Synthesis and properties of starch based biomaterials
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Chapter 6
Synthesis and Properties of Reactive Interfacial Agents for Polycaprolactone-Starch Blends

Abstract
The synthesis of two reactive interfacial agents for starch-PCL blends, PCL-g-glycidyl methacrylate (PCL-GMA) and PCL-g-diethyl maleate (PCL-g-DEM) is described. The compounds were prepared by reacting a low molecular weight PCL (Mw 3000) with glycidyl methacrylate or diethyl maleate in the presence of benzoylperoxide at 130°C. The effect of important process variables (initiator and monomer intakes as well as estimated solubility of the monomer in molten PCL) on the degree of grafting (FD) of the GMA and DEM units to the PCL backbone was explored in detail and quantified using multivariable linear regression. Highest values of the FD (up to 45 %) were observed for PCL-g-GMA, at relatively high GMA and BPO intakes. The FD values for PCL-g-DEM were considerably lower (up to 7 %). The reactive interfacial agents were tested for their performance in PCL-starch blends. Both act as compatibilizers for PCL/starch blends by improving the interfacial adhesion between the starch particles and the PCL matrix. As a result, the mechanical behavior of the compatibilized blends is in general different from that of pure PCL and of the corresponding uncompatibilized blends. In particular the elastic modulus for the compatibilized blends is significantly higher than that of uncompatibilized ones. At relatively low starch intakes, PCL-g-DEM has at least a comparable performance with respect to PCL-g-GMA, despite the expected differences (favorable to PCL-g-GMA) in the in situ formation of the compatibilizers. This discrepancy could be explained on the basis of the functional groups (GMA or DEM) distribution along the PCL backbone.

Keywords: starch-PCL blend, compatibilizer, glycidyl methacrylate, diethyl maleate, grafting
Chapter 6

6.1. Introduction

Starch is a cheap and abundantly available natural polymer with very good application perspectives in the area of biodegradable plastics. Unfortunately, the native material is very hydrophilic and important mechanical properties are inferior compared to most synthetic polymers and this hampers its direct use as packaging materials. Starch modifications to improve the product properties like enhanced hydrophobicity and mechanical properties were already reported in the early 19th century [1, 2]. One of the well known modification strategies is blending the starch with polymers displaying a stronger hydrophobic character and better mechanical properties, such as polyethylene (PE) or polystyrene (PS) [3-6]. Unfortunately, these synthetic polymers are poorly or non-biodegradable. To overcome this issue, synthetic biodegradable polymers have been applied. Among these, polyesters are considered very promising alternatives [7]. The ester bonds are susceptible to attack by water and this leads to enhanced biodegradability. A well-known biodegradable polyester, polycaprolactone (PCL), is known to be degraded with ease by microorganisms widely distributed in nature [8]. Aerobic soil-burial experiments showed that the mechanical properties of PCL films decrease rapidly in time [9]. As a consequence, PCL has gained considerable interest for possible applications in the fields of packaging materials and medical applications [10-11].

Blending of starch and synthetic biodegradable polyesters has been widely applied for the synthesis of fully-biodegradable products. However, blends of hydrophilic starch and hydrophobic biodegradable polyesters exhibit phase separation [12] due to differences in polarity of the building blocks. This phenomenon is highly undesirable and limits the application range considerably [13]. To reduce the tendency for phase separation, a compatibilizer (i.e. an interfacial agent) may be used to improve the interfacial association between the two polymer phases. In general a compatibilizer is a block-copolymer where each block displays a chemical structure equal or very similar to that of the polymers to be mixed. This leads, for starch/PCL blends, to an ideal compatibilizer having both PCL and starch blocks. Such structure is rather difficult to achieve by simple copolymerization methods and it is usually prepared in situ (i.e. upon mixing) by using a functionalized PCL. The latter displays the presence, along the backbone, of polar groups (usually epoxides or anhydrides [13-18]) able to react with the –OH groups along the starch backbone. It must be stressed here that the word “compatibilizer” is correctly used only when the block copolymer is actually able to significantly influence the dispersion of the polymers to be mixed (most probably through a steric stabilization mechanism [19]). When using ungelatinized starch as a component in the blend, as in this study, it would be actually more accurate to define the block copolymer as an “interfacial agent”, 

108
which is able to mainly improve the interfacial adhesion between the polymer and starch itself.

This chapter describes a systematic study on the synthesis of two reactive interfacial agents for starch-PCL systems, PCL-g-glycidyl methacrylate (PCL-g-GMA) and PCL-g-diethyl maleate (PCL-g-DEM). The effect of important process variables on the degree of grafting of the GMA and DEM units to the PCL backbone has been explored in detail and quantified using multivariable linear regression. The various compatibilizers have been tested for their performance in PCL-starch blends. Exploratory studies on the synthesis of PCL-g-GMA and its applications for starch/PCL blends have been published [13, 16], however, systematic studies and subsequent quantification of the functionalization reaction has not been reported to date. The synthesis and application of PCL-g-DEM is, to the best of our knowledge, an absolute novelty of the present research.

