

Synthesis and Properties of Reactive Interfacial Agents for Polycaprolactone-Starch Blends

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ABSTRACT: The synthesis of two reactive interfacial agents for starch-polycaprolactone (PCL) blends, PCL-*g*-glycidyl methacrylate (PCL-*g*-GMA) and PCL-*g*-diethyl maleate (PCL-*g*-DEM) is described. The compounds were prepared by reacting a low molecular weight PCL (M_w 3000) with GMA or DEM in the presence of benzoylperoxide (BPO) at 130°C. The effect of important process variables (initiator and monomer intakes) on the functionalization degree (FD) of the GMA and DEM units to the PCL backbone was explored in detail and quantified using multivariable linear regression. The highest FD values (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 interfa-

cial agents were tested for their performance in starch-PCL blends. The mechanical properties of the compatibilized blends differ from the uncompatibilized ones and in particular the elastic modulus for the compatibilized blends is significantly higher. At relatively low starch intakes, PCL-*g*-DEM has at least a comparable performance than PCL-*g*-GMA. These observations may be explained tentatively on the basis of the distribution of the functional groups (GMA or DEM) along the PCL backbone. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2315–2326, 2009

Key words: biomaterials; biopolymers; blends; compatibilization; mechanical properties

INTRODUCTION

Starch is a cheap and abundantly available natural polymer with very good application perspectives in the area of biodegradable plastics. Unfortunately, native starch is very hydrophilic and important mechanical properties are inferior compared to most synthetic polymers. This hampers its direct application in the field of packaging materials. Starch modifications to improve product properties like increased hydrophobicity and better mechanical properties were already reported in the early 19th century.^{1,2} One of the well-known modification strategies is blending the starch with hydrophobic polymers with better mechanical properties, such as polyethylene or polystyrene.^{3–6} Unfortunately, these synthetic polymers are poorly or nonbiodegradable. 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 is polycaprolactone (PCL), which is 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 separation¹² 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 (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 has a chemical structure equal or very similar to that of the polymers to be mixed. Thus, the ideal compatibilizer for starch/PCL blends contains both PCL and starch blocks linked to each other either in a linear or grafted fashion. This ideal structure is difficult to achieve by simple copolymerization methods. An alternative approach is the use of a functionalized PCL. The latter contains reactive polar groups (usually epoxides or anhydrides^{13–18}) able to react with the —OH groups of the starch backbone.

It must be stressed here that the word “compatibilizer” is correctly used only when the block/graft copolymer is during melt blending actually able to significantly influence the dispersion of both

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TABLE I
Overview of Experiments for the PCL-g-GMA Compatibilizers^a

| Sample | Intake (mol %) ^b | | FD (%) | T_c (°C) | ΔH_c (J/g-PCL) | T_{melt} (°C) | ΔH_m (J/g-PCL) |
|-------------|-----------------------------|-----|-------------------|------------|------------------------|-----------------|------------------------|
| | GMA | BPO | | | | | |
| PCL | – | – | – | 27 | 75 | 51 | 79 |
| PCL-g-GMA 1 | 12 | 0.6 | 5.7 | 22 | 72 | 47 | 72 |
| PCL-g-GMA 2 | 24 | 0.6 | 15.2 | 19 | 68 | 47 | 69 |
| PCL-g-GMA 3 | 36 | 0.6 | 27.9 | 29 | 67 | 48 | 68 |
| PCL-g-GMA 4 | 6 | 0.3 | 3.2 | 25 | 73 | 47 | 73 |
| PCL-g-GMA 5 | 24 | 1.1 | 45.2 ^c | 20 | 66 | 46 | 68 |
| PCL-g-GMA 6 | 12 | 0.3 | 6.3 | 28 | 71 | 47 | 67 |

^a Experiments were carried out at 130°C.

^b mol % with respect to the CL repeating units in the PCL.

^c Based on the soluble fraction of the compatibilizer.

polymers (most probably through a steric stabilization mechanism¹⁹). When using un-gelatinized starch as a component in the blend, as in this study, it would be actually more accurate to define the block/graft copolymer as an “interfacial agent”, which improves the interfacial adhesion between the polymer and starch.

This article 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 functionalization degree (FD) of the GMA and DEM units to the PCL backbone has been explored in detail and quantified using multivariable linear regression. The various reactive 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 article.

MATERIALS

Polycaprolactone (PCL, CAPA 2304, M_w = 3000) from Solvay Caprolactones, UK was used for the preparation of the reactive compatibilizers. This low molecular weight PCL grade was used without further purification. GMA (97% purity, Aldrich), DEM ($\geq 97\%$ 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 $\sim 73\%$ amylopectin and 27% amylose) was obtained from Sigma and high molecular weight PCL (CAPA 6503, M_w = 50,000) from Solvay Capro-

lactone, UK. The starch was dried for at least 24 h at 110°C under vacuum (~ 1 mbar) prior to use.

METHODS

Compatibilizer synthesis and purification

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 chamber 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 benzoylperoxide (BPO) in GMA or DEM was added drop wise over a period of 5 min. The materials were mixed for another 5 min, after which the equipment was stopped and the chamber was opened to collect the samples. Intakes for each experiment are given in Table I and II.

Work-up of PCL-g-GMA products¹³

To remove unreacted GMA monomer and GMA homopolymer, PCL-g-GMA (5 g) was dissolved in THF (50 mL), 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) until constant weight.

Work-up of PCL-g-DEM

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) until constant weight.

