further increasing the EVA50 content, super-tough PLA/EVA50 blends (notched Izod impact toughness > 60 kJ/m\textsuperscript{2}) could be obtained. The impact toughness of PLA is improved by a factor of approximately 30 after addition of 30 wt% EVA50.
Table 4.2 Mechanical properties of the PLA/EVA50 blends as a function of EVA50 content.

<table>
<thead>
<tr>
<th>PLA/EVA50 (wt/wt)</th>
<th>Notched Izod impact toughness (kJ·m⁻²)</th>
<th>Tensile yield strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Flexural modulus (GPa)</th>
<th>Hardness (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>3</td>
<td>75</td>
<td>9</td>
<td>3.7</td>
<td>86</td>
</tr>
<tr>
<td>95/5</td>
<td>2</td>
<td>68</td>
<td>310</td>
<td>3.3</td>
<td>85</td>
</tr>
<tr>
<td>90/10</td>
<td>5</td>
<td>61</td>
<td>390</td>
<td>2.9</td>
<td>84</td>
</tr>
<tr>
<td>85/15</td>
<td>32</td>
<td>54</td>
<td>430</td>
<td>2.7</td>
<td>82</td>
</tr>
<tr>
<td>80/20</td>
<td>64</td>
<td>45</td>
<td>340</td>
<td>2.4</td>
<td>80</td>
</tr>
<tr>
<td>70/30</td>
<td>83</td>
<td>37</td>
<td>400</td>
<td>1.9</td>
<td>76</td>
</tr>
</tbody>
</table>

The typical error bars for the data listed in Table 4.2 are within 10%.

The stress-strain behavior of the PLA/EVA50 blends is shown in Figure 4.8. Pure PLA fails as soon as it passes the yield stress. Apparently, pure PLA has a strong strain softening which, however, is not stabilized by strain hardening. Upon drawing, strain softening stimulates strain localization which causes the build-up of local tri-axial stresses. If the local strain cannot be delocalized, this local tri-axial stresses will induce void nucleation and crazes in the matrix leading to a brittle failure behavior. For this reason, PLA is a brittle material. Under tensile conditions, all the examined PLA/EVA50 blends show a strain softening followed by stable neck growth and strain hardening, which explains the ductility of PLA/EVA50 blends. It is worth noting that only 5 wt% EVA50 could make PLA already ductile (ε_b ≈ 300%) without obviously compromising on stiffness and yield strength of the PLA.

Figure 4.8: Stress-strain behavior of the PLA/EVA50 blends as a function of EVA50 content.
4.3.5 Toughening mechanisms

It was reported in recent studies that crystallization of the PLA matrix plays a significant role in the mechanical properties. For example, the impact toughness of PLA/EGMA (80/20) blends increased by a factor of 10 after annealing at 90 ºC for 2.5 hours upon which the PLA matrix crystallized\textsuperscript{20}. Afrifah et al.\textsuperscript{22} found that the impact toughness of semi-crystalline PLA/EAC blends was higher than that of amorphous PLA/EAC blends.

The samples used in this study were checked on crystallinity by wide angle X-ray diffraction (WAXD), as shown in Figure 4.9. The 2D-WAXD patterns show only one broad diffraction ring for either pure PLA or PLA/EVA50 blends and no crystalline reflections could be detected. Correspondingly, the 1D-WAXD patterns (Fig. 4.9 (right)) integrated from 2D-WAXD show only one broad diffraction peak for each sample. These results suggest that the specimen under the processing conditions is amorphous or the amount of crystallinity is too low to be traced. In addition, no obvious traces of orientation of molecules are indicated by the 2D-WAXD patterns. Consequently, we ruled out the effect of crystallization and orientation on the toughening behavior in our samples. The toughening mechanisms of rubber toughened plastics can be deduced from the local deformation mechanism.

![Figure 4.9: 2D-WAXD (left) and 1D-WAXD (right) patterns of (a) PLA, (b) PLA/EVA50 (90/10) and (c) PLA/EVA50 (80/20) blends.](image)

4.3.5.1 Single-edge notched three-point bending experiments

Standard Izod and Charpy impact testing are commonly used to characterize the toughness of plastics due to the convenience of these two methods. However, these two methods are limited to provide sufficient information regarding the fracture mechanism, e.g. fail to quantitatively reveal the way of energy dissipation during the impact testing. In order to
quantitatively reveal the toughening mechanism of PLA/EVA50 blends, a so-called single-edge notched three-point bending (SEN3PB) experiment was used for these samples.

Data from these tests were analyzed by a modified essential work of fracture (EWF) model based on Mai and his coworkers’ study\textsuperscript{41,42}, which originated from Broberg’s unified fracture theory\textsuperscript{43,44}. In this model\textsuperscript{45,46}, the total fracture energy, $U$, per unit fracture surfaces area, $A$, is given by equation 4-2,

$$\frac{U}{A} = u_0 + u_d \ell$$

(4-2)

where $u_0$ is the limiting specific fracture energy corresponding to the energy assuming in the inner fracture process zone (near or at the fracture surface). $u_d$ is the dissipative energy density associating with energy absorbing process, e.g. cavitation and matrix yielding, in an outer plastic zone away from the fracture surface. $\ell$ is the ligament length (as shown in Fig. 4.10). In this equation, $u_0$ and $u_d$ are considered as phenomenological parameters, not material parameters.

Figure 4.10: Schematic geometry of a single-edge notched three-point bending (SEN3PB) specimen, showing the ligament length ($\ell$), width ($W$), thickness ($t$), inner process zone ($u_0$), and outer plastic zone ($u_d$).

Figure 4.11 shows the typical load versus displacement diagrams for PLA and PLA/EVA50 blends. For each PLA specimen under the stress conditions imposed here, the load reached a maximum value immediately before sharply dropping off in the manner of brittle fracture, as shown in Figure 4.11 a. After specimen yielding, the load trails off slowly rather than dropping sharply for PLA/EVA50 blends, as shown in Figure 4.11 b. This extended tail after specimen’s yielding is typical of ductile materials. In the case of similar ligament lengths, the higher EVA50 content, the more total fracture energy was gained. The toughening effect of EVA50 content observed in SEN3PB experiments is well consistent with the results of notched Izod impact testing.
Figure 4.11: Load versus displacement diagrams for SEN3PB specimens of PLA and PLA/EVA50 blends as a function of ligament lengths (ℓ) and EVA50 content.

The total fracture energy per unit fracture area (U/A) of each specimen is plotted versus corresponding ligament lengths (ℓ), as shown in Figure 4.12 a. For the samples examined here, a good linearity of these plots was achieved. The u₀ and u_d values for each sample, as suggested above, are obtained from the slopes and intercepts of these lines respectively and are shown in Figure 4.12 b.

Figure 4.12: (a) U/A values versus ligament lengths (ℓ) and (b) u₀ and u_d for PLA and PLA/EVA50 blends as a function of EVA50 content.

The slope of the line (u_d) corresponding to pure PLA is approx 0 indicating that almost all the fracture work is done in the region near the fracture surface and very little energy is dissipated in the outer plastic zone. The u₀ of the samples increased with EVA50 content up to 10 wt% and then reduced gradually. On the other hand, the u_d values monotonically increased with increasing EVA50 content, which is consistent with the varying trend of
notched Izod impact toughness. These results indicate that a small amount of EVA50 (< 10 wt%) can contribute a certain extent to the fracture energy at the fracture surface as well as in the outer plastic zone. However, it is the $u_d$ (energy absorbing in an outer plastic zone away from the fracture surface) rather than $u_o$ that mainly accounts for the high toughness of PLA/EVA50 blends. This statement is confirmed by a large volume of stress whitening that extends below the fracture surfaces for EVA50 toughened PLA materials, while no such evidence at all for pure PLA.

4.3.5.2 Toughening mechanism under impact conditions

The impact energy of the tough PLA/EVA blends is mainly dissipated in the outer plastic zone accompanied by a considerable stress-whitening volume, as shown in Figure 4.13 b. The stress whitening, in general, is a consequence of numerous cavities and/or crazes formed during deformation. In rubber-toughened polymers two types of cavitation processes can be distinguished, i.e. internal rubber cavitation for blends with a strong interfacial adhesion in combination with a relatively low modulus of the rubber and interfacial debonding for blends with a weak interfacial adhesion. Both deformation mechanisms are beneficial for the toughness of plastic/rubber blends.

In the EAC-toughened PLA blends$^{22}$, the authors attributed the toughness of the PLA/EAC blends to a combination of different deformation mechanisms, i.e. crazing, crack bridging, interfacial debonding and matrix shear yielding, without discussing the dominating mechanism. For the PLA/PBS$^{14}$, PLA/PBAT$^{16}$ and PLA/ethylene-octene copolymer systems$^{19}$, the proposed toughening mechanisms were interfacial debonding and matrix yielding, all based on SEM observations of fracture surface.

Figure 4.13 demonstrates both the morphology at macroscopic and microscopic levels of the plastic zone of a PLA/EVA50 blend after fast deformation. In the PLA/EVA50 blends, the interfacial adhesion between the PLA and the EVA50 is relatively strong, while the EVA50 is a non-crosslinked rubber with a low modulus ($E' \approx 2$ MPa at ambient temperature as measured by DMTA). Consequently, the surface energy per unit area for the EVA50 to generate new surfaces associated with cavitation is low. This is beneficial for rubber cavitation in the presence of stress because cavitation will only be initiated if the energy gained by relieving the stress ($U_{\text{strain}}$) is greater than the energy needed to create a new surface ($U_{\text{surface}}$)$^{36}$.
Indeed, internal EVA50 rubber cavitation, which is regarded as one of the most effective ways to delocalize the stress and strain\textsuperscript{47,48}, was observed after impact testing (Figures 4.13 d – d’’). Almost no crazing or interfacial debonding occurred. When impact stress is applied, the presence of the EVA rubber particles leads to a tri-axial stress state that causes the dilatation of the EVA phase. The dilatation induces internal cavitation of EVA50 particles which releases the tri-axial stress, and prevents localization of strain in the PLA matrix\textsuperscript{40}. Simultaneously, the stress state in the thin ligaments of the PLA matrix between the cavities is converted from a tri-axial to a uni-axial tensile stress state. The new stress state is favorable for the initiation of shear bands resulting in shear yielding of the matrix\textsuperscript{36}. Such sequential yielding prevents strain softening on the microscopic level, which macroscopically results in a change in deformation mode from crazing to shear yielding and, consequently, a ductile behavior\textsuperscript{39,40}.

To obtain a tough material by releasing such tri-axial stress or delocalizing the strain, heterogeneities are needed. This explains the brittle behavior of pure PLA and PLA/EVA90 blends which have homogeneous single-phase morphologies.

\textbf{4.3.5.3 Toughening mechanism under tensile conditions}

Small-angle X-ray scattering (SAXS) has been proven to be a powerful tool to characterize the mode of local deformation of toughened plastic/rubber materials\textsuperscript{39,40,49,50}. Crazing can
result in intense scattering streaks in the tensile direction which are generally followed by scattering streaks perpendicular to the tensile direction due to a development of craze fibrils, while cavitation induces an overall increase in the scattering intensity. Therefore, crazing can be distinguished from cavitation by SAXS scattering patterns.

During tensile testing, all PLA/EVA blends, except EVA0 and EVA90, display stress-whitening followed by formation of a neck and stable growth of the neck zone. The different regions of a tensile bar after drawing are corresponding to different local deformations occurred in different tensile stages. Therefore, the local deformation mechanisms of the PLA/EVA systems can be investigated by studying the microscopic morphology over the different regions of a tensile bar after drawing.

An in-situ SAXS during tensile deformation was performed in previous studies\textsuperscript{39,49,50} which gave accurate information about the development of the local deformation. In the present work, the SAXS was performed after relaxation of stress state. This method is easier to apply, however the relaxation of the stress state may lead to changes in the morphology.

![SAXS scattering patterns](image)

*Figure 4.14: SAXS scattering patterns of the PLA/EVA50 (80/20) blends at different regions of a tensile bar: (a) un-deformed region, (b) stress whitening region and (c) the neck. The samples were drawn in the vertical direction.*

The SAXS patterns of the stress-whitening (early stage of deformation) and neck regions of a drawn tensile bar of the PLA/EVA50 (80/20) blend are shown in Figure 4.14 b and c respectively. For comparison, SAXS measurements were also performed on the same sample prior to deformation displaying an isotropic scattering pattern (Figure 4.14 a) due to the heterogeneous morphology. The overall scattering intensity of the stress-whitening region (Fig. 4.14 b) is much stronger than that of the un-deformed region, indicating the development of electron density fluctuations with no specific orientation. This is most probably the result of cavitation since no sharp crazing streaks are detected\textsuperscript{49}. As the
cavitation will relieve the tri-axial stress state in the blend, shear yielding is enhanced\textsuperscript{36}, which allows further deformation and, consequently, orientation of the cavities in the tensile direction\textsuperscript{49}. The highly oriented cavities and rubber particles resulted in an elliptically shaped SAXS scattering pattern as shown in Figure 4.14 c. Thus, the toughening mechanism for the PLA/EVA\textsubscript{50} system under tensile conditions is internal rubber cavitation in combination with matrix yielding.

Figure 4.15: Morphology of stretched PLA/EVA\textsubscript{50} (80/20) blends taken from different zones of tensile bar after necking as schematically indicated in (d).

To further support the hypothesis, the neck region of the tensile specimen (again taking the 80/20 blend as an example) was cryo-cut longitudinally and observed by SEM, as shown in Figure 4.15. To investigate the local deformation mechanism, sections (a), (b) and (c) were taken from different zones of the tensile bar, as schematically drawn in Figure 4.15 d. Cavitation occurs in the early stage of the deformation (Fig. 4.15 a) followed by elongation of the cavities and rubber particles (Fig. 4.15 b). Finally, high orientation of cavities and yielding of the matrix occur (Fig. 4.15 c). Moreover, a fibrillar structure (Fig. 4.15 c’ was detected in a few voids, which tends to bridge and retard the propagation of the voids. The fibrillation of rubber phase was regarded as an important energy absorption process in a
previous study\textsuperscript{22}, however, it is not a dominant morphology in the stretched PLA/EVA blends. The microscopic deformation observed by SEM is consistent with the SAXS results.

### 4.3.6 Temperature dependence of toughness for PLA/EVA50 blends

Figure 4.16 plots the impact toughness as a function of temperature and composition. In the experiments, no brittle-ductile transition (BDT) of pure PLA is observed as a function of temperature, because it is brittle at all the examined temperatures ($< T_g$ of PLA). The BDT temperature for an amorphous pure polymer is assumed to be situated near its $T_g$. Above $T_g$ amorphous polymers are flexible; while below $T_g$ the applied strain can not be effectively delocalized showing brittle behavior during deformation\textsuperscript{22}.