6.2. Materials and Methods

6.2.1. Materials

Polycaprolactone (PCL) CAPA 2304, M_w=3000 from Solvay Caprolactones, UK was used for the preparation of the interfacial agents. This low molecular weight PCL grade was used without further purification. Glycidyl methacrylate 97% purity (Aldrich), diethyl maleate ≥97% purity (Fluka), and benzoyl peroxide 75% (Merck, Germany) were used as received. Tetrahydrofuran (THF, >99%) was obtained from Acros, Belgium, xylene (99.8%) from Merck, Germany and methanol (99.8%) from Labscan, Ireland. Corn starch (with approx. 73% amylopectin and 27% amylase) was obtained from Sigma and high molecular weight PCL (CAPA 6503, M_w=50000) from Solvay Caprolactone, UK. The starch was dried for at least 24 h at 110°C under vacuum (approx. ~1 mbar) prior to use.

6.2.2. Methods

6.2.2.1. Compatibilizer synthesis

The compatibilizers were prepared in a Brabender Plasticorder PL2000 batch-kneader (chamber volume 35 cm³). The intake of reagents was maximally 75-80% of the volumetric volume to ensure proper mixing. The kneader was heated to 130 °C and PCL (CAPA 2304) was added while maintaining a rotational speed of 80 rpm. After the PCL was melted (1-2 minutes), a solution of BPO in GMA or DEM was added drop by drop over a period of 5 minutes. The materials were mixed for another 5 minutes, after which the equipment was stopped and the chamber was opened to collect the samples. Intakes for each experiment are given in Table 1 and 2.
6.2.2.2. Work-up of PCL-g-GMA products [13]

To remove unreacted GMA monomer and GMA homopolymer, PCL-g-GMA (5 g) was dissolved in 50 ml THF, stirred for 1.5 h, and then filtered. Methanol (450 mL) was added to the filtrate, and the product was precipitated at 6-8 °C. The solvent was decanted and the solid product was dried in a vacuum oven (40 °C, 5 mbar).

6.2.2.3. Work-up of PCL-g-DEM products

Purification of the PCL-g-DEM product was performed according to a modified procedure for PCL-g-maleic anhydride [17]. PCL-g-DEM (5 g) was dissolved in xylene and refluxed at 150 °C for 2 h. The resulting suspension was filtered and precipitated using methanol (450 mL) at 6-8°C. The solvent was decanted and the solid product was dried in a vacuum oven (40 °C, 5 mbar).

6.2.2.4. Preparation of PCL-starch blends with the reactive compatibilisers

The PCL-starch blends were prepared in a Brabender Plasticorder PL2000 batchkneader (chamber volume 35 cm³). An operation temperature of 170°C and a rotation speed of 80 rpm were applied [18]. PCL was added to the chamber followed by the addition of the starch and the reactive compatibilizer. The content was blended for 15 minutes. Subsequently, the chamber was opened and the resulting material was collected.

6.2.3. Analytical Methods

¹H-NMR measurements were performed using a 400 MHz Varian AMX Oxford NMR apparatus with CDCl₃ (99.8%, Aldrich) as the solvent. Digital Scanning Calorimetry (DSC) measurements were performed using a Q1000 TA Instruments equipped with a TA Instruments DSC cooling system. Each sample was first heated from 0 °C to 100 °C (heating rate 10 °C/min) to remove the thermal history of the material. The transition temperatures of each sample were further determined by first cooling down the samples from 100 °C to 0 °C and subsequently heating up back to 100 °C (cooling and heating rate were 10 °C/min). The error on the transition temperature is assumed to be ± 1 °C and 5 % of the calculated values for the corresponding enthalpies. Scanning Electron Microscopy (SEM) was performed using a Jeol 6320 F Scanning Electron Microscope. Before analysis, the samples were covered with a paladium/platinum conductive layer of 3 μm thickness, created using a Cressington 208 sputter coater. Infrared spectra were collected with a FT-IR apparatus in the ATR mode using a Spectrum 2000 instrument from Perkin Elmer. Tensile tests were performed using an Instron 4301.
machine. The T-bone samples were prepared using a Fontijne Holland TH 400 hot-press. For a given sample/blend, 8 different T-bones were used. For every T-bone, strain at break (\( \varepsilon \)), stress at break (\( \sigma \)) and modulus (\( E \)) were measured. The corresponding value for every blend was calculated as an average of the 8 measurements while the standard deviation was taken as absolute error on the average values.

6.2.3.1. Calculation of the Degree of Functionalization (FD) of the reactive compatibilizers

The number of moles of GMA or DEM present on the PCL backbone was quantified using the degree of functionalisation (FD). The FD is defined as:

\[
FD = \frac{\text{number of moles of GMA/DEM attached to PCL (mol)}}{\text{number of repeating units of the PCL backbone (mol)}} \times 100\%
\]  

(6.1.)