TABLE II
Overview of Experiments for the PCL-g-DEM Compatibilizers^a

| Sample | Intake (%-mol) ^b | | FD (%) | T_c (°C) | ΔH_c (J/g-PCL) | T_m (°C) | ΔH_m (J/g-PCL) |
|-------------|-----------------------------|-----|--------|------------|------------------------|------------|------------------------|
| | DEM | BPO | | | | | |
| PCL | – | – | – | 27 | 75 | 51 | 79 |
| PCL-g-DEM 1 | 15 | 0.6 | 3.5 | 27 | 70 | 44 | 72 |
| PCL-g-DEM 2 | 30 | 0.6 | 2.1 | 30 | 68 | 47 | 62 |
| PCL-g-DEM 3 | 45 | 0.6 | 7.2 | 21 | 64 | 45 | 66 |
| PCL-g-DEM 4 | 30 | 1.1 | 3.6 | 26 | 61 | 42 | 60 |
| PCL-g-DEM 5 | 60 | 1.1 | 6.5 | 25 | 63 | 41 | 66 |
| PCL-g-DEM 6 | 7.5 | 0.3 | 0.9 | 30 | 70 | 47 | 69 |

^a Experiments were carried out at 130°C.

^b mol % with respect to the CL repeating units in PCL.

Preparation of PCL-starch blends with the reactive compatibilizers

The PCL-starch blends were prepared in a Brabender Plasticorder PL2000 batch-kneader (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 min. Subsequently, the chamber was opened and the resulting material was collected and analyzed.

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 erase the thermal history of the material. The transition temperatures of each sample were determined by first cooling down the samples from 100°C to 0°C and subsequently heating up again to 100°C (cooling and heating rate were 10°C/min). The error in the transition temperature is assumed to be ±1°C and 5% for the calculated values of 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 thin palladium/platinum conductive layer created using a Cressington 208 sputter coater.

Infrared spectra were recorded on a FT-IR apparatus in the ATR mode using a Spectrum 2000 instrument from Perkin Elmer. For each sample, 30 scans were made between 4000–600 cm⁻¹ with a resolution of 4 cm⁻¹.

Tensile tests were performed using a Instron 4301 machine (Instron, MA) at 20°C and a crosshead speed of 30 mm/min. The dog-bone samples (with thickness of 2 mm) for determination of the tensile properties were prepared using a melt press apparatus (Fontijne, Netherlands), operated at 150°C and 150 bar for 3 min. For a given sample/blend, eight different dog-bones were used. For every dog-bone, strain at break (ϵ), stress at break (σ) and modulus (E) were measured. The corresponding value for every blend was calculated as an average of the eight measurements while the standard deviation was taken as the absolute error of the average values.

Calculation of the degree of functionalization of the reactive compatibilizers

The number of moles of GMA or DEM present on the PCL backbone was quantified by the FD. The FD is defined as:

$$FD = \frac{\text{number of moles of GMA/DEM attached to PCL (mol)}}{\text{number of repeating units of the PCL backbone (mol)}} \times 100\% \quad (1)$$

The FD was calculated using ¹H-NMR by comparing the area of protons belonging to the GMA (–CH< proton at $\delta = 3.2$ ppm) or DEM (–CH₂– protons at $\delta = 4.2$ ppm) side chains with that of a characteristic

proton resonance of the PCL backbone (–CH₂– protons at $\delta = 4.0$ ppm.^{13,15,16,19} A 5% relative error on the peak area of the NMR spectra was assumed, leading to a 10% relative error in the FD values.

STATISTICAL MODELING

The influence of different processing parameters on the FD values was quantified by multivariable regression on the available experimental data. The validity of the model was determined by performing an analysis of variance (ANOVA). This procedure is described in detail in the literature²⁰ and consists of calculating the sum of squares 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 are determined followed by the *P*-value. The latter is a measure of the statistical significance of the model.

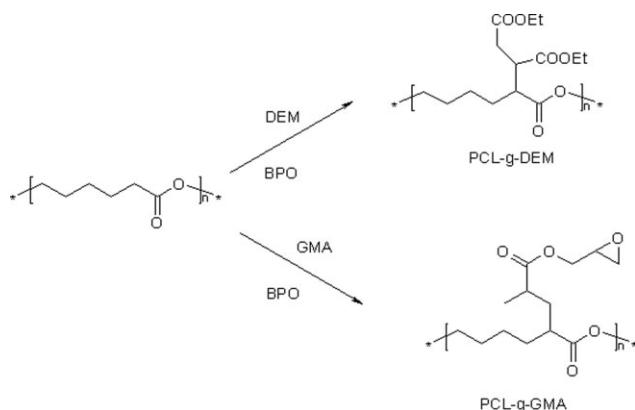
RESULTS AND DISCUSSIONS

Preparation of the reactive compatibilizers

Twelve reactive compatibilizers were prepared by either reacting GMA or DEM with low molecular PCL and benzoyl peroxide (BPO) as the radical initiator (Scheme 1). Typical ¹H-NMR spectra for the products are shown in Figure 1. Peak assignments were based on available data reported for related products.^{13,15,16,21} The FD values and the thermal properties of the products are shown in Table I (PCL-*g*-GMA) and Table II (PCL-*g*-DEM).