![Figure 4.16: Impact toughness of the PLA/EVA50 blends as a function of temperature and EVA50 content.](image)

Rubber-toughened plastics can be very brittle at very low temperatures, because the shear modulus of rubber phase dramatically increases when the temperature approaches $T_g$ of the rubber phase which promotes the resistance of rubber cavitation\textsuperscript{36}. The BDT represents a transition in major deformation mechanisms from shear yielding to crazing, or vice versa, accompanied by a sudden change in crack resistance\textsuperscript{22, 51}. For rubber-toughened plastics, there is a critical temperature at which BDT occurs. The critical temperatures (BDT) for PLA/EVA50 blends were below zero and shifted to lower values when the rubber content increased, as shown in Figure 4.16. For example, the BDT temperatures for PLA/EVA50 (80/20) and PLA/EVA50 (70/30) are approximate -10 °C and -25 °C respectively. Therefore, EVA50 enhanced the toughness of PLA also at low temperatures.
4.4 Conclusions

A commercial commodity copolymer, ethylene-co-vinyl acetate (EVA), was used to toughen PLA in this work. The macroscopic mechanical properties, especially the toughening effect of EVA and the microscopic deformation mechanism have been discussed.

The compatibility between PLA and EVA is improved with increasing the vinyl acetate (VA) content, since PLA is miscible with PVAc but immiscible with PE. The toughness of the PLA/EVA (80/20) blends firstly increased with VA content up to 50 wt% and then decreased. At low VA content large EVA particle size and weak interfacial adhesion compromised on the toughness of the PLA/EVA blends. At high VA content too small EVA particles can not cavitate under impact conditions. As a result, the optimum toughening effect of EVA on the PLA was obtained at a VA content of 50 - 60 wt%.

The EVA with VA content of 50 wt% (i.e. EVA50) was selected to study the toughening effect of EVA content in the PLA/EVA blends. Even 5 wt% EVA50 could make PLA already ductile ($\varepsilon_b \approx 300\%$), however, the notched Izod impact toughness of this blend was not obviously improved due to a strain-rate dependence of the rubber cavitation. The notched Izod impact toughness of PLA/EVA50 blends was considerably improved by 15 wt% EVA50, and further increasing the EVA50 content super-tough PLA/EVA50 blends can be obtained. The EVA50 particle size increased with EVA50 content in the blends. The increase in EVA50 particle size makes EVA50 cavitation easier, thus toughness improves.

The reason for brittleness of amorphous polymers is strain localization, which could be delocalized by the dispersed rubber phase via a (pre-)cavitation process. The morphology of PLA/EVA blends could be tuned by the VA content in the EVA copolymers, and by the EVA content in the blends. The moderate particle size and low modulus of the non-crosslinked EVA rubber particles are suitable for cavitation in the presence of tri-axial stress. Consequently, internal EVA rubber cavitation in the PLA matrix occurred under both impact and tensile conditions, which was detected by SEM, TEM and SAXS. Meanwhile, no obvious crazes were observed after deformation. Thus, internal rubber cavitation with matrix yielding is proposed to be the dominant toughening mechanism for the PLA/EVA blends.

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Reactive compatibilization of ethylene-\textit{co}-vinyl acetate/starch blends

The application of starch as a bioplastic is limited due to its poor processability and brittleness. Thermoplastic starch (TPS) is used as cheap filler as described in Chapter 1 and if dispersed finely in the matrix the TPS will not influence the overall properties in a too negative way. TPS is used in the past and present as filler in polyolefins (Cereplast, Wuhan Huali) to reduce the so-called carbon footprint. If TPS is mixed with PLA or PHB, a fully biocompostable blend is obtained.

In the previous chapter, the toughening effect of ethylene-\textit{co}-vinyl acetate copolymers (EVA) on PLA was described. EVA as such is not biocompostable but it is claimed that in the presence of starch the combination PLA/EVA/Starch is biocompostable.

In this chapter, the emphasis is on blending EVA with starch as a masterbatch for blending into PLA. In order to obtain a fine dispersion of starch in EVA, reactive EVA/starch blends were prepared by melt-extrusion in the presence of maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol. MA, BPO and glycerol play the role of coupling agent, free-radical initiator and plasticizer respectively. During the extrusion, MA was grafted onto EVA chains via a free-radical grafting mechanism, and reacted with hydroxyl groups of starch chains. As a result, EVA-g-starch copolymers were formed at the interface between the EVA and starch. The EVA-g-starch copolymer acted as a compatibilizer, leading to fine starch dispersion and strong interfacial adhesion between starch and the EVA matrix. The mechanical properties of the EVA/starch blends were enhanced by the reactive compatibilization, e.g. the tensile strength of the EVA50/starch (50/50) was increased by a factor of 6 after addition of 0.9 – 1.8 wt\% MA. The property stability of starch compounds is usually an issue, while the mechanical properties of the (compatibilized) EVA/starch blends were relatively stable during storage.
5.1 Introduction

Renewable materials have drawn great attention in the past two decades due to the environmental concern and sustainability issue. Renewable materials such as poly(lactic acid) (PLA)\(^1\), poly(hydroxyalkanoates) (PHAs)\(^2\), natural fibers\(^3,4\) and starch\(^5\) have been extensively studied.

Starch is a renewable and compostable biopolymer derived from abundant natural sources such as potato, wheat and maize\(^6\). Considering that starch is even cheaper than oil, it would be an ideal alternative for oil-based plastics. However, starch can not be processed using conventional techniques such as extrusion and injection molding because the thermal decomposition temperature of starch is lower than its melting point\(^5\) and the molar mass is far too high, see Chapter 1 (1.2.3). To process starch, it has to be gelatinized and mixed with additional additives, e.g. glycerol\(^7\). The well-accepted concept of gelatinization refers to the destruction of the crystalline structure in starch granules, which is an irreversible process\(^8\). The process includes in a broad sense and in time sequence, granular swelling, native crystalline melting (loss of birefringence) and molecular solubilization\(^9\). The combination of gelatinized starch and additives is referred to as thermoplastic starch, viz. TPS. Starch or TPS is generally used as filler for compounding with other polymers such as polyolefins. Early work in polyolefin/starch blends was to make (photo-) degradable materials due to the “white-pollution” issues, which, however, were not solved by this route\(^10,11\). In view of renewable resource, carbon footprint and competitive pricing, polyolefins/starch are still active on the market, e.g. PSM® (HL-100 series, Wuhan Huali) and Cereplast Hybrid Resins™ (Bio-polyolefins® , Cereplast, Inc.)\(^12\).

In recent years, the interest has been shifted to blends of starch with other biocompostable materials such as PLA\(^13-17\), poly(hydroxybutyrate) (PHB)\(^18-20\), poly(butylene adipate-co-terephthalate) (PBAT)\(^21,22\) and poly(caprolactone) (PCL)\(^23\). The purposes are to reduce the cost of the biocompostable materials while retaining biocompostability.

Starch is a hydrophilic material, thus, to obtain fine dispersion of starch in a hydrophobic polymer matrix is difficult. Generally, the mechanical properties of starch-related blends are not so good due to the poor affinity between starch and the other component and the coarse morphology. A common route to increase the affinity between starch and the blended polymer is compatibilization\(^13,15,16,24-26\). Compatibilization can be performed either by addition of a pre-made compatibilizer or by an in-situ reaction during blending. Pre-made compatibilizers, i.e. PLA-g-starch, were used to improve the compatibility between PLA and
starch\textsuperscript{24,27}. As a result, the tensile strength and elongation at break of the compatibilized PLA/starch blends were slightly improved in comparison with that of the blends without addition of PLA-g-starch. Also, methylenediphenyl diisocyanate (MDI)\textsuperscript{26} and maleic anhydride (MA)\textsuperscript{13,15,17,25} were used to generate an \textit{in-situ} compatibilization during melt blending of starch based materials. Compared with MDI, MA is generally preferred because it is easier to handle and has a lower toxicity\textsuperscript{13}.

Renewable materials such as corn starch have also been used as additives for rubber materials and vulcanizates\textsuperscript{28}. However, the rubber matrix was limited mainly to natural rubber (NR)\textsuperscript{29-32}. The mechanical properties such as tensile strength and elongation at break of the NR/starch blends were found to decrease with increasing starch content. The inability of starch particles to support stress transferred from elastomeric phase and a starch–rubber interface was proposed to be a reason for the decreasing trend\textsuperscript{30}.

Ethylene-\textit{co}-vinyl acetate (EVA) is a synthetic rubber material when the vinyl acetate (VA) content is between 40 and 90 wt\%. It can be reinforced by inorganic fillers, e.g. silica\textsuperscript{33} and montmorillonite (MMT)\textsuperscript{34}. To our knowledge, no studies on the reinforcement of EVA rubber by starch have been reported yet.

In addition, an important advantage of starch in packaging applications is its biocompostability, whereas EVA copolymers are not biocompostable according to various standards such as EN13432. Surprisingly, EVA copolymers in combination with starch can pass the standard tests on biocompostability\textsuperscript{35}. If EVA rubber could be reinforced by starch, then it is possible to make EVA/starch blends as useful biocompostable materials as well.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.1.png}
\caption{Schematic illustration of the proposed structure for the in-situ compatibilized EVA/starch blends showing a grafted EVA layer on the surface of starch particles.}
\end{figure}

The primary objective of this chapter is to prepare EVA/starch masterbatches with a fine dispersion of starch. The approach is using maleic anhydride (MA) and benzoyl peroxide (BPO) to initiate an \textit{in-situ} compatibilization between EVA and starch. Within this approach,
the aim is that the EVA molecules will graft onto the surface of starch particles and reduce the interfacial tension, resulting in fine starch particles coated with EVA, as schematically shown in Figure 5.1. The effect of the in-situ compatibilization on morphology and mechanical properties of the EVA/starch blends was investigated. The in-situ compatibilized EVA/starch blends are also designed to serve as a masterbatch which can be used to compound with other biocompostable polymers such as PLA, PHA, PBAT, PCL and poly(butylene succinate) (PBS). In Chapter 6, compounding of EVA/starch with PLA will be discussed.

5.2 Experimental

5.2.1 Materials

Gelatinized potato starch powder with 21 wt% amylose and 79 wt% amylopectin was supplied by Rodenburg, the Netherlands. No glycerol but 9 – 17 wt% water was used in the gelatinization process. The H₂O content in the gelatinized starch powder is around 8 wt%. Before processing, the starch was dried in a vacuum oven at 50 °C over night and the H₂O content in dried starch is around 2 wt% according to TGA measurements. The structures of amylose and amylopectin were shown in Figure 1.3 (Chapter 1). EVA50 under the trade name of Levapren® was supplied by Lanxess Chemical Co., Ltd. in the form of pellets. The data for EVA50 are listed in Table 4.1 (Chapter 4). Maleic anhydride (MA) as a coupling agent was supplied by Fluka® with purity ≥ 99.0%. Benzoyl peroxide (BPO) used as a free-radical grafting initiator was supplied by Aldrich® with a half-life time of approximately 1 min at 131 °C. Glycerol as a plasticizer for starch was supplied by Rodenburg, the Netherlands. All the chemicals were used as received without further purification. The structures of additives are shown in Figure 5.2.

![Figure 5.2: The structures of additives: (a) maleic anhydride, (b) benzoyl peroxide and (c) glycerol.](image-url)
5.2.2 Blend preparation

Since powders are easier to pre-mix with additives, the EVA50 pellets and starch powder with a weight ratio of 50/50 were first ground using a Retsch ZW100 grinder (14000 rpm and mesh size of 0.5 mm). Before the grinding procedure, EVA50 and starch were immersed in liquid nitrogen. Dry EVA50/starch powders (in a vacuum oven at 50 °C over night) with different amounts of additives (i.e. glycerol, MA and BPO) were then compounded on a twin-screw extruder (D = 16 mm, L/D = 20) at 135 °C. A fixed screw rotation speed of 100 rpm was used. The configuration of the twin-screw including transport, compression, reversing and mixing regions, is shown in Figure 5.3. The compositions of the samples are listed in Table 5.1. As general processing of starch, glycerol was used as a plasticizer of starch in this study. Since the water content in dried starch is only around 2 wt% (including hydrogen bonded H\textsubscript{2}O), the effect of H\textsubscript{2}O is not discussed although water is also a good plasticizer of starch. The residence time of materials in the extruder was 2 - 3 min as checked by using color masterbatch. In view of the limited residence time in the extruder and the half-life time of BPO (t\textsubscript{0.5} ≈ 1 min), the extrudates were granulated and re-extruded under the same processing conditions. The extrudates were pelletized and compression molded into sheets (0.8 mm in thickness) at 135 °C for 3 min and then quenched to room temperature. The compression-molded samples were used for further characterization.

**Table 5.1: Compositions of the EVA50/starch blends.**

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>EVA50 (wt%)</th>
<th>Starch (wt%)</th>
<th>Glycerol (wt%)</th>
<th>MA (wt%)</th>
<th>BPO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>45.5</td>
<td>45.5</td>
<td>9.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>#2</td>
<td>45.5</td>
<td>45.5</td>
<td>9.0</td>
<td>0.23</td>
<td>0.023</td>
</tr>
<tr>
<td>#3</td>
<td>45.0</td>
<td>45.0</td>
<td>9.0</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td>#4</td>
<td>45.0</td>
<td>45.0</td>
<td>9.0</td>
<td>0.90</td>
<td>0.090</td>
</tr>
<tr>
<td>#5</td>
<td>44.5</td>
<td>44.5</td>
<td>9.0</td>
<td>1.78</td>
<td>0.178</td>
</tr>
<tr>
<td>#6</td>
<td>45.5</td>
<td>45.5</td>
<td>9.0</td>
<td>0</td>
<td>0.181</td>
</tr>
</tbody>
</table>

*Note: the spread of the composition of EVA50, starch and glycerol is within 0.5 wt%.*
5.2.3 Characterization

**Polarized optical microscope (POM):** The crystal morphology of native and gelatinized starch powders was studied using POM (Zeiss Axioplan 2 microscope) equipped with a Zeiss AxioCam camera. The images were analyzed with the accompanied Axio Vision v3.06 software.

**Scanning electron microscope (SEM):** SEM (Quanta 600-F-ESEM, FEI, the Netherlands) was used to characterize the phase morphology of the EVA50/starch blends. The compatibilized EVA50/starch samples were microtomed at -40 °C using a glass knife to obtain sections with 3 μm in thickness. The thin sections were firstly stained with saturated I$_2$/KI solution, and then sputter-coated with a thin gold layer. For the sample-#1, the microtomed bulk-surface was characterized with SEM, since thin-section of this sample was difficult to obtain due to large starch particles and poor interfacial adhesion between starch and EVA50 matrix.