The FD was calculated using 1H-NMR by comparing the area of protons belonging to the GMA (\(-\text{CH}<\) proton at \( \delta \) 3.2 ppm) or DEM (\(-\text{CH}_2-\) protons at \( \delta \) 4.2 ppm) side chains with that of a characteristic proton resonance of the PCL backbone (\(-\text{CH}_2-\) protons at \( \delta \) 4.0 ppm [13, 15-16, 19]. A 5% relative error in the peak area of the NMR spectra was assumed, leading to a 10% relative error in the FD values.

6.2.4. Statistical Modeling

The influence of different processing parameters on the FD values has been determined by performing a multivariable regression procedure on the available data. As a result we were able to obtain a model for the FD of the reaction. The validity of the model was determined by performing an analysis of variance (ANOVA, Table 3). This procedure is described in detail in the literature [23] and consists of calculating the sum of squares (SS) for the model and the error. When the relative degrees of freedom (DF) are known, it is possible to calculate the mean square (MS) for the model and the error. On the basis of the latter values, the F-value for the model is determined followed by the P-value. The latter is a measure of the statistical significance of the model.
6.3. Results and Discussions

6.3.1. Preparation of the ReactiveCompatibilizers

Twelve compatibilizers were prepared by either reacting glycidyl methacrylate (GMA) or diethyl maleate (DEM) with low molecular PCL as the starting polymer and benzoyl peroxide (BPO) as the radical initiator (Scheme 6.1.).

Scheme 6.1. Functionalization reactions (only showing reactivity for the >CH₂ in α position on PCL backbone)

Typical ¹H-NMR spectra for the products are shown in Figure 6.1.
Figure 6.1. Typical $^1$H-NMR spectra of PCL-g-GMA (top) and PCL-g-DEM (bottom)

Peak assignments were based on available data reported for related products [13, 15-16, 20]. The FD values and the thermal properties of the products are shown in Table 6.1. (PCL-g-GMA) and Table 6.2. (PCL-g-DEM).
Table 6.1. Overview of experiments for the PCL-g-GMA compatibilisers \(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intake ((^\circ)-mol) (^b)</th>
<th>FD (%)</th>
<th>T (_{\text{cryst.}}) ((^\circ)C)</th>
<th>(\Delta H) (_{\text{cryst.}}) (J/g-PCL)</th>
<th>T (_{\text{melt.}}) ((^\circ)C)</th>
<th>(\Delta H) (_{\text{melt.}}) (J/g-PCL)</th>
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<tbody>
<tr>
<td></td>
<td>GMA</td>
<td>BPO</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PCL</td>
<td>-</td>
<td>-</td>
<td>27</td>
<td>75</td>
<td>51</td>
<td>79</td>
</tr>
<tr>
<td>PCL-g-GMA 1</td>
<td>12</td>
<td>0.6</td>
<td>22</td>
<td>72</td>
<td>47</td>
<td>72</td>
</tr>
<tr>
<td>PCL-g-GMA 2</td>
<td>24</td>
<td>0.6</td>
<td>19</td>
<td>68</td>
<td>47</td>
<td>69</td>
</tr>
<tr>
<td>PCL-g-GMA 3</td>
<td>36</td>
<td>0.6</td>
<td>29</td>
<td>67</td>
<td>48</td>
<td>68</td>
</tr>
<tr>
<td>PCL-g-GMA 4</td>
<td>6</td>
<td>0.3</td>
<td>25</td>
<td>73</td>
<td>47</td>
<td>73</td>
</tr>
<tr>
<td>PCL-g-GMA 5</td>
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<td>1.1</td>
<td>20</td>
<td>66</td>
<td>46</td>
<td>68</td>
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<tr>
<td>PCL-g-GMA 6</td>
<td>12</td>
<td>0.3</td>
<td>28</td>
<td>71</td>
<td>47</td>
<td>67</td>
</tr>
</tbody>
</table>

\(^a\) Experiments were carried out at 130 \(^\circ\)C.