One of the PCL-*g*-GMA compatibilizers (PCL-*g*-GMA 5, see Table I), was only partly soluble in CDCl₃, 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 are much higher than those of PCL-*g*-DEM (0.9–7.2%). This may be either due to the difference in mutual solubility of the GMA and DEM in PCL or



Scheme 1 Functionalization reactions (only showing reactivity for the $>\text{CH}_2$ in α position on PCL backbone).

differences in the molecular mechanism of the grafting reaction. The mutual solubility may be expressed in terms of the differences in solubility parameters of PCL and the reagents. The value for GMA and PCL is $0.29 \text{ cal}^{1/2}\text{cm}^{-3/2}$, which is much lower than calculated for DEM and PCL ($6.3 \text{ cal}^{1/2}\text{cm}^{-3/2}$).²¹ Thus, GMA is expected to be much better soluble in PCL, leading to higher FD values of the products, as confirmed by our experiments. However, the higher FD values for PCL-*g*-GMA may also be rationalized by considering the reaction mechanism for the preparation of the compatibilizers. 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 represents basically a propagation step and leads to longer GMA grafts on a PCL backbone.¹³ A simplified representation of the reactivity of GMA is shown in Figure 2.

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 occurs. Based on the analogy, the length of a DEM graft is expected to be unity whereas longer grafts are possible for GMA. Our experimental findings, higher FD values for GMA than for DEM, are in line with this explanation and support the proposed molecular reaction mechanisms.

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

The effect of the substrate (GMA or DEM) to the PCL ratio on the FD was studied by changing the GMA/DEM intake at constant PCL intake. Two different BPO intakes were explored. The results are graphically provided in Figure 3. When considering GMA as the substrate, it is clear that higher GMA intakes lead to higher FD values. This trend is independent of the BPO intake and is in agreement 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 (Fig. 2). Thus, an increase in the GMA intake will likely lead to longer GMA grafted chains and thus to higher FD values.

The experimental trends for DEM are different. The FD values are within a rather narrow range, although a slight increase in the FD values might be appreciated. Such behavior is somewhat in contrast to what was observed for MA.^{13,15,17} Here, a leveling off and eventually a decrease of the FD values for relatively high MA intakes were observed. This discrepancy is probably related to the relatively low

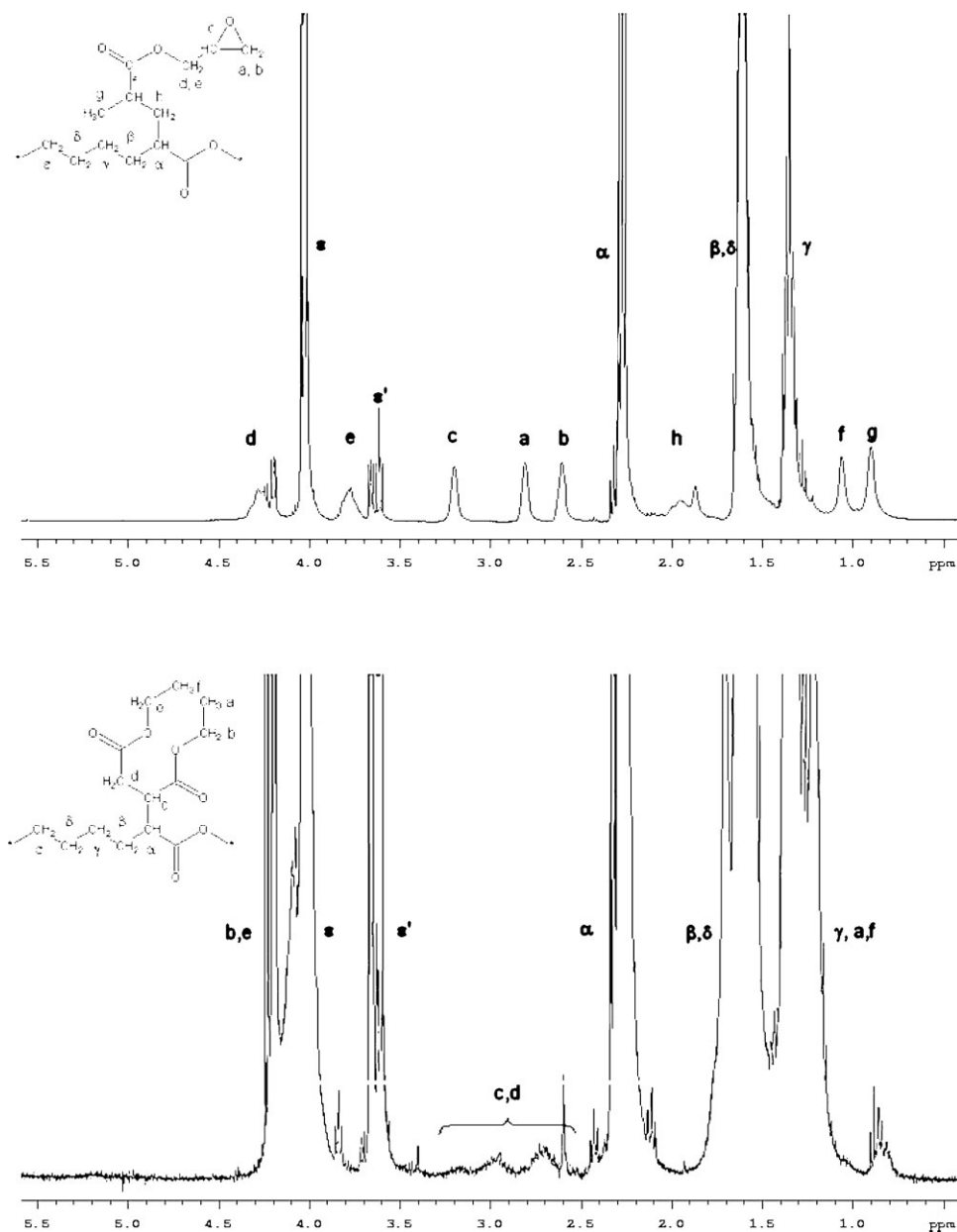


Figure 1 Typical $^1\text{H-NMR}$ spectra of PCL-g-GMA (top) and PCL-g-DEM (bottom).