**Solvent extraction:** Chloroform is a good solvent for EVA50 but not for starch. The residues from EVA50/starch blends after extraction, viz. starch and starch with grafted EVA50 blends were obtained by Soxhlet extraction in boiling chloroform for three days. The obtained residues were dried overnight at 50 °C in a vacuum oven for further analysis.

**Fourier transform infrared spectroscopy (FTIR):** The residues obtained from extraction of starch and the EVA50/starch blends were analyzed on a FTIR spectrometer (Excalibur 3000 spectrometer) using an attenuated total reflection (ATR) mode. The final spectrum of
each sample was an average of 100 scans at a resolution of 4 cm\(^{-1}\). The data were analyzed using the Varian Resolutions Pro 4.0 software.

**Thermogravimetric analysis (TGA):** To determine the existence and the amount of grafted EVA50 in the extracted residues, TGA was performed on a TA Q500 instrument. The residues were heated from 20 to 700 °C at 10 °C/min under nitrogen atmosphere.

**Molau experiment:** A sample of 1.1 g of each EVA50/starch blends (with different MA concentrations) was dipped into 20 mL chloroform. The solutions were sealed in glass bottles for a couple of days and digital photos were taken to compare the emulsifying effect of EVA50 on the starch phase at different MA concentrations.

**Dynamic mechanical thermal analysis (DMTA):** DMTA was carried out on a DMA Q800 (TA Instrument, USA) using a tensile-film mode. Specimens (13.0 × 6.5 × 0.8 mm\(^3\)) were measured from -65 to 270 °C at a frequency of 1 Hz, with constant amplitude of 10 μm and at a heating rate of 3 °C/min. The storage modulus and tan δ were recorded as a function of temperature.

**Mechanical properties measurements:** The tensile properties were measured using a Zwick Z100 tensile tester at a crosshead speed of 10 mm/min. The narrow parallel-sided portion of the dumbbell-shaped tensile bar was 12 mm in length, 0.8 mm in thickness and 2 mm in width. The tests were carried out at ambient temperature.

5.3 Results and discussion

5.3.1 Morphology of starch

The crystal morphology of native starch and gelatinized starch was first studied using polarized optical microscopy (POM), as shown in Figure 5.4 a and b. Under polarized light, the crystals have a bright contrast. Native potato starch is found in the form of granules with oval or egg shapes and size from 15 to 70 μm in diameter, as shown in Figure 5.4 a. The native starch shows typical cross extinction patterns due to its crystalline order. Because of strong hydrogen bonding between starch molecules, the granules without plasticizers are not easy to break-up during processing. This crystal structure can be successfully destroyed by a so-called gelatinization process in the presence of heat, shear force and plasticizer(s) (e.g. H\(_2\)O). The crystal morphology of gelatinized starch is shown in Figure 5.4 b. The crystal order of gelatinized starch was disrupted to a large extent, therefore, hardly any cross extinction are observed. However, a small amount of crystal is still present (Fig. 5.4 b). A
SEM image of the gelatinized starch is shown in Figure 5.4 c, indicating the particle size of gelatinized starch from several tens to several hundreds micrometers. The gelatinized starch particles are even larger than native starch granules due to agglomerations of starch particles during the gelatinization process. The gelatinized starch is easier to process than native starch as mentioned before and is used in this work.

![Figure 5.4: Polarized optical microscopic images of (a) native starch and (b) gelatinized starch, and a SEM image of (c) gelatinized starch. The particle size noted in the images was measured directly by the accompanied software (see section 5.2.3).](image)

### 5.3.2 Effect of compatibilization on phase morphology of the EVA50/starch blends

The SEM images of the EVA50/starch blends with different MA concentrations are shown in Figure 5.5. Since the EVA50 matrix and starch have different phase contrasts after staining with I₂/KI solution, they can be easily distinguished. The bright phase in the SEM images is starch while the dark matrix is the EVA50 phase.

In the absence of MA, starch was non-uniformly dispersed in the EVA50 matrix with large particle sizes (from 40 to 300 μm), as shown in Figure 5.5 a. The size is similar to that of the gelatinized starch (Fig. 5.4 c). This phenomenon implies that the gelatinized starch was almost not broken-up (fragmented) during melt blending with EVA50, or the gelatinized starch was broken-up but agglomerated again during blending. In addition, voids are observed between starch particles and the EVA50 matrix indicating a rather weak interfacial adhesion between the two components.

However, the particle size was reduced by a factor of about 100 after addition of 0.45 wt% MA. The starch particles with a sub-micron dimension are dispersed uniformly in the EVA50 matrix when 0.45 - 1.8 wt% MA is added (Fig. 5.5 b - d). In a shear field, large (plasticized) starch particles could break up into small pieces thanks to the use of glycerol as a plasticizer, offering more fresh interfaces. Then EVA-g-starch copolymers are formed *in-situ* at the fresh
interfaces preventing agglomeration (coalescence) of the fine starch particles during the subsequent processing.

Figure 5.5: SEM images of the EVA50/starch blends with different MA concentrations. The images (a) - (d) correspond to samples #1, #3, #4 and #5 (Table 5.1) respectively. The diameter of the starch particles are indicated in the images.
5.3.3 Mechanisms of the reactive compatibilization

It is already known that a free radical grafting reaction is able to occur between EVA and MA with peroxide\textsuperscript{36-38}. On the other hand, an esterification reaction is expected between the grafted MA and the hydroxyl groups of starch chains\textsuperscript{15}. Therefore, these two reactions may occur simultaneously during melt blending with EVA50, starch, MA and BPO. In Figure 5.6, the main chemical reactions in the melt blending are proposed. However, the situation is complex especially in the presence of glycerol and water (contained in starch).

Reactive compatibilization reactions in processing

(1) Formation of the initiator radicals

\[
R-O-O-R \xrightarrow{135^\circ C} 2 R-O-\cdot
\]

(2) Formation of macro-radicals

\[
\left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right) + R-O-\cdot \xrightarrow{135^\circ C} \left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right) + R-OH
\]

(3) Grafting MA onto EVA polymer chains

\[
\left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right) + \text{CO} \xrightarrow{135^\circ C} \left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right)
\]

(4) Combination reaction between EVA and starch via MA

\[
\left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right) + \text{H}_2\text{O} \xrightarrow{135^\circ C} \left(\frac{\text{CH}_2-\text{CH}_2}{x}\left(\frac{\text{CH}_2-\text{CH}_2}{y}\right)\text{CH}_2-\text{C}^\cdot_n\right)
\]

Figure 5.6: Proposed main reactions between EVA50 and starch in the presence of MA and BPO. (R represents C\textsubscript{7}H\textsubscript{5}O).

Firstly, the maleated EVA50 could react with hydroxyl groups present at the starch particle surface forming ester linkages\textsuperscript{15}. Secondly, the presence of glycerol would interfere with starch - MA reactions, as MA grafts could react with hydroxyl groups of glycerol as well.
Thirdly, recombination of two polymer radicals (i.e. EVA•) may occur. Fourthly, the humidity (water) in the starch phase may cause the ring opening of the MA. Although the opened MA (i.e. acids) can still react with hydroxyl groups of starch, its reactivity is much lower than that of anhydride. The first two possible reactions are both helpful in improving compatibility and interfacial adhesion between the EVA50 and starch phases, while the last two are side reactions. Considering the greatly improved interfacial properties and the fine dispersion of starch in the EVA50 matrix (Figs. 5.5 b – d), the reaction between maleated EVA50 and hydroxyl groups on the starch surface is mainly proposed.

During melt free-radical grafting of MA onto polymers, the grafting degree increases with MA concentration\(^ {36} \). As a result, at a low MA concentration, EVA50-g-starch copolymers are the dominant reaction products which are responsible for the fine dispersion of starch. However, the high grafting degree of MA at a high MA concentration could result in a network between starch and EVA50, in which the starch particles could act as crosslink points. The effect and mechanism of the \textit{in-situ} compatibilization for the EVA50/starch/MA/BPO blends are schematically illustrated in Figure 5.7. Since the starch particles act as crosslink points, the network could be fragmented in a shear force field during melt blending.

![Figure 5.7: Schematic illustration of the in-situ compatibilization effect on the morphology and the interfacial structures of the EVA50/starch/MA/BPO blends.](image)
In order to prove the above described *in-situ* compatibilization mechanism, gelatinized starch and the EVA50/starch blends (with varied MA concentrations) were subjected to soxhlet extraction using boiling chloroform for 3 days. The residues were dried and then characterized using FTIR spectroscopy and TGA.

Figure 5.8 shows FTIR spectra of EVA50 and the extracted starch. Two distinctive characteristic vibration bands at 2918 and 2849 cm\(^{-1}\) are observed for EVA50 due to the presence of C-H stretching. A sharp characteristic IR band at 1733 cm\(^{-1}\) is also observed, corresponding to the vibration of the carbonyl groups (C = O) of EVA50\(^{39}\). On the other hand, starch has a broad stretching vibration peak in the region of 3013 - 3646 cm\(^{-1}\) relating to the -OH groups\(^{40}\).

Chloroform is a good solvent for EVA50, but not for starch. During extraction, non-reacted EVA50 molecules are extracted into chloroform, since EVA50 is the continuous phase in the blends. The FTIR spectra of the residues are presented in Figure 5.9. No characteristic band relating to the carboxyl group (C = O) is observed for the residues of the non-compatibilized blend (Fig. 5.9, curve a). This indicates that all EVA50 in this blend was extracted into chloroform. In contrast, the C = O absorption band at approximately 1736 cm\(^{-1}\) is present for the residues of the compatibilized blends (Fig. 5.9, curves b - e). The EVA50 content in the residues increases with an increase in the MA concentration, as evidenced by an enhancement in the peak intensity. The FTIR results confirm that EVA50 was grafted onto starch chains in the presence of MA and BPO. In the ATR-FTIR, the depth of penetration of infrared light...
into the residues is similar however the composition of the residues is changed with MA concentration, resulting in different intensity of the FTIR spectra.

The reactions between EVA50 and starch are further confirmed by TGA. In Figure 5.10 a, the decomposition of pure EVA50 was analyzed, showing two decomposition steps. Poly(ethylene) (PE) and poly(vinyl acetate) (PVAc) are used as references for the backbone and side groups of EVA50 chains respectively. The TGA decomposition curves for the references are shown in the inset of Figure 5.10 a. Taking into account that the weight percent of backbones in the EVA50 copolymer is 66 % and the decomposition temperature of PE is around 500 °C, it can be concluded that the second-step decomposition corresponds to the backbones of EVA50 chains.

The decomposition temperature of starch is around 300 °C, as shown in Figure 5.10 b/curve (1), which is similar to that of CH₃-COO- groups of the EVA50 copolymer. No traces of EVA50 are detected in the residues of the non-compatibilized blend (Fig. 5.10 b/curve (2)). On the other hand, a decomposition of the EVA50 backbone is observed for the extracted residues of the compatibilized blend (sample #4), as shown in Figure 5.10 b/curve (3). This, again, proves that EVA50 was chemically bonded to starch chains during the \textit{in-situ} compatibilization. Based on the weight lose (11 wt %) between 400 and 500 °C (Fig. 5.10 b/curve (3)), the grafted EVA50 content is estimated about 17 wt% in the residues of the sample #4.

The in-situ compatibilizer, EVA50-g-starch, is proposed to stabilize the fine morphology of the EVA50/starch blends. A Molau test\textsuperscript{41} was carried out to evaluate the stabilization and emulsifying effect of the EVA50-g-starch. In this test, EVA50/starch blends were immersed...
into chloroform and stored in different bottles, and digital photos were taken after 3 days, as shown in Figure 5.11. The sample #1 (as a reference) is dissolved in chloroform, showing an obvious phase separation (Fig. 5.11 a). As indicated, starch particles aggregate on the top layer of the solution. The blends with MA 0.9 wt% (#4) is found to retain as a milky and colloidal suspension solution (Fig. 5.11 b). It indicates that the emulsifying function of the EVA50-g-starch copolymers stabilizes the suspension solution. At a MA concentration of 1.8 wt%, the sample (#5) is swollen to a certain extent, but is not dissolved completely, as shown in Figure 5.11 c. A few small insoluble pieces are also observed on the top of the solution B (Fig. 5.11 b). These results indicate that (1) the in-situ compatibilization proposed above is effective and (2) EVA50-g-starch copolymer is the major reaction product at low MA concentration (≤ 0.9 wt%), while EVA50-crosslink-starch network is dominant at high MA concentrations.

EVA50 itself can also form a crosslink-network with peroxide\textsuperscript{38}. The highest peroxide (BPO) concentration used in this study is 0.18 wt%. An EVA50/starch blend with 0.18 wt% BPO but without MA (i.e. sample #6) was prepared under the same processing conditions. The Molau test shows similar phase separation as presented in Figure 5.11 a. In addition, the EVA50 matrix was completely dissolved and no gel was observed. These results indicate that 0.18 wt% BPO alone cannot initiate a crosslink network in the EVA50/starch blends. Thus, the network is mainly resulted from the chemical reactions between starch and EVA50 in the presence of MA and peroxide.

![Figure 5.11: Molau test of the EVA50/starch blends with MA concentration: (A) 0, (B) 0.9, and (C) 1.8 wt%. (A), (B) and (C) correspond to samples #1, #4 and #5 (Table 5.1) respectively.](image-url)
5.3.4 Effect of compatibilization on properties of the EVA50/starch blends

5.3.4.1 Dynamic mechanical thermal analysis

The storage moduli ($E'$) of the EVA50/starch blends and pure EVA50 were measured by DMTA, as presented in Figure 5.12. The storage modulus of EVA50 was enhanced significantly after addition of 50 wt% starch regardless of the in-situ compatibilization. For the compatibilized blends, higher $E'$ values were measured in comparison with the non-compatibilized blend.

![Figure 5.12: Storage moduli of the EVA50/starch blends and the pure EVA50 as a function of temperature.]