\(^b\) \(^\circ\)-mol with respect to the CL repeating units in the PCL

\(^c\) based on the soluble fraction of the compatibilizer

Table 6.2. Overview of experiments for the PCL-g-DEM compatibilisers \(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intake ((^\circ)-mol) (^b)</th>
<th>FD (%)</th>
<th>T (_{\text{cryst.}}) ((^\circ)C)</th>
<th>(\Delta H) (_{\text{cryst.}}) (J/g-PCL)</th>
<th>T (_{\text{melt.}}) ((^\circ)C)</th>
<th>(\Delta H) (_{\text{melt.}}) (J/g-PCL)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>DEM</td>
<td>BPO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCL</td>
<td>-</td>
<td>-</td>
<td>27</td>
<td>75</td>
<td>51</td>
<td>79</td>
</tr>
<tr>
<td>PCL-g-DEM 1</td>
<td>15</td>
<td>0.6</td>
<td>27</td>
<td>70</td>
<td>44</td>
<td>72</td>
</tr>
<tr>
<td>PCL-g-DEM 2</td>
<td>30</td>
<td>0.6</td>
<td>30</td>
<td>68</td>
<td>47</td>
<td>62</td>
</tr>
<tr>
<td>PCL-g-DEM 3</td>
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<td>21</td>
<td>64</td>
<td>45</td>
<td>66</td>
</tr>
<tr>
<td>PCL-g-DEM 4</td>
<td>30</td>
<td>1.1</td>
<td>26</td>
<td>61</td>
<td>42</td>
<td>60</td>
</tr>
<tr>
<td>PCL-g-DEM 5</td>
<td>60</td>
<td>1.1</td>
<td>25</td>
<td>63</td>
<td>41</td>
<td>66</td>
</tr>
<tr>
<td>PCL-g-DEM 6</td>
<td>7.5</td>
<td>0.3</td>
<td>30</td>
<td>70</td>
<td>47</td>
<td>69</td>
</tr>
</tbody>
</table>

\(^a\) Experiments were carried out at 130 \(^\circ\)C

\(^b\) \(^\circ\)-mol with respect to the CL repeating units in the PCL

One of the PCL-g-GMA compatibilizers (PCL-g-GMA 5, see Table 6.1.), was only partly soluble in CDCl\(_3\), and therefore the FD is based on the soluble fraction of the compatibilizer only. The presence of an insoluble fraction, combined with a relatively broad molecular weight distribution (as shown by GPC, but not shown here for brevity), suggests that cross-linking occurred during this experiment.

In general, the FD of the PCL-g-GMA (3.2-45.2\%) products is much higher than those of PCL-g-DEM (0.9-7.2\%). This difference may be either due to the difference in mutual solubility of the GMA and DEM in PCL or differences in the molecular
mechanism of the grafting reaction. The mutual solubility may be expressed in terms of the differences of solubility parameters of PCL and the reagents [18]. The difference between the solubility parameters of GMA and PCL is 0.29 cal$^{1/2}$ cm$^{-3/2}$, while it is much higher (6.3 cal$^{1/2}$ cm$^{-3/2}$) for DEM and PCL [20]. Thus, GMA is likely better soluble in PCL, leading to higher values for FD of the products, as confirmed by our experiments. However, the higher experimental grafting efficiencies for PCL-GMA may also be rationalised by considering the reaction mechanism for the preparation of the compatibilisers. GMA molecules may either react directly with a radical at the PCL backbone or with a radical present on an already coupled GMA molecule. The latter leads to longer GMA grafts on a PCL backbone [13]. A simplified representation of the reactivity of GMA is shown in Figure 6.2.

![Figure 6.2. Simplified scheme of the GMA Grafting Reaction Mechanism [12]](image)

The reactivity of DEM in radical reactions is expected to be different from that of GMA. Previous studies on maleic anhydride (MA), a compound resembling the
chemical structure of DEM, showed that MA reacts easily with a radical on the PCL backbone. However, subsequent reactions of MA to an already grafted MA molecule hardly occur. Hence, the length of a MA graft is always unity whereas longer grafts are possible for GMA. Our experimental findings, i.e. higher FD values for GMA than for DEM are in line with this explanation and support the proposed molecular reaction mechanisms.

6.3.1.1. Effect of substrate (GMA/DEM) to PCL ratio on the FD

The effect of the substrate (GMA or DEM) to PCL ratio on the FD was studied by changing the GMA/DEM intake at different BPO amounts. The results are graphically provided in Figure 6.3.

![Figure 6.3](image)

**Figure 6.3.** Effect of GMA and DEM to CL-units ratio (mol/mol) on the FD of the products (constant PCL intake, 130°C)

Higher GMA intakes lead to higher FD values. This trend is independent of the BPO amount and matches with data reported by other groups [13, 22]. It is most probably related to the fact that GMA is able to propagate to longer grafted chains when reacted with PCL (Figure 6.2.). Thus an increase in the GMA intake will provide more monomer available for the growing of the grafted chains leading to higher FD values.
The experimental trend for DEM is different. The FD values are within a rather narrow range, although a slight increase in the FD values might be appreciated. Such behavior is slightly in contrast to what observed for maleic anhydride [13, 15, 17], for which a levelling off and eventually a decrease of the FD values for relatively higher MA amounts has been observed. Such discrepancy is probably related to the relatively low intake of DEM as well as to the different reactivity of DEM compared to MA [22].

6.3.1.2. Effect of the BPO intake on the product FD

The effect of the BPO intake on the FD was studied by using different intakes of BPO (Figure 6.4.).