intake of DEM in our experiments as well as to differences in reactivity of DEM compared to MA.²²

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 at a constant PCL-GMA/DEM intake (Fig. 4). For high GMA to PCL ratios (24%-mol/mol CL units), doubling the amount of initiator results in considerably higher FD values for the products. These results are in line with earlier work.^{15,17} Application of higher initiator concentrations will lead to higher concentrations of primary radicals, giving a higher proportion of PCL radicals by hydrogen abstraction from the polymer

backbone and leading to higher FD values. However, at relatively lower GMA intakes, no detectable influence of the BPO intake on the FD is observed (Fig. 4). Apparently, there is an optimum ratio between the BPO concentration and available monomer (GMA in this case) on the FD. When large amounts of radicals are created in the system (relatively high BPO intakes) at low GMA intakes, the possibility of side reactions will become significant. In particular the occurrence of "cage effects", i.e. the recombination of radicals, as well as several transfer reactions may take place and lead to the experimentally observed trend.²²

The data for PCL-g-DEM shows a similar trend as for the experiments with a high GMA to CL ratio

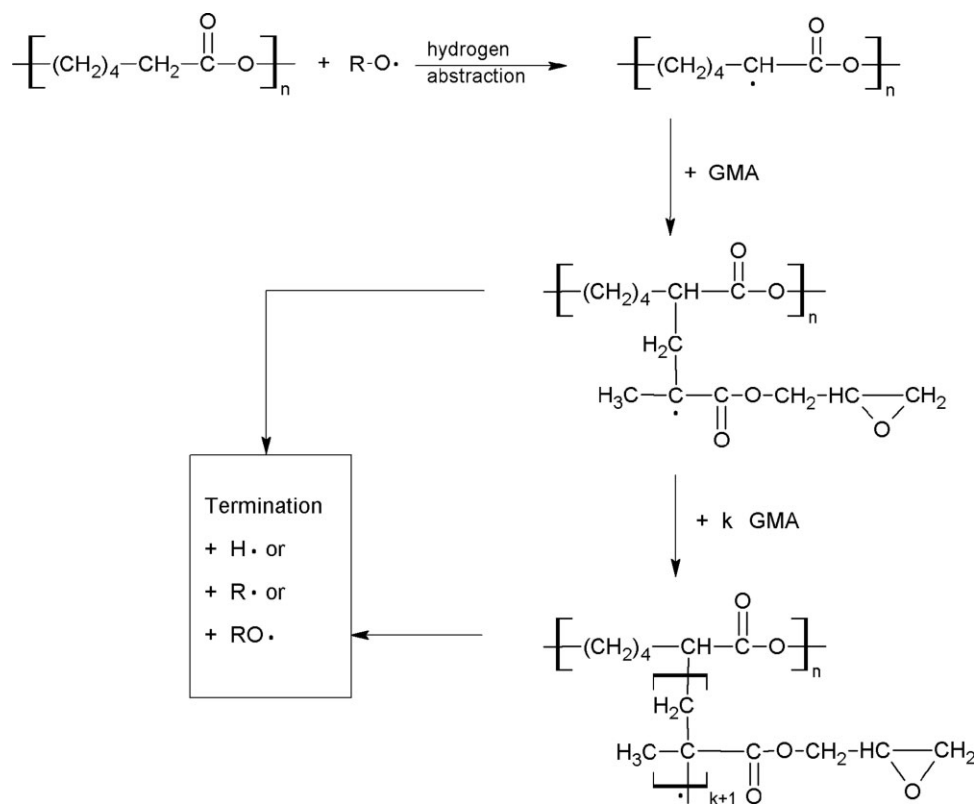


Figure 2 Simplified reaction mechanism for the GMA grafting reaction.¹²

(24%-mol/mol CL units), namely an increase in the BPO intake results in products with a higher 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 discussed earlier.

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

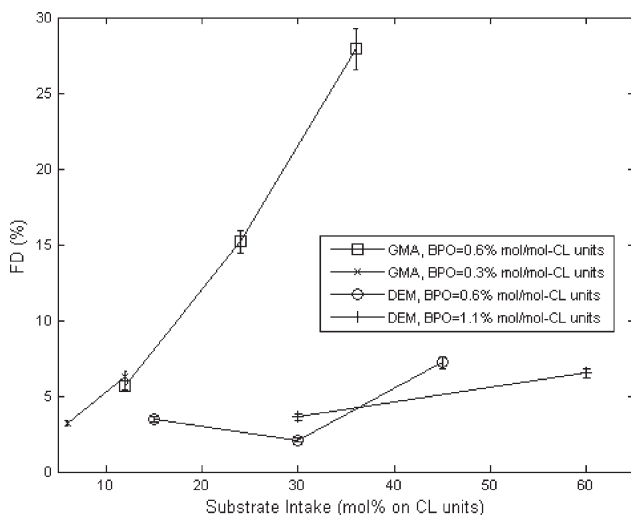


Figure 3 Effect of GMA and DEM to CL-units ratio (mol/mol) on the FD of the products (constant PCL intake, 130°C).