The three principal contributions responsible for the reinforcement in polymer composites are: (i) substitution of soft polymer matrix by stiff filler, (ii) immobilization of polymer molecules on filler particle surfaces as a consequence of filler-polymer interaction and (iii) stress transfer from the matrix to the filler. Moreover, accompanying effects such as particle aggregation, residual stresses, or presence of defects in the polymer matrix or at the matrix-filler interface can complicate the prediction of elastic moduli\textsuperscript{42}. Starch is a rigid filler. In the glassy region ($< -20^\circ\text{C}$, $T_{g-EVA50}$), the thermal mobility of EVA50 main chain is negligible, hence, adding starch can only affect the secondary transitions. As a result, the reinforcement by addition of starch at low temperature is mainly attributed to the substitution mechanism, where part of the soft matrix is replaced by the stiffer starch filler. However, the segmental and/or molecular immobilization becomes the primary reinforcing mechanism at temperatures well above the $T_g$ of EVA50\textsuperscript{42}. The chain mobility close to the filler surface is reduced due to an intensive polymer-filler interaction\textsuperscript{43}, leading to reinforcement of the
rubber matrix. The extent of interaction of the polymer chains with the filler surface depends on the characteristics of the surface like energy distribution, roughness and surface area\(^{44}\). After the *in-situ* compatibilization, the starch particle size was reduced accompanied by an increase in specific surface area of starch (filler) and an enhancement in interfacial adhesion between the starch and EVA50 matrix, which may be responsible for the higher storage modulus of the compatibilized EVA50/starch blends.

Upon heating, the compatibilized blends showed an increase in storage modulus at approximately 220 °C. This behavior suggests a certain extent of network may exist in these blends which is consistent with the above discussion (Molau test). In rubber/filler systems, an increased storage modulus was also attributed to a filler network formation bridged with polymers between adjacent filler particles\(^{44, 45}\). The existence of the network in the compatibilized blends could also be responsible for their higher storage modulus.

![Figure 5.13: Thermal relaxation of the EVA50/starch blends as a function of MA concentration.](image)

Glycerol plasticized starch usually consists of a starch-rich phase and a glycerol-rich phase. A \(\alpha\) relaxation of starch-rich phase and a \(\beta\) relaxation of glycerol-rich phase were reported at around 50 °C and -50 °C respectively in literature\(^{46-48}\). The \(\alpha\) relaxation associated with the glass transition corresponds to a translational diffusion of starch chain/segments, while the \(\beta\) relaxation is due to the motions of groups or short segments such as local rotations of side groups or crank shaft motions along the backbone. Figure 5.13 shows the thermal relaxation behavior of the EVA50/starch blends. The \(T_g\) of the EVA50 phase in the blends was not affected so much by the compatibilization (Fig. 5.13 a). Due to the good affinity between starch and glycerol, the glycerol is expected to distribute mainly in starch phase. The \(\beta\) relaxation of glycerol plasticized starch phase shifted to lower temperatures after the
compatibilization, as shown more clearly in Figure 5.13 b. Sarazin et al.\textsuperscript{47} reported that the $\beta$ relaxation temperature of TPS36 (with glycerol content of 36 wt\% to starch) was 10 °C lower than that of TPS24 (with glycerol content of 24 wt\% to starch). Therefore, the slight decrease in the $\beta$ relaxation temperature, as shown in Figure 5.13 b, may imply a better plasticization effect of glycerol on the starch component in the compatibilized blends. This could be resulted from a facilitated penetration of glycerol into the starch phase due to the larger starch surface area after compatibilization.

5.3.4.2 Tensile properties

Macroscopic properties of a rubber blend relates to its structures. For a non-crosslinked rubber, it usually exhibits a high elongation at break (> 1000 \%) and a very low tensile strength (except NR because of strain-induced crystallization). However, the tensile strength can be enhanced by addition of active fillers such as carbon black which could form a network with rubber\textsuperscript{49}. Simultaneously, the elongation at break is usually reduced.

![Figure 5.14: (a) Tensile properties and (b) typical stress-strain curves of the EVA50/starch blends as a function of MA concentration.](image)

The tensile properties and stress-strain curves of the EVA50/starch blends are presented in Figure 5.14 a and b respectively. The physical blend (#1) exhibits a rubbery behavior with high elongation at break (1100 \%) and low tensile strength (1 MPa) which is similar to pure EVA50 ($\varepsilon_b = 1600\%$ and $\sigma = 2.2$ MPa). Apparently, the tensile properties of EVA50 were not improved by addition of the starch. Thus, starch plays a role of inert filler in the EVA50/starch blend\textsuperscript{49}. After the \textit{in-situ} compatibilization, the EVA50 rubber is reinforced as
evidenced by an increase in the tensile strength (Fig. 5.14 a). Starch became active in the presence of MA. The more MA was used, the larger reinforcing effect was obtained. Meanwhile, the elongation at break of the EVA50/starch blends decreases with MA concentration, and levels off at MA 0.9 wt% (Fig. 5.14 a).

In a starch-reinforced NR system, unmodified starch acted as essentially inert filler causing a decrease in tensile strength, tear strength and elongation at break of the NR matrix. In contrast, the modified starch (grafted with poly(butylacrylate)) showed an obvious reinforcement of both NR matrix and the NR/starch composites, which was ascribed to an improvement on the dispersion of starch and the interfacial adhesion between starch and the NR matrix after modification. Similarly, the reinforcement of starch combined with the in-situ compatibilization on the EVA50 matrix is attributed to the fine dispersion of starch particles, the strong interfacial adhesion between starch and the EVA50 matrix and the formation of a certain extent of crosslink network. The blends with MA 0.45 - 1.8 wt% show a continuous and steep increase in stress with strain, which is very different from the blends with MA ≤ 0.23 wt% (Fig. 5.14 b). The stress-strain curves of the compatibilized blends (at MA ≥ 0.9 wt%) exhibit some characteristics of a thermoplastic vulcanizate due to the network of starch filler and the network between the EVA50 and starch.

**5.3.5 Property stability of the EVA50/starch blends**

Property instability with time is an issue for starch-based materials. In the present study, the EVA50/starch samples were sealed in a desiccator at ambient temperature. The tensile tests were applied after different storage times to evaluate the property stability with time. The tensile properties of the EVA50/starch blends obtained at different storage times are presented in Figure 5.15. These tensile properties measured after three and nine months are normalized to those of the one-day-old samples. The normalized data are plotted in Figure 5.16. The tensile strength (σ) of the blends was increased slightly after several months, as shown in Figure 5.15 a. The largest change in σ is observed for the blend with MA 1.8 wt%, the σ of which was increased by ~ 1 MPa after 3 months and then leveled off. The elongation at break of these blends shows a certain fluctuation with time (Fig. 5.15 b). The property changes could be induced by moisture sensitivity of the starch phase, migration of glycerol, starch retrogradation and the relaxation of amorphous EVA50 matrix during storage.
The storage stability of injection-molded starch/zein (a type of protein) plastics using glycerol and H$_2$O as plasticizers was studied by Lim et al.\textsuperscript{51}. In their study, both the tensile strength and the elongation at break of the blends were decreased (typically) by 50\% after one-week storage in a dry environment (11\% RH). It was also found that the blends kept their properties better under a humid condition (93\% RH) in comparison with under the dry condition. In a previous study in our group\textsuperscript{52}, a poly(vinyl acetate)/starch (40/60) blend (where starch is still a dispersed phase plasticized with 3 wt\% H$_2$O and 10 wt\% glycerol) became brittle after two-day storage, e.g. the elongation at break was reduced by a factor of 9. The changes in properties of the EVA50/starch blends are within 25\% in 9 months (Fig. 5.16). In comparison with the reported results, the mechanical properties of all the examined EVA50/starch blends regardless of compatibilization were relatively stable over a period, at least, of 9 months.
5.4 Conclusions

EVA50/starch blends were prepared via a reactive extrusion in the presence of maleic anhydride (MA), benzyol peroxide (BPO) and glycerol. The compatibility between the hydrophobic EVA50 and the hydrophilic starch is rather poor leading to a very coarse morphology of their blends. During the reactive extrusion, MA was grafted onto EVA50 chains via a free-radical grafting mechanism and also reacted with the hydroxyl groups of starch. The chemical bonding between the EVA50 and starch phases was confirmed by FTIR and TGA results. The in-situ formed EVA50-g-starch copolymers acted as a compatibilizer in the EVA50/starch blends. The compatibility between the EVA50 and starch was then improved as evidenced by a dramatic reduction in starch particle size and an improvement of the interfacial adhesion. Generally, starch compromises on the tensile strength and elongation at break of the other blend component\textsuperscript{15,20,30}. In this study, the mechanical properties of the EVA50/starch blends were improved after the reactive extrusion. A reinforcement effect of starch on the EVA50 matrix was observed after the in-situ compatibilization. The reinforcement was attributed to a fine dispersion of starch, a strong interfacial adhesion between starch and the EVA50 matrix and a formation of crosslink network between the EVA50 and starch. Therefore, the morphology and mechanical properties of the EVA50/starch blends can be tailored by the in-situ compatibilization.

5.5 References

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Chapter 6

Reactive compatibilization of poly(lactic acid)/ethylene-co-vinyl acetate/starch blends

Poly(lactic acid)/ethylene-co-vinyl acetate/starch (PLA/EVA/starch) ternary blends were prepared by a multiple-step melt processing. First, EVA/starch pre-compounds were prepared by reactive extrusion in the presence of maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol. An in-situ compatibilization was induced between the EVA and starch, i.e. MA was grafted onto EVA chains and reacted with hydroxyl groups on the starch chains forming EVA-g-starch copolymers at the interface. Then, PLA was physically melt-blended with the EVA/starch pre-compounds. The effect of MA concentration on the morphology and properties of the PLA/EVA/starch blends was studied. A significant reduction in starch particle size was induced in the PLA/EVA/starch blends by the in-situ compatibilization. With compatibilization, starch could be dispersed in the ternary blends with a dimension of 0.5 - 2.5 μm. As a result, the toughness of the blends was improved. For instance, the elongation at break increased from 10 % of the non-compatibilized blends to 100 % of the compatibilized blend with MA 0.45 wt%. Since property stability of starch is an issue, the tensile properties of these blends were measured at different storage time and the blends showed good property stability with time.
Chapter 6

6.1 Introduction

Poly(lactic acid) (PLA) is a renewable and biocompostable material with good processability and reasonable mechanical properties. However, the application is limited due to its brittleness, low heat distortion temperature and high price (comparing to conventional polymers)\(^1\). To reduce the price, PLA could be blended with starch or thermoplastic starch (TPS) which is cheap, renewable and biocompostable\(^2\).

A lot of works were done to prepare PLA/starch blends to reduce the high cost of PLA and to increase the biocompostable rate of PLA\(^3\)-\(^11\). The properties of PLA/starch blends are usually poor due to a lack of affinity between the two components\(^5\),\(^12\),\(^13\). Therefore, diisocyanates\(^6\),\(^14\),\(^15\), PLA-g-starch\(^12\), poly (vinyl alcohol)\(^16\) and maleic anhydride\(^3\),\(^5\),\(^13\),\(^17\) were used to improve the compatibility between PLA and starch. However, the toughness of these blends was only improved to a certain extent probably because of the brittle natures of both PLA and starch. For example, the elongation at break of PLA/starch blends after compatibilization was still less than 5\(^%\)\(^5\),\(^14\), which is comparable to that of pure PLA. A possible approach to increase the ductility of PLA/starch blends is via plasticization of the PLA matrix\(^7\),\(^18\) or via plasticization of the starch phase\(^7\). The elongation at break of a PLA/starch/MA (60/40/1) blend was reported around 100\(^\%\), when 15\(^\%\) of acetyl triethyl citrate (ATC) was used as a plasticizer\(^7\), while the tensile strength of the blends was decreased to around 15 MPa. A high plasticizer concentration is usually required to obtain sufficient plasticization effect, which leads to the property instability due to the migration of plasticizers.

Considering that both PLA and starch are relatively brittle, introduction of a toughening modifier as a third component to PLA/starch blends may improve the toughness. Poly(caprolactone) (PCL) is a ductile and biodegradable material which was used to toughen PLA\(^19\),\(^20\). PCL was added to PLA/TPS blends and the toughness of the blends was increased obviously after addition of 5 - 10\(^\%\) PCL\(^21\), e.g. the strain at break of the PLA/PCL/starch ternary blends was increased to 10 - 50\(^\%\) and the notched Izod impact strength was increased to 25 - 70 J/m dependent on the amount of glycerol in the TPS. The tensile strength and elongation at break of PLA/PCL/starch ternary blends were even higher when (PLA/PCL)-g-acrylic acid compatibilizer was used\(^20\). An elongation at break of 250\(^\%\) and a tensile strength of 35 MPa for the (PLA/PCL)-g-acrylic acid/starch (starch, 50\(^\%\)) ternary blends were reported. Ren et al.\(^22\) studied the properties of ternary blends with PLA, TPS and poly(butylene adipate-co-terephthalate) (PBAT). They found that both physical and
compatibilized (by using an anhydride functionalized compatibilizer) PLA/PBAT/TPS blends exhibited an increase in the elongation at break (from 2 to 20 %) and a decrease in the tensile strength (from 25 to 10 MPa) with increasing PBAT content up to 50 wt%. Hence, blending with a flexible polymer may lead to a ternary PLA/TPS/flexible-polymer blend with promising properties. These flexible polymers play an import role in improving interfacial adhesion and toughness. Unfortunately, flexible polymers usually only affect one component in the blends and could not produce a perfect interfacial adhesion between all components. Recently, a glycidyl methacrylate grafted poly(ethylene-co-octene) (i.e. GPOE) was introduced to PLA/TPS blends to improve the interfacial adhesion of components. GPOE was proposed to react with carboxyl and hydroxyl groups of PLA and TPS creating better affinity among the components. As a result, the toughness of the blends was improved by the addition of the rubbery GPOE. The optimum tensile strength and the optimum elongation at break of the PLA/GPOE/TPS blends were reported to be 30 MPa and 350 % respectively at TPS 20 wt% and GPOE 15 wt%.

In Chapter 4, ethylene-co-vinyl acetate (EVA) copolymer with a VA content of 50 wt% (i.e. EVA50) is found to be an excellent toughening modifier for PLA. Therefore, a good performance of PLA/EVA50/starch blends was expected as well. However, the mechanical properties of the PLA/EVA50/starch blends are not satisfying because of the large starch particle size and the weak interfacial adhesion between starch and the PLA matrix. To obtain good ultimate properties, improvement on the morphology and the interface between the PLA and starch is needed. In Chapter 5, the grafting of EVA50 chains onto the surface of the starch particles was described, thus the fine particle size of starch could be retained during a subsequent blending with PLA because the agglomeration of starch particles was prevented by grafted EVA50 layers. Therefore, a morphology of starch particles coated with EVA50 in the PLA matrix is expected, as schematically illustrated in Figure 6.1. The EVA50 shell can prevent the agglomeration of the fine starch particles during blending with the PLA and, simultaneously, enhance the toughness of the PLA matrix.