For high GMA to CL ratio (24%-mol/ mol CL units), doubling the amount of initiator results in considerable higher product FD. These results are in line with earlier work [15, 17]. The use of higher initiator concentrations will result in an increase in the number of formed radicals. This will lead to a higher proportion of PCL radicals by hydrogen abstraction from the polymer backbone and thus to higher FD values. However, at relatively lower GMA intakes, no detectable influence of the BPO amount on the FD is observed (Figure 6.4.). Apparently, there
is an optimum ratio between the BPO concentration and available monomer (GMA in this case) on the FD. If many macroradicals are created in the system (relatively high BPO intakes) at low GMA intake, the possibility of side reactions will become significant. In particular the occurrence of “cage effects”, i.e. recombination of (macro) radicals, as well as several transfer reactions might be responsible for the observed trend [22].

The data for PCL-g-DEM shows a similar trend as for the experiments with a high GMA to CL ratio (24%-mol/mol CL units), namely an increase in the BPO intake results in higher product FD. The effect is however much less pronounced than for GMA. A doubling of the initiator intake for PCL-g-DEM only results in a 70% increase in the FD (compared to 300% for PCL-g-GMA). This phenomenon is likely related to the different nature of the radical grafting mechanism of GMA and DEM on PCL as mentioned before.

6.3.1.3. Modeling of the combined effects of the GMA/DEM and BPO intakes on the FD

Previous studies showed the importance of the initiator to monomer ratio on the FD values [15, 17]. However, these investigations focused on a better understanding of the individual variables by studying the effect of higher peroxide and monomer intakes while keeping for example their ratio constant. The results described in the previous paragraph imply that the mutual interaction between these variables and not the absolute value itself determines the final FD values to a great extent. To quantify synergic effects of monomer and initiator molar intakes on the FD of GMA and DEM on the PCL backbone, a statistical model has been developed by performing a multivariable linear regression on the data reported in Table 6.1. and 6.2. Here, the BPO and monomer intakes are considered as independent parameters. In addition, the mutual solubility of DEM in PCL and DMA in PCL was included in the model by using a parameter $\delta$, defined as the difference in solubility parameters between PCl and the substrates. This leads to the following equation:

$$FD = f(n_m, n_i, \delta)$$  \hspace{1cm} (6.2.)

where $n_m$ is the molar amount of monomer in the feed, $n_i$ the molar amount of initiator in the feed and $\delta$ the difference in solubility parameters calculated using group contributions [21].

The model provided in eq. 6.3. gives the best description of the experimental data:

$$FD = -1.8875 + 0.0325n_m\delta + 0.5431n_i\delta + 1.6022n_mn_i - 0.2729n_mn_i\delta$$  \hspace{1cm} (6.3.)
The analysis of variance data are given in Table 6.3. The very low P-value implies that the model is statistically significant. This was also confirmed by inspection of the residue distribution by a normal probability plot (not reported here for brevity) [23]. The $R^2$ value for the model (0.957) and its closeness to the adjusted $R^2$ (0.941) also suggests that all important variables have been included in the model.

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
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<td>Model</td>
<td>1828</td>
<td>4</td>
<td>456.908</td>
<td>44.928</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>Error</td>
<td>81.358</td>
<td>8</td>
<td>10.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1909.358</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The value of the coefficients in the model imply that the FD is positively influenced by the interaction between monomer and initiator intake ($n_n n_i$), the interaction between (PCL-monomer) intake and solubility parameter difference ($n_{in} \delta$) and the interaction between the latter factor and the initiator intake ($n_{i} \delta$).

Graphical representation of the FD models for PCL-g-GMA and PCL-g-DEM are given in Figure 6.5. and Figure 6.6., respectively.

**Table 6.3.** Analysis of variance for the FD model provided in eq 6.3.

![Graphical representation of the FD model for PCL-g-GMA.](image)

**Figure 6.5.** Graphical representation of the FD model for PCL-g-GMA.

a. 3D plot. 

b. Contour plot.
Remarkable is once more the different trends for the two substrates. While for GMA an increase in BPO or monomer intakes invariably leads to higher FD values, for DEM a clear transition is observed. For relatively high DEM intakes (> 30 % mol/mol), a higher BPO intake leads to a reduction of the FD values while an opposite trend is observed at lower DEM intakes. These differences in dependency of the FD values on the DEM and GMA intakes may be explained on the basis of the different grafting mechanisms as previously discussed. From a more practical point of view, the statistical model provides besides a reliable description of the experimental data also a good mathematical description to modulate the FD values of the two substrates by changing the chemical composition (monomer, radical initiator and PCL intakes).