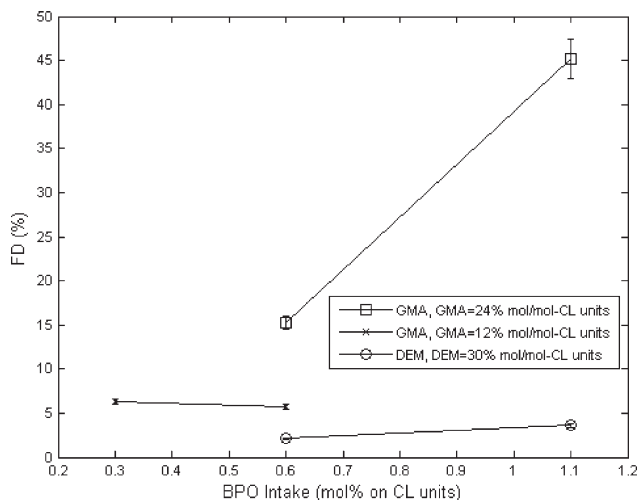


Figure 4 Effect of the BPO intake on the product FD (130°C, constant substrate to PCL ratio).

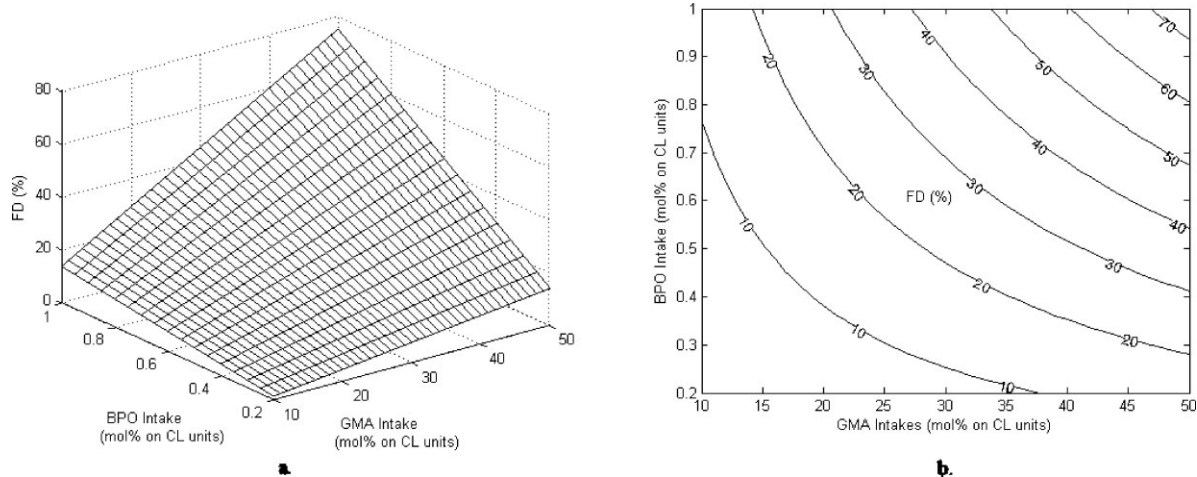


Figure 5 Graphical representation of the FD model for PCL-g-GMA. (a) 3D plot. (b) Contour plot.

understanding of the individual variables by studying the effect of higher peroxide and monomer intakes while keeping for example their ratios 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 or DEM on the PCL backbone, a statistical model has been developed by performing a multivariable linear regression on the data reported in Table I and II. Here, the BPO and monomer intakes are considered as independent parameters. The type of monomer (GMA or DME) is included in the model by a solubility parameter δ . This parameter is different for both monomers and is defined as the difference in solubility parameters between PCL and the monomers. The values were calculated using group contributions.²³ This leads to the following equation:

$$\text{FD} = f(n_m, n_i, \delta) \quad (2)$$

where n_m is the molar intake of monomer, n_i the molar intake of initiator and δ the solubility parameter.

The model provided in eq. (3) gives the best description of the experimental data:

$$\text{FD} = -1.8875 + 0.0325 n_m \delta + 0.543 \ln_i \delta + 1.6022 n_m n_i - 0.2729 n_m n_i \delta \quad (3)$$

An ANOVA for this model gives a very low P -value ($<10^{-9}$), which implies that the model is statistically significant. This is also confirmed by inspection of the residuals distribution and a normal probability plot (not reported here for brevity).²⁰ 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.

The values of the coefficients in the model imply that the FD is positively influenced by the interaction between monomer and initiator intake ($n_m n_i$), the interaction between (PCL-monomer) intake, the solubility parameter difference ($n_m \delta$) 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 Figures 5 and 6, respectively. The trends for the FD is remarkably different for both monomers. Whereas for GMA an increase in the BPO or monomer intake invariably leads to higher FD values, a clear transition is observed for DEM. At 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. The statistical model may be applied to determine the required intakes (monomer, radical initiator and PCL) for the synthesis of reactive compatibilizers with desired FD values.

Thermal properties of the reactive compatibilizers

The thermal properties (Table I and II) of the reactive compatibilizers were determined by DSC. The melting temperature and the relative enthalpy for all samples were lower than for pure PCL. The crystallization temperature and enthalpy are not a clear function of the FD values, although both properties are significantly lower than those of the virgin PCL used in the preparation. The differences in thermal properties of the reactive compatibilizers and virgin PCL may be caused by the introduction of grafts on the PCL chains. These induce irregularities and are expected to result in a lowering of the T_c and