![Figure 6.1: Schematic illustration of a proposed morphology for the compatibilized PLA/EVA50/starch blends showing a core-shell structure of EV50/starch particles.](image-url)
The primary objective of this chapter is to obtain fine morphology and good properties of PLA/EVA50/starch ternary blends via a multiple-step processing. Compatibilization and plasticization were carried out during the preparation of EVA50/starch pre-compounds. The effect of the compatibilization on the morphology and properties of the PLA/EVA50/starch ternary blends was studied.

6.2 Experimental

6.2.1 Materials

PLA, 7000D, was supplied by Natureworks LLC., USA, with \( M_w = 210 \) KDa and \( M_w/M_n = 1.7 \). Gelatinized potato starch with 21 wt% amylose and 79 wt% amyllopectin was supplied by Rodenburg, the Netherlands. No glycerol but 9 – 17 wt% water was used in gelatinization process. The H\(_2\)O content in the gelatinized starch powder is around 8 wt%. Before processing, the starch was dried in a vacuum oven at 50 °C over night and the H\(_2\)O content in dried starch is around 2 wt% according to TGA measurements. EVA, with a VA content 50 wt% (i.e. EVA50), under the trade name of Levapren\(^\circledR\) was supplied by Lanxess Chemical Co., Ltd. The material data of EVA50 was listed in Table 4.1, Chapter 4. Maleic anhydride (MA) was supplied by Fluka\(^\circledR\) with purity \( \geq 99.0\% \). Benzoyl peroxide (BPO) was supplied by Aldrich\(^\circledR\) with a half-life time of approximate 1 min at 131 °C. Glycerol was supplied by Rodenburg, the Netherlands. All the materials and chemicals were used as received without further purification.

6.2.2 Blend preparation

The EVA50/starch pre-compounds were prepared via reactive extrusion in the presence of additives such as glycerol, MA and BPO. The MA concentration varied from 0 to 2.0 wt\%, and the BPO concentration was fixed at 10 wt\% to MA, while the content of glycerol was fixed at 20 wt\% to starch. The preparation method for the EVA50/starch pre-compounds was the same as described in section 5.2.2 (Chapter 5). The PLA/EVA50/starch ternary blends were prepared by blending dry PLA with the EVA50/starch pre-compounds on a twin-screw extruder \((D = 16 \text{ mm}, L/D = 20)\) at 167 °C. A screw rotation speed of 130 rpm was used. The configuration of the twin-screw is shown in Figure 5.3 (Chapter 5). The extrudates of PLA/EVA50/starch blends were pelletized and compression-molded into sheets (0.8 or 3.6
mm in thickness) at 170 °C for 3 min. The compression-molded samples were used for further characterization. The approximate compositions of the final PLA/EVA50/starch blends are listed in Table 6.1.

Table 6.1: The compositions of the PLA/EVA50/starch/glycerol/MA/BPO blends.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PLA (wt%)</th>
<th>EVA50 (wt%)</th>
<th>Starch (wt%)</th>
<th>Glycerol (wt%)</th>
<th>MA (wt%)</th>
<th>BPO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
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<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>#2</td>
<td>50</td>
<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0.13</td>
<td>0.013</td>
</tr>
<tr>
<td>#3</td>
<td>50</td>
<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0.25</td>
<td>0.025</td>
</tr>
<tr>
<td>#4</td>
<td>50</td>
<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td>#5</td>
<td>50</td>
<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0.90</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Note: the spread for the composition of PLA, EVA50 and starch is < 0.5 wt%.

6.2.3 Characterization

**Scanning electron microscope (SEM):** SEM (Quanta 600-F-ESEM, FEI, the Netherlands) was used to characterize the phase morphology of the PLA/EVA50/starch blends. The samples were first cut by a glass (or diamond) knife at -40 °C to get smooth surfaces. The surfaces were then etched by hydrochloric acid (HCl, 1.0 mol/l) for 3 hours at ambient temperature, or stained with a saturated I2/KI solution. The treated surfaces were observed after drying and sputter-coating with a thin gold layer. The ImageJ software was used to analyze the average particle size based on the SEM images. The area of each particle ($A_i$) was measured and then converted to an equivalent diameter ($d_i$) of a sphere via $d_i = 2 \cdot (A_i / \pi)^{1/2}$. The number-average diameter ($d_n$) and volume-average diameter ($d_v$) were calculated via $d_n = \sum d_i / N$ and $d_v = \sum d_i^3 / \sum d_i^3$, respectively, where $N$ is the number of analyzed particles.

**Atomic force microscope (AFM):** AFM with a Smena P47H (NT-MDT Ltd, Moscow, Russia) was used to examine the morphology of blend-#4 in a chloroform emulsion. The AFM was operated in a semi-contact mode under an air atmosphere using a silicon cantilever (NSG 11 NT-MDT), which was coated with a gold layer for a higher laser beam reflectivity. The resonance frequencies applied were 115-190 kHz. The blend was dissolved in chloroform (~ 6.5 mg/mL) and then spin-coated onto a glass slide via a spin coater at 1000 rpm for 30 seconds. The spin-coated film was used for AFM characterization.
Transmission electron microscope (TEM): TEM was used to evaluate the phase morphology of PLA/EVA50/starch blends. Transmission electron microscopy was performed using a Tecnai 20 microscope, operated at 200 kV. Ultrathin sections (~ 70 nm) were prepared at -35 °C using a Leica Ultracut S/FCS microtome.

Molau experiment: Samples of about 1.1 g from PLA/EVA50/starch blends (i.e. #1, #3, #4, and #5) were dipped into 20 mL chloroform. The solutions were sealed in glass bottles. After a couple of days, digital photos were taken. The emulsifying effect of EVA50 on starch was compared in terms of MA concentration.

Mechanical properties measurements: The tensile properties were measured using a Zwick Z100 tensile tester at a crosshead speed of 10 mm/min. The narrow parallel-sided portion of the dumbbell-shaped tensile bar was 12 mm in length, 0.8 mm in thickness and 2 mm in width. Izod impact toughness was tested using an impact analyzer (Zwick 5102, Germany) according to ASTM D256. The dimension of the specimen for impact testing was 63.5×12.7×3.6 mm³. The tests were carried out at ambient temperature.

Dynamic mechanical thermal analysis (DMTA): Dynamic mechanical thermal analysis was carried out on a DMAQ800 (TA Instrument, USA) with a tensile-film mode. Specimen (13.0 × 6.5 × 0.8 mm³) were measured from - 65 to 150 °C at a frequency of 1 Hz, with a constant amplitude of 10 μm and a temperature ramp of 3 °C/min. The storage modulus and tan δ were recorded as a function of temperature.

Differential scanning calorimetry (DSC): Cold crystallization and melting behavior of PLA in the PLA/EVA50/starch blends were investigated by DSC (TA Instrument, USA). The samples were heated from 20 to 180 °C at a heating rate of 10 °C/min under nitrogen atmosphere. To check the crystallinity of PLA after processing and to correlate the DSC and the DMAT results, the thermal properties of PLA in the PLA/EVA50/starch blends was evaluated from the first heating DSC curves.

6.3 Results and discussion

6.3.1 Effect of compatibilization on the morphology of PLA/EVA50/starch blends

The morphology of PLA/EVA50/starch blends was studied by SEM. Figure 6.2 demonstrates the effect of MA on the morphology of the PLA/EVA50/starch blends. HCl solution (1.0 mol/mL) was used to remove starch from the blends, since HCl solution is a
good solvent for starch but not for PLA and EVA50. As a result, starch was removed, leaving black cavities in the PLA matrix.

![SEM images of the PLA/EVA50/starch blends with different magnifications and with different MA concentrations. Images (a, a'), (b, b', b''), (c, c', c''), (d, d', d'') and (e, e', e'') correspond to the samples #1, #2, #3, #4 and #5 respectively. Starch was etched by HCl (1.0 mol/L at ambient temperature for 3 hours) as indicated by the dark spots.](image)
In the absence of MA, starch dispersed non-uniformly in the PLA matrix with large dimensions (Fig. 6.2 a). It was also observed from the cryo-fractured surface (the SEM images are not shown here) that EVA50 was finely dispersed in the PLA matrix. The starch particle size was considerably reduced by addition of 0.13 wt% MA, while the dispersion of starch was still non-uniform (Fig. 6.2 b). When the MA concentration was higher than 0.25 wt%, a much finer morphology and more uniform dispersion of starch particles were obtained, as shown in Figure 6.2 c - e. This fine phase morphology is attributed to an emulsifying effect of grafted EVA50 on the surface of the starch particles. Figure 6.3 presents the emulsifying effect on particle size (diameter, \(d\)) as a function of MA concentration. Taking into account that starch places much more weight in big particles, both the number-average diameter (\(d_n\)) and volume-average diameter (\(d_v\)) were analyzed. Figure 6.3 shows a classical emulsifying behavior for the compatibilization of immiscible polymer blends, i.e. the particle size reduces steeply with increasing MA concentration up to 0.25 wt% and then levels off. When the MA concentration is higher than 0.25 wt%, the critical micelle (or grafted EVA50 in this case) concentration may be reached and the interface might be saturated with the EVA-g-starch copolymers.

![Figure 6.3: Emulsification curves for the PLA/EVA50/starch blends with different MA concentrations: (■) number average diameter; (○) volume average diameter.](image)

A very interesting phenomenon is observed in the SEM images of the compatibilized blends, i.e. the components around starch particles were also removed during the etching process. Although pure EVA50 is not dissolvable in the HCl solution, the grafting reaction might enhance the solubility of EVA50 (or EVA50-g-starch) molecules. Considering that
EVA50 was chemically bonded onto the surface of the starch particles, the removed components surrounded starch particles are inferred to the EVA50 phase.

**Figure 6.4:** SEM images of the PLA/EVA50/starch blends with different MA concentrations. Images (a, a’) (b, b’), (c, c’) and (d, d) correspond to samples #1, #3, #4 and #5 respectively. The surfaces were cryo-cut with a diamond knife and stained with a saturated I₂/KI solution before observation. The starch particle size is indicated in the images.
The morphology of these samples was also studied with SEM using an I$_2$/KI solution to stain the cryo-cut surfaces which supplied a better contrast for the three components. The SEM images of these stained samples are shown in Figure 6.4, which are consistent with the etched morphology of the corresponding samples as shown in Figure 6.2. The etched SEM images show core-shell-like (or starch-in-EVA50) morphology for the compatibilized EVA50/starch phase. At MA concentrations of 0.45 and 0.90 wt%, EVA50 in combination with starch forms an interpenetrating or (partially) co-continuous morphology in the ternary blends (Figs. 6.2 d’ and e’). These arguments are supported by the images shown in Figure 6.4. Comparing Figures 6.2 d’ and e’ with Figures 6.4 c’ and d’ respectively, it confirms that starch in combination with EVA50 was removed during etching process with HCl solution.

The above hypothesis about the morphology of the compatibilized PLA/EVA50/starch blends is confirmed further by the TEM images. Figure 6.5 shows TEM images of the PLA/EVA50/starch blend (MA 0.45 wt%). The three components, i.e. PLA, EVA and starch, can be distinguished using TEM due to their different electron density contrasts even without any staining. The bright domains with an oval shape are starch particles. The partially continuous phase with a dark contrast corresponds to the EVA50 component. PLA is the matrix as indicated in the images. Clearly, starch particles with a diameter of 0.4 - 1.3 μm are well embedded in the EVA50 phase. In other words, starch particles are coated with EVA50 (or starch-in-EVA50) in the PLA matrix. Due to the interconnection of EVA50 phase, EVA50 in combination with starch are partially continuous in this blend. In addition, a few fine EVA50 domains are observed in the TEM images, however, no bare starch particles are founded in the PLA matrix.

![Figure 6.5: TEM images of the PLA/EVA50/starch blend (#4) with MA 0.45 wt%](image-url)
Chloroform is a good solvent for both PLA and EVA50, but not for starch. To study the emulsifying effect of grafted EVA50 on starch, Molau experiments were carried out for the PLA/EVA50/starch blends using chloroform as a solvent. The results are shown in Figure 6.6. For the physical blend, there is no chemical bonding between PLA and starch or EVA50 and starch. Thus, both PLA and EVA50 are dissolved in chloroform, leaving visible starch particles as a top layer on the PLA/EVA50 solution (Fig. 6.6 a). For modified blends, no chemical bonding between PLA and other components is expected, since the in-situ compatibilization was done during blending of EVA50 with starch. When MA concentration was moderate (0.25 ~ 0.45 wt%), stable emulsions of the ternary blends were obtained, as shown in Figure 6.6 b and c. This phenomenon indicates that the emulsifying function of EVA-g-starch copolymer effectively stabilized the starch particles in the chloroform. PLA was dissolved in chloroform in any case. The reacted EVA50 chains could also be dissolved but were chemically bonded onto the surfaces of starch particles. This structure is schematically illustrated in Figure 6.6 e. As a result, the starch particles were not agglomerated or didn’t precipitate out from the emulsion. However, at MA 0.90 wt%, the samples were not totally dissolved (Fig. 6.6 d), because the EVA50/starch pre-compound had a network structure (see Chapter 5) and was (partially) continuous in this blend. These results agree with the above morphology study.

**Figure 6.6:** Molau test of the PLA/EVA50/starch blends with MA concentrations: (A) 0, (B) 0.25 wt%, (C) 0.45 wt%, and (D) 0.90 wt%. A proposed structure of starch particles with grafted EVA50 in the emulsions is illustrated in (E).

More information about the emulsion is provided by Atomic Force Microscopy (AFM). The emulsion from bottle C (Figure 6.6) was spin-coated onto a glass slide, which was then investigated by AFM. The AFM phase-angle images are shown in Figure 6.7, showing a
matrix-droplet morphology. The dark region in the phase-angle images corresponds to lower phase angles or a higher stiffness, which is the PLA matrix. The bright region corresponds to higher phase angles or a lower stiffness, which is the dispersed EVA50 and EVA50 coated starch phases. The dimension of dispersed particles is in the range of 0.1 - 1.5 μm. The AFM images indicate a fine dispersion of particles and an isolated state of the particles. These images again prove an emulsifying effect of the grafted EVA50 on the starch particles. It also proves that no large-scale crosslink-network (EVA/starch) exists in the emulsion. In addition, a few relatively large particles (d ≈ 5 μm) were detected by AFM, as shown in Figure 6.7 (left).