6.3.1.4. Thermal properties of the compatibilizers

The thermal properties (Table 6.1. and 6.2.) of the compatibilizers were determined by DSC. For all samples, the melting temperature and the relative enthalpy decrease with respect to pure PCL. Furthermore, the crystallization temperature and enthalpy are not a clear function of the FD values, although both properties are significantly lower than those of pure PCL. Such changes in the thermal properties compared to pure PCL may be caused by the introduction of grafts on the PCL chains. This induces irregularities and is expected to result in a lowering of the $T_c$ and the $T_m$. Similar observations have also been made by Kim, et al [13] working with PCL-g-GMA. The random behavior of the $T_c$ as function of the FD values is probably the result of two concurring effects: the presence of irregularities, which is expected to lead to a $T_c$ reduction, and a favored nucleation
of the PCL chains in the compatibilizers compared to virgin PCL (higher \( T_c \)) induced by the presence of polar groups.

The lower crystallization and melting enthalpy of the compatibilizers compared to virgin PCL is possibly caused by the presence of side chains on the PCL backbone which are expected to have a negative effect on the crystallinity of the products.

6.3.2. Synthesis and Properties of Starch- PCL Blends

The two compatibilizers (PCL-g-GMA and PCL-g-DEM) were further used as interfacial agents in blends of PCL with starch. A total of 12 blends were prepared: a series of binary ones (not containing any compatibilizers) constituting our reference points, a series with PCL-g-DEM (different intakes of the latter at fixed starch/PCL ratio) and two series with PCL-g-GMA (one with different intakes of PCL-g-GMA at a fixed starch/PCL ratio and one with a fixed compatibilizer intake at three different starch/PCL ratios). An overview of all prepared blends together with their thermal and mechanical (tensile tests) properties is given in Table 6.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \sigma ) (MPa)</th>
<th>( \varepsilon ) (%)</th>
<th>( E ) (MPa)</th>
<th>( T_c ) (°C)</th>
<th>( \Delta H_c ) (J/gPCL)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta H_m ) (J/gPCL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
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Table 6.4. Thermal and mechanical properties of starch/PCL blends

*PCL-g-DEM has an FD of 1.7 %. PCL-g-GMA has an FD of 9.6%.

Our experimental design allows comparisons of thermal and mechanical properties as function of the starch content for binary blends (no compatibilizer) and intake of PCL-g-DEM and of PCL-g-GMA.
6.3.2.1. Binary blends of starch and PCL

For binary blends (no compatibilizer is added) a monotonous decrease of the stress and strain at break is observed as function of the starch intake, respectively from 16.43 MPa and 640.5 % for pure PCL to 7.1 MPa and 341.8 % at 30 % starch content. The simultaneous increase in the modulus (from 270.2 MPa up to 341.8 MPa) clearly indicates that the rigidity of the blends increases at higher starch contents. This is in agreement with the data previously reported on PCL/starch blends and related to the lack of interfacial adhesion between the starch particles and the PCL matrix [18]. The thermal behavior is characterized by no significant changes in the $T_m$ and $T_c$ values but unreported trends of the corresponding enthalpies as function of the starch content (Figure 6.7.).

![Figure 6.7. Melting and crystallization enthalpy as function of the starch content for binary blends with PCL.](image)

The two trends are remarkably mirroring each other and are both characterized by an increase of $\Delta H_m$ and $\Delta H_c$ with respect to pure PCL at 10 % starch content followed by a monotonous decrease of both quantities as function of the starch intake. This is most probably due to a nucleation effect of the starch on PCL as observed also for other kinds of polymer blends [27]. The thermal and mechanical properties indicate no or very little interaction of the starch particles with the PCL.
Synthesis and Properties of Reactive Interfacial Agents for Polycaprolactone-Starch Blends

matrix. This is visually confirmed by the morphology of the prepared blends (Figure 6.8).

![Figure 6.8. Morphology of starch/PCL binary blends.](image)

Indeed starch particles are clearly dispersed in the PCL matrix but no interaction (adhesion) between the two phases is actually detected. Thus, the starch particles are simply inserted into voids of the PCL matrix. The presence of these voids was also observed for sago starch/PCL blends [25, 26] and explained by assuming that the voids are formed by water in the starch. Evaporation of the water during blend preparation, either by heating or in combination with mechanical stress [24], and the lack of interface adhesion cause void formation.