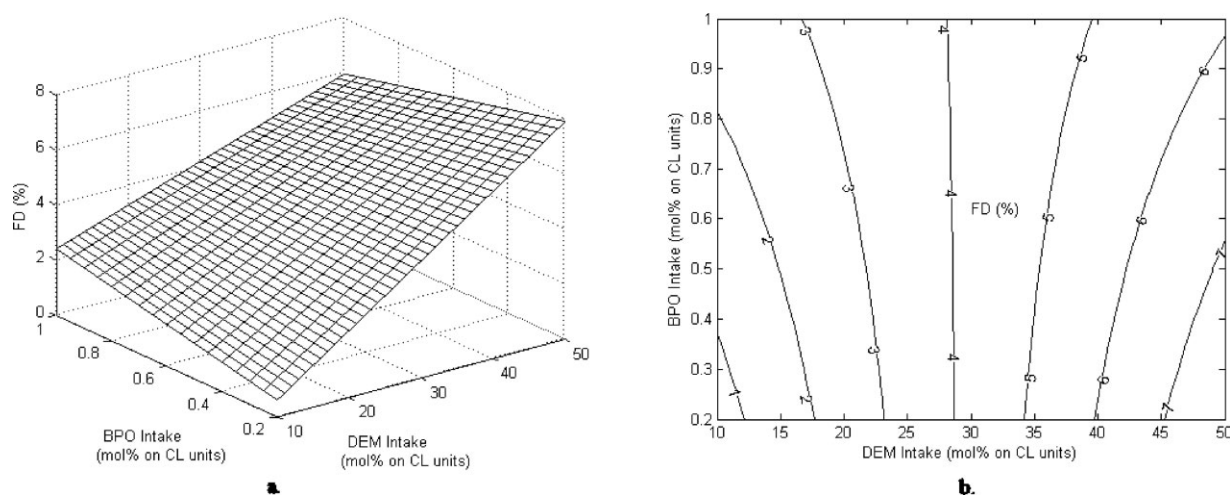


Figure 6 Graphical representation of the FD model for PCL-g-DEM. (a) 3D plot. (b) Contour plot.

the T_m . Similar observations were made by Kim et al.¹³ for PCL-g-GMA. A clear relation between the T_c and the FD value of the product is absent. This is probably the result of two concurring effects: the presence of irregularities, which is expected to lead to a T_c reduction, and enhanced nucleation of the PCL chains in the compatibilizers compared to virgin PCL (higher T_c), induced by the presence of polar groups, leading to higher T_c values.

Synthesis and properties of starch-PCL blends

The two reactive compatibilizers (PCL-g-GMA and PCL-g-DEM) were evaluated as interfacial agents in starch-PCL blends. A total of 12 blends were prepared: a series of binary blends not containing any compatibilizer (reference series), a series with PCL-g-DEM (different intakes of the latter at a fixed starch to PCL ratio) and two series with PCL-g-GMA (one with different intakes of PCL-g-GMA at a fixed starch to PCL ratio and one with a fixed com-

patibilizer intake at three different starch to PCL ratios). This experimental lay-out allows a comparisons of the thermal and mechanical properties as function of the starch content for binary blends (no compatibilizer) and blends with various intakes of PCL-g-DEM and PCL-g-GMA. An overview of all prepared blends together with their thermal and mechanical properties is given in Table III.

Binary blends of starch and PCL

For the binary blends without compatibilizers a monotonous decrease of the stress and strain at break is observed as a function of the starch intake, respectively from 16.43 MPa and 640.5% for virgin PCL up to 7.1 MPa and 341.8% for the blend with 30% of starch. The rigidity of the blends increases at higher starch contents, as in indicated by an increase in the modulus (from 270.2 MPa up to 341.8 MPa) when increasing the starch intake. This is in agreement with previous data on starch-PCL blends and is

TABLE III
Thermal and Mechanical Properties of Starch/PCL Blends^a

| Sample | σ (MPa) | ε (%) | E (MPa) | T_c (°C) | ΔH_c (J/g-PCL) | T_m (°C) | ΔH_m (J/g-PCL) |
|--------------------------|----------------|-------------------|-----------|------------|------------------------|------------|------------------------|
| PCL | 16.3 | 640.5 | 270.2 | 35 | 55 | 57 | 62 |
| S/PCL 10/90 | 15.3 | 489.5 | 321.2 | 36 | 69 | 57 | 68 |
| S/PCL 20/80 | 10.5 | 425.4 | 337.0 | 36 | 51 | 57 | 53 |
| S/PCL 30/70 | 7.1 | 230.0 | 341.8 | 36 | 40 | 57 | 43 |
| S/PCL/PCL-g-DEM 20/80/1 | 11.1 | 401.8 | 371.2 | 30 | 52 | 57 | 46 |
| S/PCL/PCL-g-DEM 20/80/2 | 10.9 | 384.9 | 342.8 | 30 | 54 | 57 | 50 |
| S/PCL/PCL-g-DEM 20/80/5 | 11.0 | 379.5 | 329.9 | 30 | 55 | 57 | 52 |
| S/PCL/PCL-g-GMA 20/80/1 | 9.2 | 357.2 | 368.3 | 29 | 53 | 57 | 51 |
| S/PCL/PCL-g-GMA 20/80/2 | 9.6 | 343.4 | 380.8 | 31 | 58 | 58 | 54 |
| S/PCL/PCL-g-GMA 20/80/5 | 11.7 | 431.6 | 372.6 | 30 | 57 | 57 | 50 |
| S/PCL/PCL-g-GMA 20/80/10 | 10.1 | 305.9 | 386.0 | 29 | 63 | 57 | 60 |
| S/PCL/PCL-g-GMA 10/90/2 | 13.6 | 424.6 | 332.0 | 28 | 54 | 58 | 51 |
| S/PCL/PCL-g-GMA 30/70/2 | 5.5 | 168.9 | 430.3 | 29 | 55 | 56 | 48 |

^a PCL-g-DEM has an FD of 1.7%, PCL-g-GMA 9.6%.