![Figure 6.7: AFM phase-angle images of a spin-coated sample from the emulsion which is shown in Figure 6.6 (C).](image)

To summarize, the in-situ compatibilization has a significant effect on the morphology of the PLA/EVA50/starch blends, which is schematically illustrated in Figure 6.8. In the absence of compatibilization, very coarse (three-phase) morphology of the ternary blend is obtained (Fig. 6.8 B). The particle size of the starch reduces by a factor of around 100 after addition of 0.25 - 0.90 wt% MA. In the compatibilized blends, the grafted EVA50 and starch have starch-in-EVA50 structures in the PLA matrix (Fig. 6.8 D). At high MA concentration (0.45 - 0.90 wt%), EVA50 in combination with starch particles is (partially) continuous.

In fact, glycerol also plays an important role in morphology control. The plasticization by glycerol and compatibilization by MA provide a synergistic effect on generating a fine morphology and good mechanical properties, see the Appendix.
6.3.2 Effect of compatibilization on properties of the PLA/EVA50/starch blends

Figure 6.9 shows the mechanical properties of the PLA/EVA50/starch blends. The maximum tensile strength of the blends was decreased with increasing MA concentration from 0.13 to 0.45 wt% (Fig. 6.9 a). On the other hand, the elongation at break was increased dramatically with increasing MA concentration from 0.13 to 0.45 wt%. The impact toughness as a function of MA concentration (Fig. 6.9 b and c) showed a similar trend to the elongation at break. With further increasing MA concentration, the mechanical properties varied less pronounced. As studied in Chapter 4, the PLA/EVA50 binary blends, with a ratio similar to that in the PLA/EVA50/starch blends, showed a high notched Izod impact strength (60 - 70 kJ/m²) and high tensile strength (40 MPa). Comparing with the properties of the PLA/EVA50 binary blends, the overall mechanical properties of the ternary blends were deteriorated by starch. However, the mechanical data presented in Figure 6.9 indicate that the toughness of the PLA/EVA/starch blends was improved after addition of MA. The variety of properties relates to the changes in morphology. When MA concentration increased from 0.13 to 0.45 wt%, the EVA50 in combination with starch gradually changed from isolated particles (disperse phase) in PLA matrix to a partially co-continuous phase. Therefore, the mechanical properties were changed considerably in this MA range. Once a (partially) co-continuous...
morphology was formed, the morphology did not change too much with further increasing MA concentration, resulting in relatively steady mechanical properties. The mechanical properties of the physical blend (#1) showed some deviation from the above trends. This could be due to huge differences in morphology between blend #1 and the other blends, as shown in Figures 6.2 and 6.4. For the blend #1, the EVA50 was finely dispersed in the PLA matrix and seldom EVA50 was coated on the surface of large starch particles. For the compatibilized blends, the EVA50 was mainly coated on the surface of fine starch particles. The ultimate properties of the ternary blends are affected by both the toughening effect of EVA50 on the PLA matrix and the influence of the dispersion of starch.

Figure 6.9: Mechanical properties of the PLA/EVA50/starch blends with different MA concentrations: (a) maximum tensile strength and elongation at break (b) notched Izod impact toughness (c) un-notched Izod impact toughness and (d) stress-strain behavior.

Figure 6.9 d shows the typical stress-strain curves of the PLA/EVA50/starch blends. The blends with MA ≤ 0.13 wt% show obvious strain softening. However, the samples failed
quickly after yielding, indicating a brittle fracture behavior. This brittle behavior might be resulted from the large starch particles and poor interfacial adhesion (indicated in Figure 6.2 a, b). The blends with MA 0.25 – 0.45 wt% underwent a stable cold-drawn process. A noteworthy stress-whitening of the tensile bar was also observed during tensile testing, showing ductile behavior. The blend with MA 0.90 wt% exhibits a different stress-strain curve from the others. No strain softening is present for this blend (as shown in Figure 6.9 d), since its stress increases monotonously with strain until the specimen fails. This tensile behavior is similar as a thermoplastic vulcanizate (TPV)\textsuperscript{27}. The TPV-like tensile behavior for this blend is attributed to the existence of partially continuous rubber network referring to the EVA50/starch phase (indicated in Figure 6.2 e and e’).

6.3.3 Dynamic mechanical thermal analysis

The dynamic mechanical properties of the PLA/EVA50/starch blends as a function of MA content were measured using dynamic mechanical thermal analysis (DMTA). The curves of storage modulus (\(E'\)) and tan \(\delta\) versus temperatures are presented in Figure 6.10 a and b. After addition of MA, the blends have higher \(E'\) values at low temperatures (< -25 °C, \(T_g\) of EVA50), but have lower \(E'\) values above -25 °C. The higher \(E'\) at low temperature may be attributed to the finer dispersion of starch and the enhanced interfacial adhesion between starch and EVA50. Stress could be sufficiently transferred from one phase to another when the interfacial adhesion is high, leading to higher storage modulus. At room temperature, the \(E'\) is controlled by PLA as long as PLA is the continuous phase, because PLA is rigid while EVA50 is rubbery (\(E'_{EVA50} = 1\sim10\) MPa), as shown in the insert of Figure 6.10 a. As discussed above (Fig. 6.2 and Fig. 6.6), the EVA50 in combination with starch gradually changes from a dispersed phase to a co-continuous phase with increasing MA content. The larger EVA50/starch domains or (partially) continuous EVA50/starch phase result in the lower \(E'\) values of the blends at room temperatures.

The storage moduli of the blends were found to drop steeply at a temperature around 60 °C (the \(T_g\) of PLA), and then increased to a certain extent due to cold crystallization of PLA. This phenomenon is shown in Figure 6.10 a. The cold crystallization was not affected significantly by the compatibilization according to these results.
The cold crystallization and melting behavior of the PLA/EVA50/starch blends were also studied by DSC at a temperature ramp of 10 °C/min. The thermal parameters are listed in Table 6.2. The overall thermal behavior of the PLA in the blends was not influenced significantly by the in-situ compatibilization. The cold crystallization temperature of PLA ($T_{cc}$) decreased slightly with MA content up to 0.45 wt%, but increased at MA 0.90 wt%. The very similar crystallization enthalpy ($\Delta H_c$) and fusion enthalpy ($\Delta H_m$) values for each sample indicate that the PLA component is primarily amorphous after processing. The blend with MA 0.90 wt% had the highest $T_{cc}$ but lowest $\Delta H_c$ and $\Delta H_m$ values. This indicates that the crystallization of PLA in this blend was slower than that of PLA in the other blends, which may be attributed to its co-continuous morphology.

Table 6.2: Thermal parameters of PLA in the PLA/EVA50/starch blends from the 1st heating DSC curves.

<table>
<thead>
<tr>
<th>MA content (%)</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58</td>
<td>117</td>
<td>-7</td>
<td>9</td>
<td>145</td>
</tr>
<tr>
<td>0.13</td>
<td>58</td>
<td>117</td>
<td>-5</td>
<td>6</td>
<td>145</td>
</tr>
<tr>
<td>0.25</td>
<td>58</td>
<td>116</td>
<td>-5</td>
<td>6</td>
<td>145</td>
</tr>
<tr>
<td>0.45</td>
<td>58</td>
<td>114</td>
<td>-7</td>
<td>8</td>
<td>145</td>
</tr>
<tr>
<td>0.90</td>
<td>56</td>
<td>120</td>
<td>-3</td>
<td>4</td>
<td>145</td>
</tr>
</tbody>
</table>

$T_g$, glass transition temperature; $T_{cc}$, cold-crystallization temperature; $\Delta H_c$, crystallization enthalpy; $\Delta H_m$, fusion enthalpy; $T_m$, melting temperature.
Figure 6.10 b presents the glass transition peaks of EVA50 and PLA in the PLA/EVA50/starch blends. The glass transition temperatures ($T_g$) are obtained from the tan $\delta$ peak temperatures of corresponding components. The tan $\delta$ peaks for the starch component are absent in blends (Fig. 6.10 b). The $T_g$ of TPS was reported to be between -8 and 50 °C dependent on the amount of plasticizers$^{21,28,29}$. However, the $T_g$ of starch in the blends was seldom detected by DSC or DMTA$^{6,13,14,17}$, probably because the hydrogen bonds among starch molecules are so strong that the mobility of starch chains are limited. The $T_g$ of PLA in the blends is around 60 °C and did not change significantly after addition of MA, while the $T_g$ of EVA50 shifted to higher temperatures, e.g. from -27 °C in the absence of MA to -22 °C with 0.90 wt% MA (inset of Fig. 6.10 b). In order to understand the changes in $T_g$ of EVA50 in the blends, the $T_g$ of EVA50 in different systems were measured and are presented in Table 6.3. It is interesting to notice, from Table 6.3, that EVA50 always has a low $T_g$ (~ - 27 °C) if the EVA50 is a fine dispersed phase in the PLA matrix. On the contrary, EVA50 always has a high $T_g$ (~ - 20 °C), close to the $T_g$ of pure EVA50 (~ 19 °C), when it is a matrix or a (partly) continuous phase.

Table 6.3: Glass transition temperature ($T_g$) of EVA50 in different systems.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ of EVA50 (°C)</th>
<th>Morphology of EVA50 phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA50</td>
<td>- 19</td>
<td>pure matrix</td>
</tr>
<tr>
<td>PLA/EVA50 (2/1)</td>
<td>- 26</td>
<td>fine domains</td>
</tr>
<tr>
<td>PLA/EVA50/starch (2/1/1)</td>
<td>- 27</td>
<td>fine domains</td>
</tr>
<tr>
<td>PLA/EVA50/starch (2/1/1) with MA 0.9 wt%</td>
<td>- 22</td>
<td>partially continuous</td>
</tr>
<tr>
<td>EVA50/starch (1/1)</td>
<td>- 19</td>
<td>matrix</td>
</tr>
<tr>
<td>EVA50/starch (1/1) with MA 2.0 wt%</td>
<td>- 20</td>
<td>matrix</td>
</tr>
</tbody>
</table>

*Note: $T_g$ is obtained from the peak temperatures of tan $\delta$ measured by DMTA.*

Therefore, the $T_g$ of EVA50 in PLA/EVA50-related blends correlates to the phase morphology or dispersion of EVA50 in the blends. To confirm this statement and to make the system simple, PLA/EVA50 binary blends with different weight ratios were prepared by melt blending using a mini-extruder (170 °C, 4 min and 90 rpm) and their $T_g$s were measured with DMTA, as shown in Figure 6.11 a. With decreasing EVA50 content from 100 to 20 wt%, the morphology of EVA50 phase changes gradually from a continuous matrix to a fine dispersed
phase. Correspondingly, the $T_g$ of EVA50 phase decreases gradually from -19 °C to -31 °C, while the $T_g$ of PLA is not affected significantly. It is worthy to mention that PLA/EVA50 blends with different weight ratios were also prepared by solvent (chloroform) casting, and the $T_g$ of PLA and EVA50 showed the same trend as that presented in Figure. 6.11 a. Furthermore, another grade of EVA, i.e. EVA70 with an average vinyl acetate (VA) content of 70 wt%, was also used to melt-blend with PLA, and again the same trend was obtained as that presented in Figure. 6.11 a.

![Figure 6.11: (a) $T_g$ of EVA50 and PLA in the PLA/EVA50 blends as a function of EVA50 content and (b) $T_g$ of pure EVA copolymers as a function of ethylene segment content.](image)

The most common explanation for the change of $T_g$ in a polymer blend is the phenomenon of (partial) miscibility. If two polymers are miscible, their blend has a single $T_g$. If two polymers are immiscible, they keep their own $T_g$ in the blends. If two polymers are partially miscible, their $T_g$ shifts to each other after blending. After blending PLA and EVA50, the $T_g$ of PLA did not change much while the $T_g$ of EVA50 decreased to lower temperatures instead of shifting to the $T_g$ of PLA. Apparently, the decrease in $T_g$ of EVA50 in the PLA/EVA50 blends can not be explained by the (partial) miscibility between the EVA50 and PLA.

Since the decrease in $T_g$ of EVA50 in the PLA/EVA50 blends mainly occurs at a low EVA50 content (20 wt%), i.e. EVA50 is a very fine dispersed phase, the interface effect has to be taken into account. The $T_g$ of ultra-thin film such as poly(styrene) and poly(methyl methacrylate) (PMMA) is strongly influenced by the free surface and by the substrate\textsuperscript{30,31}. The effect of free surface is to decrease the density and to enhance the mobility of the polymer chains near to the interface, reducing the $T_g$ of the polymer (the thinner of the film, the lower $T_g$), while the effect of substrate is usually to increase the $T_g$ value due to the
interaction between the substrate and the polymer. However, the interfacial effects only occur when the film thickness is less than 70 nm. In the PLA/EVA50 (80/20) blend the number average particle size of EVA50 is about 300 nm (the TEM images are shown in Figure 6.12), thus the interfacial effect could be important. However, no free surface of the EVA50 phase exists in this blend. If the interface between the EVA50 and PLA affect the $T_g$ of EVA50, PLA should play a role of substrate which will confine or immobilize the EVA50 chains near to the interface, resulting in a higher $T_g$ of EVA50.

![TEM images of the PLA/EVA50 (80/20) blend with different magnifications showing the morphology of EVA50 and the interface between the EVA50 and PLA.](image)

A possible reason for the decreased $T_g$ of EVA50 in the PLA/EVA50 blends, notably when EVA50 is a fine dispersed phase, is the composition variety in the EVA50 domains.

EVA50 is a random copolymer with an average VA content of 50 wt% in the copolymer which is measured by TGA. The reactivity of the two monomers is so similar that they should be statistically distributed throughout the copolymer chains. However, in an industrial reactor diffusion of monomers will be a problem up on polymerization due to an increased solution-viscosity at high polymerization degrees. Therefore, in practice, the VA content may not be the same for every chain and the sequence of monomers may not be perfectly random in a single chain. This might be result in VA-reach chains or VA-reach segments in the EVA50 materials.

It is already known that PLA is miscible with poly(vinyl acetate) (PVAc) and ethylene-co-vinyl acetate (EVA) with VA content of > 85 wt%\textsuperscript{32}. Therefore, VA segments or VA-rich chains in the EVA50 domains could move to the interface between PLA and EVA50 during melting blending. Although it is not very convincing, Figure 6.12 (right) shows gradient
changes at the interface between the PLA and the EVA phases. As a consequence, the ethylene content inside of the EVA50 domains would be higher than 50 wt%, resulting in a lower $T_g$ of EVA50 because the $T_g$ of EVA copolymer decreases with increasing ethylene content, as shown in Figure 6.11 b. It has to be mentioned that according to the data supplied by the EVA producer (Lanxess)\textsuperscript{33}, the $T_g$ of EVA only slightly decreased (by few degrees) when the ethylene content increases from 50 to 80 wt%. Therefore, if this proposed reason is correct, the significant drop (~ 10 °C) in $T_g$ of EVA50 in the PLA matrix (Fig. 6.11 a) indicates a very high ethylene segment content inside of the EVA50 domains, however, experimental evidence is lacking.