6.3.2.2. Ternary blends compatibilized with PCL-g-DEM

PCL-g-DEM, whose synthesis is described for the first time in this work, was used as compatibilizer for the preparation of ternary blends with starch and PCL. The thermal behavior is characterized (Table 6.4.) by constant values of the $T_m$ (with respect to pure PCL) while the $T_c$ is slightly lower (30 vs 35 °C) than that of pure PCL and it is independent of the compatibilizer content. The latter trend is also valid for the corresponding enthalpies: i.e. a decrease with respect to pure PCL is observed and then a substantial invariance as function of the PCL-g-DEM content. Such behavior is consistent with the hypothesis that the starch particles hinder the melting and crystallization processes of the PCL chains. However, in order to fully understand the role of PCL-g-DEM, the corresponding binary blend (S/PCL 20/80) constitutes a better reference point compared to pure PCL. In this respect the thermal properties remain substantially unchanged with the exception of the $T_c$, for which a 6 °C drop is observed when using PCL-g-DEM. As consequence one might expect a slight different structure of these ternary blends as compared to the corresponding binary one. This is confirmed by examination of the blend morphology by SEM (Figure 6.9.).
Figure 6.9. Morphology of ternary blends compatibilized with PCL-g-DEM.
(a) S/PCL/PCL-g-DEM 20/80/1
(b) S/PCL/PCL-g-DEM 20/80/2
(c) S/PCL/PCL-g-DEM 20/80/5

Indeed starch particles in the ternary blends display a smoother interface with
the PCL matrix compared to the corresponding binary blends (Figure 6.9.). A
closer inspection of the SEM pictures reveals that the starch particles are clearly
embedded in the PCL matrix with almost no void spaces at the interface. As a
result of the different morphology also the mechanical behavior display
differences with the virgin PCL and the binary blend. The stress and strain at
break remain constant as function of the compatibilizer intake while the modulus
display an optimum as function of the compatibilizer intake (Figure 6.10.).

At 1 %-wt of PCL-g-DEM in the blends the modulus increases with respect to
the binary blend (0 %-wt compatibilizer in Figure 6.10.). This can be explained by
the improved interfacial adhesion [14] between PCL and starch, which will hinder
the flowability and fibre forming ability of PCL matrix under cold drawing,
resulting in more rigid material with higher modulus. At higher PCL-g-DEM
intakes the lower average molecular weight of the compatibilizer as compared to
the one of the unmodified PCL used in the blends (3000 vs 50000) is probably
responsible for the observed decrease in the E values.
6.3.2.3. Ternary blends compatibilized with PCL-g-GMA

When using PCL-g-GMA as compatibilizer two possible comparisons can actually be made: one at fixed starch/PCL ratio and changing the amount of PCL-g-GMA and one at different starch/PCL ratios but with fixed amount of PCL-g-GMA (2 %-wt).

The first comparison as function of the PCL-g-GMA intake (ternary blends with starch/PCL ratio of 20/80) results in quite similar considerations as the ones made for PCL-g-DEM. In particular also in the case of PCL-g-GMA, by taking as reference the corresponding binary blend (S/PCL 20/80), it can be observed that:

1) the melting temperature as well as the crystallization and melting enthalpies do not change significantly (discrepancies in the values are within the boundary defined by the experimental error);

2) the crystallization temperature experiences a drop of about 5-6 °C;

3) the stress and strain at break are lowered and hardly a function of the PCL-g-GMA amount;

4) the modulus is higher and hardly a function of the compatibilizer amount.

Remarkable is that in the case of PCL-g-GMA no optimum is found in the modulus as function of the compatibilizer intake. However, in all cases (i.e. at all PCL-g-GMA contents) there is a clear increase of the modulus with respect to the
binary blend, clearly indicating that also PCL-\(g\)-GMA (like PCL-\(g\)-DEM) acts as compatibilizer in the blends. Such hypothesis is partially and qualitatively confirmed by the blends morphology (Figure 6.11.).

![Figure 6.11. Morphology of ternary blends S/PCL/PCL-\(g\)-GMA. (a) S/PCL/PCL-\(g\)-GMA 20/80/1 (b) S/PCL/PCL-\(g\)-GMA 20/80/2 (c) S/PCL/PCL-\(g\)-GMA 20/80/3](image)

In this case we observe structural features (partially smooth interface between the components, presence of voids, partial interfacial adhesion) which render these ternary blends a kind of “intermediate” case between the binary ones and those compatibilized with PCL-\(g\)-DEM. This is surprising if one takes into account the different FD values: 9.8 % for PCL-\(g\)-GMA against 1.7 % for PCL-\(g\)-DEM. Thus, despite a much more favourable FD value for PCL-\(g\)-GMA with respect to PCL-\(g\)-DEM and even despite a relative low reactivity of ester groups towards the –OH groups on starch and nucleophilic groups in general [27, 28, 29], PCL-\(g\)-DEM is at least as active as compatibilizer (compare modulus values in Table 6.4. and morphologies in Figures 6.9. and 6.11.) than PCL-\(g\)-GMA for blends containing 20 %-wt of starch. These differences in compatibilizing effect are not yet fully understood. However, one might speculate that the longer length of the GMA grafts compared to DEM (vide supra) plays a negative role in the in situ formation of the compatibilizer. As given schematically in Figure 6.12. (left) the structure of PCL-\(g\)-GMA is inhomogeneous at the molecular level with long poly(GMA) branches pending from the PCL backbone. This confines all reactive GMA groups in relatively “isolated” spots along the PCL backbone. As a result, upon reaction of PCL-\(g\)-GMA with one of the –OH groups on the surface of the starch particles the remaining GMA groups are actually scarcely available for further reaction with other –OH groups spatially distant from the reacted one.
On the other hand (right of Figure 6.12.) PCL-g-DEM has much less reactive groups (lower FD) than PCL-g-GMA; but since DEM is preferentially grafted as monomer, the distribution of the reactive group along the PCL backbone is more “homogenous”. As consequence, once PCL-g-DEM has reacted with one –OH groups on the starch particle, other groups will presumably remain available (arrows in Figure 6.12.) for further reaction, thus probably ensuring a better coverage of the surface.