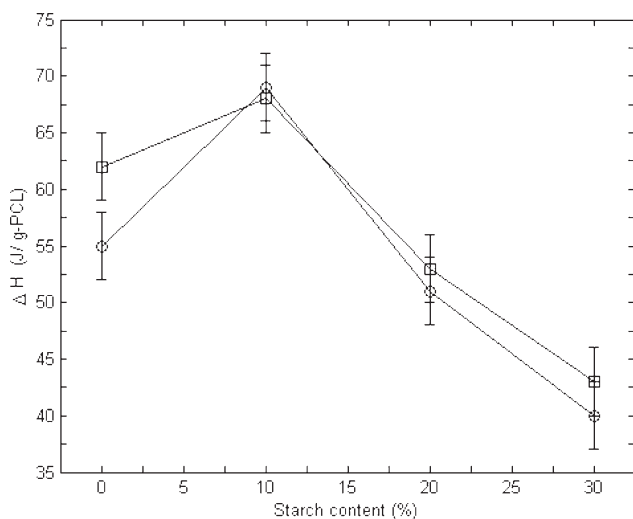


Figure 7 Melting and crystallization enthalpy as function of the starch content for binary blends with PCL. \circ : ΔH_c , \square : ΔH_m .

related to the lack of interfacial adhesion between the starch particles and the PCL matrix.¹⁸ Thermal analysis shows no significant changes in the T_m and T_c values as a function of the starch intake. However, unreported trends for the corresponding enthalpies as a function of the starch content were observed (Fig. 7). Both the ΔH_m and ΔH_c values increase when going from pure PCL to a blend with 10% starch and decrease monotonously when further increasing the starch intake. This is most probably due to a nucleation effect of the starch on the PCL matrix, as also observed for other polymer blends.²⁴

The thermal and mechanical properties indicate that starch particles have no or very limited interaction with the PCL matrix. This is visually confirmed by SEM pictures of the prepared blends (Fig. 8). It is clear that the starch particles are dispersed in the PCL matrix and that interactions (adhesion) between the two phases are actually absent. Thus, the starch particles are simply present as isolated particles in voids in the PCL matrix. The presence of these voids was also observed for sago starch-PCL blends.^{25,26}

The voids are likely formed during blend preparation due to evaporation of residual water in the starch.²⁷

Ternary blends of starch-PCL compatibilized with PCL-g-DEM

A number of starch-PCL blends with PCL-g-DEM as the reactive compatibilizer were prepared and analyzed. The thermal behavior is characterized (Table III) by constant values of the T_m while the T_c is slightly lower (30 vs. 35°C) than for virgin PCL and independent of the compatibilizer content. The latter trend is also valid for the corresponding enthalpies. Such behavior is consistent with the hypothesis that the starch particles hinder the melting and crystallization processes of the PCL chains.

To gain a better understanding of the role of the reactive compatibilizer PCL-g-DEM, the corresponding binary blend (S/PCL 20/80) constitutes a better reference point than pure PCL. The thermal properties of the binary and ternary blend are essentially similar, with the exception of the T_c , for which a 6°C drop is observed when using PCL-g-DEM. As a consequence, differences in structure between the ternary and binary blends are expected. This is confirmed by the blend morphology as determined by SEM (Fig. 9). The starch particles in the ternary blends display a smoother interface with the PCL matrix compared to the corresponding binary blends (Fig. 9). A closer inspection of the SEM pictures reveals that the starch particles are clearly embedded in the PCL matrix with almost no voids at the interface. The mechanical properties of the ternary blends differ from that of virgin PCL and the binary blends. 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 (Fig. 10). Ternary blends with 1 wt % of PCL-g-DEM have a higher modulus compared to the binary blends (Fig. 10). This may be explained by assuming a higher interfacial adhesion¹⁴ between PCL and starch when using the

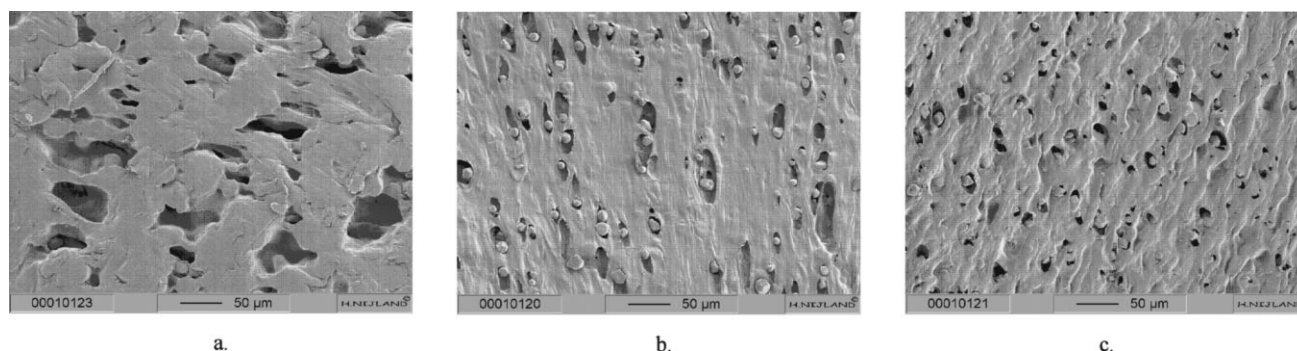


Figure 8 Morphology of starch/PCL binary blends. (a) S/PCL 10/90, (b) S/PCL 20/80, (c) S/PCL 30/70.