6.3.4 Property stability of the PLA/EVA50/starch blends

Property instability is an issue of plasticized starch and its blends. The property instability is usually caused by the typical drawbacks of plasticized starch such as moisture sensitivity, plasticizer migration, and starch retrogradation.\textsuperscript{3} For a polymer/starch/glycerol blend, the embrittlement with time might be induced by migration of glycerol out of the starch phase. The resulted embrittlement of starch phase could deteriorate the overall mechanical properties of the blends.\textsuperscript{3} In this study, all the samples were sealed in a desiccator at ambient temperature. Tensile tests were applied on these samples after different storage time to trace the property changes with time.

![Figure 6.13: Comparison in tensile properties of the PLA/EVA50/starch blends with different MA concentrations: (a) maximum tensile strength, and (b) elongation at break. The properties were measured 4 days, 3 months and 9 months respectively after compression molding.](image-url)
The tensile properties of the PLA/EVA50/starch ternary blends obtained after different storage time are presented in Figure 6.13. Obviously, the samples retained their properties with time, except the blend with 0.90 wt% MA. In the blends, starch is capsulated in the PLA and EVA50 phases, i.e. glycerol is sealed in the starch phase. In addition, the glycerol concentration in these blends is low (20 wt% to starch). Thus, the migration of glycerol is insignificant. However, rubbery EVA50 in combination with starch is a co-continuous phase at MA 0.90 wt%, which might supply a better leaching way for glycerol. Therefore, the elongation at break of this blend was dropped by 35% after 3 months (Fig. 6.13 b).

6.4 Conclusions

PLA/EVA50/starch ternary blends were prepared via a multiple-step processing. A plasticization of starch (by glycerol) and an in-situ compatibilization (by MA and BPO) between EVA50 and starch phases were carried out first in preparation of EVA50/starch pre-compounds. A fine dispersion of starch in the EVA50 matrix was obtained due to the in-situ compatibilization, which was discussed in Chapter 5. Since EVA50 was chemically grafted onto the surface of starch particles, the fine starch particles could not agglomerate with each other during the subsequent blending with PLA. As a consequence, a fine dispersion of starch ($d = 0.5 - 2 \mu m$) was obtained in the PLA/EVA50/starch blends. With the in-situ compatibilization starch was mainly dispersed in the EVA50 phase in the PLA/EVA50/starch blends instead of dispersing in the PLA matrix directly, which is confirmed by SEM and TEM images. The blends can form stable emulsion in chloroform when the MA concentration is between 0.25 and 0.45 wt% thanks to the grafted EVA50 shell on the surface of starch particles. The EVA50 that was coated on the surface of starch particles not only stabilized the fine morphology of starch but also beneficial to the toughness of the blends. The fine starch morphology, the improved interfacial properties between starch and EVA50 and the toughening effect of EVA50 resulted in a higher elongation at break and impact toughness of the PLA/EVA50/starch blends after the compatibilization. Therefore, a starch-in-EVA50 type morphology of the PLA/EVA50/starch can be achieved by a multiple-step processing. The morphology and mechanical properties of the PLA/EVA50/starch ternary blends can be controlled by the in-situ compatibilization in the step of making EVA50/starch pre-compounds.

The glycerol and starch content are also important in controlling the morphology and mechanical properties, which will be discussed in the Appendix.
6.5 References

Appendix

Effect of glycerol and starch on the morphology and mechanical properties of poly(lactic acid)/ethylene-co-vinyl acetate/starch blends

Poly(lactic acid)/ethylene-co-vinyl acetate/starch (PLA/EVA/starch) ternary blends were prepared by a multiple-step melt processing, as described in Chapter 6. The effect of glycerol and starch content on the morphology and properties of the PLA/EVA/starch blends was studied. A significant reduction in starch particle size was induced in the PLA/EVA/starch blends by the in-situ compatibilization in the presence of sufficient glycerol. The compatibilization (via MA) and plasticization (via glycerol) in the blends provide a synergistic effect on generating a fine morphology and good mechanical properties. In this appendix, fine starch dispersion can be retained at high starch loading, e.g. 40 wt%, indicating an effective emulsifying effect of the grafted EVA50. The yield tensile strength and E-modulus of the ternary blends were increased with starch, however, accompanied by a reduction in toughness. DMTA results showed that the storage modulus of the blends was gradually increased with the starch content, especially at a temperature higher than $T_g$ of the PLA, which could broaden the application range of PLA in terms of temperature.

A.1 Introduction

Poly(lactic acid) (PLA) is a renewable and biocompostable polymer with good processability and reasonable mechanical properties. However, the application is limited due to its brittleness, low heat distortion temperature and high price\(^1\). As an alternative, starch is cheap (less than 1 euro/kg), renewable and biocompostable\(^2\). Therefore, blending PLA with starch can reduce the cost of resulting materials, without sacrificing their renewable and biocompostable natures. A lot of works have been done to prepare PLA/starch blends to offset the high cost and to increase the biocompostable rate of PLA\(^3\)-\(^{11}\). The properties of the PLA/starch blends are usually poor, ascribing to the lack of affinity between PLA and starch\(^5,12,13\).

In our previous study, ethylene-co-vinyl acetate rubber (i.e. EVA50) was introduced to PLA/starch system. Reactive PLA/EVA/starch ternary blends were prepared with maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol in Chapter 6. Maleated EVA50 was
reacted with hydroxyl groups of starch molecules, and formed a shell-layer on the surfaces of starch particles. This structure (as drawn in Figure 6.1, Chapter 6) resulted in fine dispersion of starch ($d = 0.5 - 2.5 \mu m$) and toughness of the blends.

Plasticizer, i.e. glycerol, plays an important role on the properties of starch especially when glycerol is used as the sole plasticizer. Starch lacks of flowability due to strong hydrogen bonding and a very high molecular weight. The mobility of starch chains (or segments) could be enhanced, and the secondary bonds among starch chains could be weakened by addition of glycerol. Consequently, the viscosity of starch phase was reduced. The morphology of the PLA/EVA50/starch blends will be influenced by glycerol concentration, since the morphology of a polymer blend is determined by a complex interplay among the viscosity of the components, the interfacial properties, the composition and the processing conditions. In addition, a percolation phenomenon in terms of plasticizer concentration was reported in PLA/starch blends. Whether the percolation phenomenon exists in the PLA/EVA/starch system is not known yet. Therefore, it is of interest to study the effect of glycerol on the morphology and mechanical properties of the PLA/EVA/starch blends.

Starch content is another important factor affecting the performances of starch-based blends. The higher starch loading, the lower material cost. However, high starch loading generally leads to poor mechanical properties due to the inherent poor performance of starch. As a filler, agglomeration of starch is enhanced at high loadings. Whether the in-situ compatibilization mentioned above is effective at high starch loading has not been clear yet.

The effect of MA concentration (compatibilization) on the morphology and mechanical properties of the PLA/EVA/starch blends was studied in Chapter 6. As an extension to Chapter 6, the prime objective of this appendix is to discuss the effect of glycerol and starch content on the morphology and mechanical properties of the in-situ compatibilized PLA/EVA/starch blends.

A.2 Experimental

A.2.1 Materials

Materials used in this study such as PLA7000D, gelatinized potato starch, EVA50 (Levapren®), maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol are the same as the used in Chapter 6 and were described in section 6.2.1 (Chapter 6). All the materials and chemicals were used as received without further purification.
A.2.2 Blend preparation

Two series of EVA50/starch pre-compounds were prepared, viz.

(1) EVA50/starch (50/50) blends with glycerol content varying from 0 to 20 wt% to starch. The MA concentration was 2.0 wt% to EVA50, while the BPO was fixed at 10 wt% to MA.

(2) EVA50/starch blends with different weight ratios. The MA concentration was 2.0 wt% to EVA50, BPO concentration was 10 wt% to MA, while the glycerol content was 20 wt% to starch.

The EVA50/starch pre-compounds were prepared by a reactive extrusion in the presence of additives such as glycerol, MA and BPO. The preparation method was the same as described in section 5.2.2 (Chapter 5). The PLA/EVA50/starch ternary blends were prepared by blending dry PLA with the EVA50/starch pre-compounds on a twin-screw extruder (D = 16 mm, L/D = 20) at 167 °C. A screw rotation speed of 130 rpm was used. The extrudates of PLA/EVA50/starch blends were pelletized, and compression-molded into sheets (0.8 or 3.6 mm in thickness) at 170 °C for 3 min. The compression-molded samples were used for further characterization. The compositions of the final PLA/EVA50/starch blends are listed in Table A.1.

Table A.1: The composition of the PLA/EVA/starch blends.

<table>
<thead>
<tr>
<th>series</th>
<th>Sample Code</th>
<th>PLA (wt%)</th>
<th>EVA50 (wt%)</th>
<th>Starch (wt%)</th>
<th>Glycerol (wt%)</th>
<th>MA (wt%)</th>
<th>BPO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>#1</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>0</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
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<td>24</td>
<td>24</td>
<td>1.2</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>50</td>
<td>24</td>
<td>24</td>
<td>2.5</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>50</td>
<td>23</td>
<td>23</td>
<td>4.5</td>
<td>0.45</td>
<td>0.045</td>
</tr>
<tr>
<td>(2)</td>
<td>#5</td>
<td>47</td>
<td>21</td>
<td>26</td>
<td>5.0</td>
<td>0.45</td>
<td>0.045</td>
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<tr>
<td></td>
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<td>6.0</td>
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<tr>
<td></td>
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<td>7.0</td>
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<td>16</td>
<td>39</td>
<td>8.0</td>
<td>0.33</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Note: the spread for the composition of the PLA, EVA and starch is within 0.5 wt%.

A.2.3 Characterization

Scanning electron microscopy (SEM): SEM (Quanta 600-F-ESEM, FEI, the Netherlands) was used to characterize the phase morphology of the PLA/EVA50/starch blends. The
samples were first cut using a glass (or diamond) knife at -40 °C to get smooth surfaces. The surfaces were then etched by hydrochloric acid (HCl, 1.0 mol/l) for 3 hours at ambient temperature, or stained with a saturated I₂/KI solution. The treated surfaces were observed after drying and sputter-coating with a thin gold layer.

**Mechanical properties measurements:** The tensile properties were measured using a Zwick Z100 tensile tester at a crosshead speed of 10 mm/min. The narrow parallel-sided portion of the dumbbell-shaped tensile bar was 12 mm in length, 0.8 mm in thickness and 2 mm in width. Izod impact toughness was tested using an impact analyzer (Zwick 5102, Germany) according to ASTM D256. The dimension of the specimens for impact testing was 63.5×12.7×3.6 mm³. The tests were carried out at ambient temperature.

**Dynamic mechanical thermal analysis (DMTA):** Dynamic mechanical thermal analysis was carried out on a DMA Q800 (TA Instrument, USA) with a tensile-film mode. Specimens (13.0 × 6.5 × 0.8 mm³) were measured from -65 to 150 °C at a frequency of 1 Hz, with constant amplitude of 10 μm and a temperature ramp of 3 °C/min.

### A.3 Results and discussion

#### A.3.1 Effect of plasticization on the compatibilized PLA/EVA50/starch blends

Glycerol plays an important role in the compatibilized PLA/EVA50/starch ternary blends. The ternary blends (i.e. #1 - #4) with different glycerol contents are studied, and the effect of glycerol content on the morphology and mechanical properties of the blends is discussed. The glycerol content mentioned in this part is based on the weight of starch.

#### A.3.1.1 Morphology of the PLA/EVA50/starch blends with different glycerol contents

Figure A.1 shows the phase morphology of the PLA/EVA50/starch blends with different glycerol contents. Clearly, the morphology of the blends is very coarse at glycerol ≤ 5 wt% (Figure A.1 a and b). The starch particle size in those blends is as large as the original starch particles which are shown in Figure 5.3c (Chapter 5). It indicates that a small amount of glycerol can not plasticize starch sufficiently. Therefore, no break-up of the starch particles occurred during the mixing. At the same loading of starch, a large particle size means a small starch surface area where the *in-situ* reaction occurs. As a consequence, the *in-situ* compatibilization was ineffective. At glycerol 10 wt%, starch is partially plasticized but still
could not flow as a normal thermoplastic melt. Therefore, both big and small starch particles are present, as shown in Figure A.1 (c). When 20 wt% of glycerol was added, a very fine and uniform dispersion of starch is obtained (Fig. A.1 d).

Starch has highly branched molecules (amylopectin) and high molecular weight, e.g. amylopectin has around 20,000 branches in average molecules, and has a weight average molecular weight up to 50 - 500 $\times 10^6$ g/mol. Furthermore, strong hydrogen bonds exist within and among the starch molecules. As a result, starch can not be processed as a normal thermoplastic before gelatinization and plasticization\textsuperscript{16,17}.

Starch did not exhibit any viscosity plateau even with glycerol in an investigated shear rate range (1-100 s$^{-1}$) and was highly shear thinning\textsuperscript{3}, which are typical of branched or highly entangled polymer melts. Consequently, the starch or TPS is difficult to deform and disperse in hydrophobic polymers. It was reported that addition of sufficient glycerol could induce a considerable drop of the viscosity\textsuperscript{3,18}. Therefore, the morphology of polymer/starch blends will be influenced by decreasing the viscosity of starch phase via glycerol.

The decrease in starch particle size at high glycerol content is associated with the lower viscosity of starch phase\textsuperscript{3}. With increasing glycerol content, the viscosity of starch phase was

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Figure A.1: SEM images of the PLA/EVA50/starch blends with glycerol content to starch: (a) 0, (b) 5 wt%, (c) 10 wt%, and (d) 20 wt%. a – d correspond to samples # 1 - # 4 (Table A.1) respectively. Starch was etched by HCl solution (1.0 mol/L at ambient temperature for 3 hours), as indicated by the dark holes.
decreased, resulting in a lower viscosity ratio of the dispersed starch to the EVA matrix ($\eta_d/\eta_m$). This changes the critical capillary number ($Ca_{crit}$) of the blends, which could enhance the driving force of break-up of starch particles. When 20 wt% of glycerol was added, the starch particles could be deformed and broken up more easily. Consequently, new and larger interfaces were generated via the break-up process, forming fine morphology which was subsequently stabilized by the *in-situ* formed compatibilizers at the new interfaces. Although the *in-situ* compatibilization occurred at the interface between EVA50 and starch in the absence of glycerol as well, starch could not be broken up easily to generate new surfaces; without stabilizing effect of the *in-situ* compatibilization, small starch particles coalesce to be large ones during a subsequent blending. Therefore, the *in-situ* compatibilization and plasticization provide a synergistic effect to this system. The effect of plasticization and compatibilization on the morphology development of starch phase during the processing is schematically illustrated in Figure A.2.