The proposed explanation implies however that at relatively higher starch contents (> 20 %-wt) the segregation of the poly(GMA) chains in “isolated” spot along the PCL backbone would become less important. Indeed, at higher starch contents more –OH groups would be available for reaction with the GMA groups, thus attenuating the effect discussed above. In order to check this we compared blends with the same amount of PCL-g-GMA (2 %-wt) but with different starch intakes (10, 20 and 30 %-wt respectively). Concerning the thermal behavior (Table 6.4.), the T_c decreases (with respect to the corresponding binary blends) while all other factors (T_m and enthalpies) remain virtually unchanged with respect to the binary blends and also as function of the starch intake. Moreover, for all starch amounts (Table 6.4.), when comparing ternary blends (compatibilized with PCL-g-GMA) with the binary ones, the stress and strain at break decrease while the modulus is unchanged at low starch contents and increases significantly for S/PCL blends with 30 %-wt starch. The latter result (from a modulus of 341.8 MPa for S/PCL 30/70 up to 430.3 MPa for S/PCL/PCL-g-GMA 30/70/2) clearly indicates that the efficiency of PCL-g-GMA as compatibilizer becomes more relevant at relatively higher starch contents (>30 %) [25]. This is in agreement with the hypothesis made above (Figure 6.12.) and relating the “coverage” of the starch particle surface upon reaction with PCL-g-GMA with the compatibilization efficiency. We can therefore conclude that the efficiency of PCL-g-GMA in the
compatibilization of starch/PCL blends can be significantly improved by changing the blend composition.

6.4. Conclusions

A systematic study, including statistical modeling, has been performed on the synthesis of two reactive compatibilisers, PCL-g-glycidyl methacrylate (PCL-g-GMA) and PCL-g-diethyl maleate (PCL-g-DEM). The proposed model to quantify the effects of process variables (monomer and initiator intake, mutual solubility of the monomer into the molten polymer) on the FD adequately described the experimental results ($R^2=0.957$, $P$-value $≤10^{-4}$). The most important variable for the final product FD is the interaction between the amount of monomer and initiator used. This represents an unreported mathematical confirmation of the fact that these kinds of functionalization reactions are mainly governed by the synergy between the different process variables and only slightly by their individual values. The PCL-g-GMA and PCL-g-DEM compatibilizers display lower melting temperatures and melting enthalpies compared to virgin PCL.

The reactive compatibilizers were used in blends of starch with PCL. At a fixed starch content (20 %-wt) PCL-g-DEM seems to have slightly more efficient compatibilizing effect than PCL-g-GMA as shown by blends morphology and elastic modulus values. This is in contrast with chemical reactivity and amount of chemical groups along the PCL backbone (both factors favorable to GMA as compared to DEM) but it is explainable on the basis of the group distribution along the PCL backbone. The latter hypothesis is indirectly confirmed by the observation that PCL-g-GMA becomes more efficient at relatively higher starch contents in the blends. From a more practical point of view it can be concluded that the newly synthesized PCL-g-DEM, firstly reported in this work, can replace PCL-g-GMA as compatibilizer at relatively low starch contents offering at the same time the advantage of a less pronounced modification of the polymer backbone and a reduced consumption of polar groups to be grafted on PCL.

6.5. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$E$</td>
<td>initial modulus [MPa]</td>
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<tr>
<td>$FD$</td>
<td>functionalization degree, moles of GMA or DEM present per mole of CL repeating units</td>
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<tr>
<td>$n_i$</td>
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<tr>
<td>$n_m$</td>
<td>amount of monomer GMA or DEM intake [mol% on CL units]</td>
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Synthesis and Properties of Reactive Interfacial Agents for Polycaprolactone-Starch Blends

\[ T \] : temperature [°C]
\[ T_c \] : crystallization temperature [°C]
\[ T_m \] : melting temperature [°C]

Greek symbols:
\[ \Delta H_c \] : enthalpy of crystallization [J/g-PCL]
\[ \Delta H_m \] : enthalpy of melting [J/g-PCL]
\[ \delta \] : solubility parameter [cal^{1/2}cm^{-3/2}]
\[ \sigma \] : stress at break [MPa]
\[ \varepsilon \] : strain at break [%]

6.6. References