![Figure A.2: Schematic illustration of the morphology development of starch phase, showing the synergistic effect of plasticization and compatibilization.](image-url)
A.3.1.2 Mechanical properties of the PLA/EVA50/starch blends with different glycerol contents

Figure A.3 shows the tensile properties of the PLA/EVA50/starch blends as a function of glycerol content. It is found that the maximum tensile strength of the blends is not affected significantly by incorporation of glycerol (Fig. A.3 a). It is reasonable, since the glycerol affects mainly on the starch phase, not on the PLA matrix. The elongation at break of the blends keeps constant at glycerol \( \leq 10 \) wt\%, but increases from 15 % to 90 % when the glycerol content rises from 10 to 20 wt\% (Figure A.3 b). These results are associated with the morphology of the blends and the properties of the dispersed starch phase. An improved interfacial adhesion between starch and the matrix was observed after the \textit{in-situ} compatibilization even in the absence of glycerol, as shown in Figure A.4. However, the morphology of the blends was coarse at glycerol content \( \leq 10 \) wt\%, (Fig. A.1). The large starch particles were stiff with cracks inside (Fig. A.4 b) which deteriorated the toughness of the blends. At high glycerol content, the ductility of the finely dispersed starch particles was enhanced. Consequently, a large amount of energy could be dissipated by the ductile starch particles during a deformation, leading to an increase in the elongation at break. In addition, the improvement of interfacial properties by compatibilization is also important, since the improved interface enables the stress transmission from one phase to the other easily\textsuperscript{19}. 

![Graph](image)

\textit{Figure A.3: Tensile properties of the PLA/EVA50/starch blends as a function of glycerol content: (a) maximum tensile strength and (b) elongation at break.}
Figure A.4: SEM images of the PLA/EVA50/starch/MA blend in the absence of glycerol. The surface was cryo-cut with a diamond knife and stained with a saturated I$_2$/KI solution before observation.

In polymer/plasticizer blends, a critical volume fraction of plasticizer exists, at which the mechanical properties change suddenly. The plasticizer concentration at the critical volume fraction is referred to as a percolation threshold. This sudden jump is usually attributed to a formation of critical continuous network or phase$^{20}$. Such percolation phenomenon was reported in PLA/starch/MA blends using acetyl triethyl acetate (ATC) as a plasticizer$^7$, viz.

\[
\begin{align*}
\varepsilon_b &\approx \varepsilon_0 \quad \text{when } p < p_c \\
\varepsilon_b &\propto (p - p_c)^\mu \quad \text{when } p \geq p_c
\end{align*}
\]

where $\varepsilon_b$ is the elongation at break at ATC concentration, $\varepsilon_0$ is the initial elongation at break; $p_c$ is the percolation threshold, and $\mu$ is the exponent for cubic dimensions. This expression indicates a critical plasticizer content ($p_c$) for elongation at break. Below $p_c$, no increase in elongation at break was observed. Above $p_c$, the elongation increased considerably. The $P_c$ is observed at around 8 wt% in the PLA/starch/MA/ATC system. Since the ATC is a good plasticizer for PLA matrix but not for starch phase, the tensile strength of the blends showed a monotonic decrease with ATC content.

In our PLA/EVA50/starch system, a percolation phenomenon for elongation at break was also observed in terms of glycerol content (Figure A.3 b). The $p_c$ for these blends is between 10 and 20 wt%. In literatures, a critical content of glycerol for PLA/PCL/starch blends and PLA/starch/MA blends was reported to be between 24 – 36 wt% and 33 – 36 wt%, respectively$^{3,15}$. In their studies, native starch was used which might be a reason for their higher $p_c$ values.
A.3.2 Effect of starch content on the compatibilized PLA/EVA50/starch blends

Starch is much cheaper than PLA, thus, it is interesting for single-use applications to increase the content of starch in the blends. It is also of interest to study the effectiveness of the in-situ compatibilization at high starch contents. The PLA/EVA50/starch blends (i.e. #4 - #8) with different starch contents were studied. The weight ratio of PLA to EVA50 in these blends is approximately constant, while the starch content is varied.

A.3.2.1 Morphology of the PLA/EVA50/starch blends with different starch contents

![Figure A.5: SEM images of the PLA/EVA50/starch blends (PLA/EVA50 ≈ 2.2/1) with starch content in the blends: (a) 23, (b) 26, (c) 35, and (d) 40 wt%. a – d correspond to samples # 4, #5, #7 and #8 (Table A.1) respectively. The surfaces were cryo-cut with a diamond knife and stained with a saturated I$_2$/KI solution before observation.](image)

Figure A.5 shows the morphology of PLA/EVA50/starch blends with starch content from 23 to 40 wt%. The definition for different phases was indicated in the images. At low starch content, the fine starch particles are well embedded in the EVA50 phase. In addition, EVA50 in combination with starch particles has an interpenetrating morphology in the PLA/EVA50/starch blends. This type of morphology (i.e. core-shell-like or starch-in-EVA50) has been discussed in detail in Chapter 6, and is shown again in Figures A.5 a and b. At
starch content $\geq$ 35 wt%, numerous isolated domains are observed, as shown in Figures A.5 c and d. These domains are starch particles with a thin EVA50 layer on the surface.

When the starch content is increased, the amount of grafted EVA50 reduces correspondingly. Meanwhile, the overall content of EVA50 in the ternary blends is decreased. As a result, the EVA50 shells may be too thin to be connected with each other in the ternary blends. Although the grafted EVA50 layer is estimated to be thin, it is effective enough to emulsify the starch particles in the blends. Therefore, a fine dispersion of starch ($d = 0.5 - 2 \mu m$) can be obtained at starch content, at least, up to 40 wt%, as shown in Figures A.5 c and d.

A.3.2.2 Properties of the PLA/EVA50/starch blends with different starch contents

![Graphs showing mechanical properties](image)

Figure A.6: Mechanical properties of the PLA/EVA50/starch blends ($PLA/EVA50 \approx 2.2/1$) with different starch contents. (a) yield tensile strength and E-modulus, (b) elongation at break, (c) un-notched Izod impact toughness, and (d) notched Izod impact toughness.

Figure A.6 shows the mechanical properties of the PLA/EVA50/starch blends with different starch contents. The yield tensile strength and E-modulus of the blends were
increased with an increase in starch content (Fig. A.6 a). However, the elongation at break was decreased monotonically (Figs. A.6 b). A sharp change was observed for these tensile properties when the starch content was increased from 30 to 35 wt% due to an obvious variety in morphology (Figs. A.5). The impact toughness of these blends was also decreased monotonically with increasing starch content (Figs. A.6 c and d). Starch gradually becomes a dominate component with increasing its content up to 40 wt%. Meanwhile, the content of EVA50 coated on the starch particles, acting as a toughening modifier for PLA, is reduced. As a consequence, the blends show brittle behaviors at high starch contents, e.g. the toughness of the blend is comparable to pure PLA at a starch content of 40 wt%.

Dynamic mechanical properties of the PLA/EVA50/starch blends as a function of starch content and temperature were studied using DMTA. The storage modulus ($E'$) versus temperature is plotted in Figure A.7. For all the blends, the $E'$ was dropped at a temperature around - 25 °C and a temperature around 60 °C, corresponding to the glass transitions ($T_g$) of the EVA50 and PLA components respectively. Since the crystallization rate of PLA is low, no back-up of the modulus can be obtained from crystallinity at a temperature higher than its $T_g$. Thus, PLA, as known, has a low heat distortion temperature (HDT). This limits its hot-package applications such as coffee cups. The $E'$ of the blends increases with increasing starch content at all examined temperatures, more strikingly at temperatures higher than the $T_g$ of PLA (Figure A.7). It, thus, supplies a possible approach to improve the HDT of PLA materials.

![Dynamic mechanical properties of the PLA/EVA50/starch blends](image)

*Figure A.7: Dynamic mechanical properties of the PLA/EVA50/starch blends (PLA/EVA50 ≈ 2.2/1) with different starch contents.*
A.4 Conclusions

Glycerol and starch play an important role in morphology and property control of the starch-based blends. Plasticization and compatibilization provided a synergetic effect to this system, since a fine and uniform morphology can only be obtained in the presence of both MA and a sufficient amount of glycerol. A percolation phenomenon in terms of the elongation at break of the blends was observed. The critical glycerol concentration for the PLA/EVA50/starch system was found to be between 10 and 20 wt% (to starch). PLA/EVA50/starch blends with high starch loading were also studied. Fine dispersion of starch with a particle size of 0.5 - 2 μm was retained at a starch content, at least, up to 40 wt%. The E-modulus and yield tensile strength was increased while the toughness of the blends was reduced with an increase in starch content. Meanwhile, the storage modulus of the blends, especially at a temperature higher than the $T_g$ of PLA, was improved considerably with increasing starch content, indicating a potential way to enhance the HDT of PLA materials.

A.5 References

Conventional oil-based plastics such as poly(propylene) (PP) and poly(ethylene) (PE) have shown an almost exponential growth during the past few decades. Considering the sustainability in view of oil depletion and environmental issues, bio-based and/or biocompostable plastics have become a topic of interest throughout the world.

One has to distinguish between bio-based plastics for durable applications (engineering plastics) and single-use applications, notably in packaging. In the area of biocompostable packaging, only 6 commercially available biocompostable polymers exist in the market which can be subdivided into:

- Bio-based and biocompostable: PHB [poly(hydroxyl butyrate)], PLA [poly(lactic acid)] and TPS (thermoplastic) Starch;
- Oil-based and biocompostable: PCL [poly(ε-caprolactone)], PBAT [poly(butylene adipate-co-terephthalate)] and PBS [poly(butylene succinate)].

The performance of notably bio-based and biocompostable polymers, viz. PHB, PLA and starch compounds, is rather poor. The inherent drawbacks are temperature instability, lack of processability, brittleness and high price, notably PHB, limiting their developments and applications as a substitute for oil-based plastics.

The main objective of the thesis is improving the properties of bio-based and biocompostable polymer blends. Polymer blending is an engineering route to develop new materials with desired properties by mixing two or even more components, which can be easily carried out in the polymer processing industry.

PHB and PLA are both brittle thermoplastics. The brittleness of PHB and PLA could be improved by blending with a ductile polymer such as PBS. Since PHB and PLA are not compatible with PBS, the mechanical properties of the PHB/PBS and PLA/PBS blends could be improved further by compatibilization. In Chapters 2 and 3, we addressed a general toughening method for bio-based and biocompostable polymer blends, i.e. reactive compatibilization with dicumyl peroxide (DCP) as a free-radical grafting initiator. During reactive processing, the compatibilizer (i.e. graft copolymers and a certain extent of network
consisting of both components) can be made *in-situ*. The morphology can be tuned by processing conditions and the use of DCP, which leads to tough(er) PHB/PBS and PLA/PBS blends. This modification method is economic, since no extra process for compatibilization is necessary because it is performed during the blending in an extruder or compounding equipment. Therefore, the reactive extrusion with peroxide is of interest for a large-scale production, providing possibilities for biocompostable plastics with enhanced performance. However, side products, i.e. branched molecules and crosslinked networks may compromise on the processability of the resulting materials to a certain extent but in this study, processability was still feasible after compounding with DCP.

The toughness of PLA could be highly improved by physical blending with ethylene-co-vinyl acetate (EVA) which are, in fact, random copolymers. Since PLA is miscible with poly(vinyl acetate) (PVAc) but immiscible with PE, the compatibility and morphology of PLA/EVA blends can be tuned by the ratio of ethylene and vinyl acetate in the EVA copolymers. EVA domains in a sub-μm size in the PLA matrix can be easily obtained even without any additional compatibilizer. As a consequence, highly toughened PLA/EVA blends can be obtained at a certain vinyl acetate content (~ 50 wt%) (Chapter 4). The toughening effect of EVA is much more efficient in comparison with optimized commercial toughening modifiers such as Biomax®-Strong-100 (Dupont). For example, the notched impact toughness of PLA/EVA (80/20, wt/wt) and PLA/Biomax®-Strong-100 (80/20, wt/wt) blends is 65 kJ/m² and < 10 kJ/m² (i.e. ~ 100 J/m) respectively³. In addition, PLA retains a reasonable optical clarity after addition of EVA due to a good compatibility and a small EVA domain size, which is attractive in package application. All grades of EVA used in the thesis are commercially available and the preparation of PLA/EVA blends is rather simple (i.e. physical compounding), thus, the production of tough PLA/EVA blends can be easily scaled up to an industrial scale.

Since PLA/EVA (or EVA) can be biocompostable in the presence of starch, attempts were made in the last part of the thesis to prepare PLA/EVA/starch blends with fine dispersion of starch and attractive properties⁴. Due to the hydrophilic nature of starch and its poor processability, coarse morphology of PLA/starch blends is usually observed with starch particle size from several micrometers to several tens micrometers⁵,⁶,⁷. It is shown in
Chapters 5 – 6 that starch can be finely dispersed in EVA and PLA matrixes (potentially with a diameter of ~ 1 μm) by reactive compatibilization. Fine dispersion of starch (with d = 0.5 - 2 μm) can be obtained at starch content up to, at least, 40 wt%. Compatibilized EVA/starch pre-compounds were first prepared in the presence of maleic anhydride (MA), benzoyl peroxide (BPO) and glycerol. Then the pre-compounds were physically blended with PLA to make PLA/EVA/starch ternary blends. As a result, much better mechanical properties were obtained in comparison with the non-compatibilized blends. Although multiple steps are used to prepare the starch compounds in the thesis, it is feasible to combine the multiple steps in one step on an optimized large-scale extruder via mid-feeding. During the study, few large starch particles were observed also in the compatibilized blends, which might be resulted from the relatively low shear force of the lab-scale extruder. Thus, an even finer morphology of the starch compounds is expected via an optimized large-scale extruder. Moreover, addition of starch could effectively reduce the cost of the resulting materials, which makes the research more interesting and industrially viable.

References

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Curriculum Vitae

The author, Piming Ma, was born on November 13th 1980 in Jiaozhou, Qingdao, China. After finishing his bachelor study in 2005 at the South China University of Technology in Guangzhou, he studied Polymer Materials and Science at the Jiao Tong University in Shanghai and obtained his master degree in 2008 in the group “Plastic & Rubber Technology” under the supervision of prof. dr. Yong Zhang. During his master thesis he investigated the modification of poly(β-hydroxybutyrate-co-β-hydroxybutyrate).

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