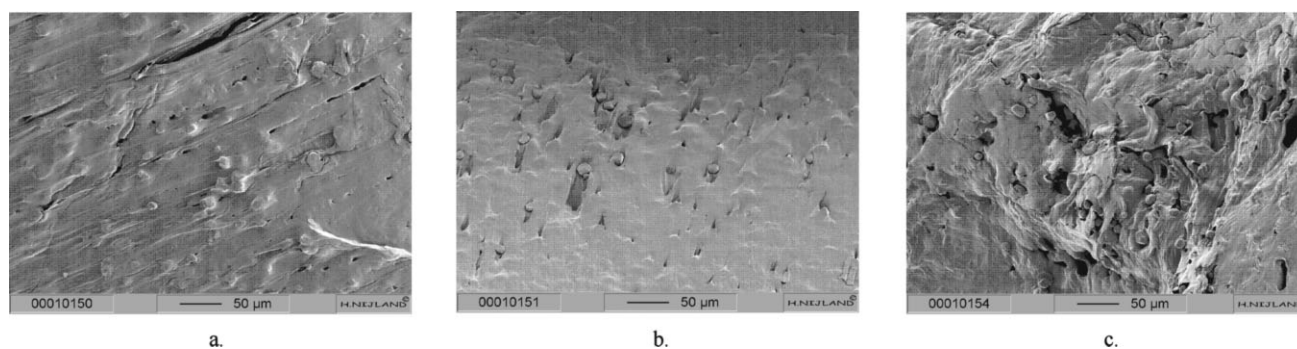


Figure 9 Morphology of ternary blends compatibilized with PCL-g-DEM. (a) S/PCL/PCL-g-DEM 20/80/1, (b) S/PCL/PCL-g-DEM 20/80/2, (c) S/PCL/PCL-g-DEM 20/80/5.

reactive compatibilizer. This will hinder the flow ability and fiber forming ability of PCL matrix under cold drawing conditions, resulting in a more rigid material with a higher modulus. At higher PCL-g-DEM intakes, the lower average molecular weight of the compatibilizer as compared to the unmodified PCL used in the blends (3000 vs. 50,000) is probably responsible for the observed decrease in the E values.

Ternary blends of starch-PCL compatibilized with PCL-g-GMA

For PCL-g-GMA two possible comparisons can be made with the available dataset: a comparison at fixed starch to PCL ratio and a variable amount of PCL-g-GMA and a comparison at different starch to PCL ratio's but with a fixed intake of PCL-g-GMA (2 wt %).

The results for the experiments with a fixed starch to PCL ratio (20–80) and a variable intake of PCL-g-GMA are very similar to those for PCL-g-DEM. The melting temperature as well as the crystallization and melting enthalpies do not change significantly (discrepancies within the experimental error). The crystallization temperature is 5–6°C lower than the corresponding binary blend. In addition, the stress and strain at break are lower than the binary blend but not a function of the PCL-g-GMA intake. Furthermore, the modulus of the ternary blends is higher than the binary system and hardly a function of the compatibilizer intake.

In contrast to PCL-g-DEM, an optimum in the modulus as a function of the compatibilizer intake is not observed. However, for all PCL-g-GMA contents, the modulus is higher than for the binary blend. As for PCL-g-DEM, this clearly indicates that PCL-g-GMA acts as compatibilizer (improved interfacial adhesion) in the blends. This hypothesis is partially and qualitatively confirmed by the morphology of the blends (Fig. 11). Here, structural features are observed (partially smooth interface between the

components, presence of voids, partial interfacial adhesion) which renders these ternary blends “intermediate” between the binary ones and those compatibilized with PCL-g-DEM. The difference in performance between PCL-g-GMA and PCL-g-DEM is surprising when taking into account the FD values: 9.8% for PCL-g-GMA versus 1.7% for PCL-g-DEM. Thus, despite a much lower FD value for PCL-g-DEM and despite the relative low reactivity of ester groups towards the starch —OH groups and nucleophilic groups in general,^{24,28,29} PCL-g-DEM is at least as good as a compatibilizer than PCL-g-GMA for blends containing 20 wt % of starch. These differences in performance of both reactive compatibilizers are not yet fully understood. However, one might speculate that the longer length of the GMA grafts compared to DEM (*vide supra*) has a negative effect on its properties. As given schematically in Figure 12 (left) the structure of PCL-g-GMA is inhomogeneous at the molecular level with poly(GMA) grafts pending from the PCL backbone. This confines all reactive GMA groups in relatively concentrated spots along the PCL backbone. As a result,

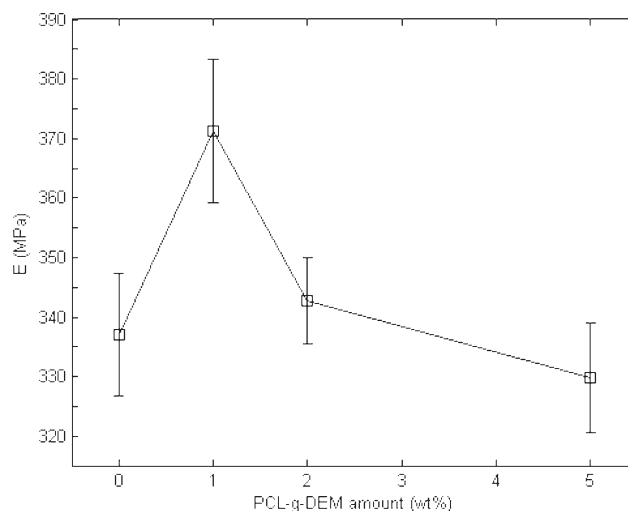


Figure 10 Modulus of ternary blends S/PCL/PCL-g-DEM as a function of the PCL-g-DEM intake.

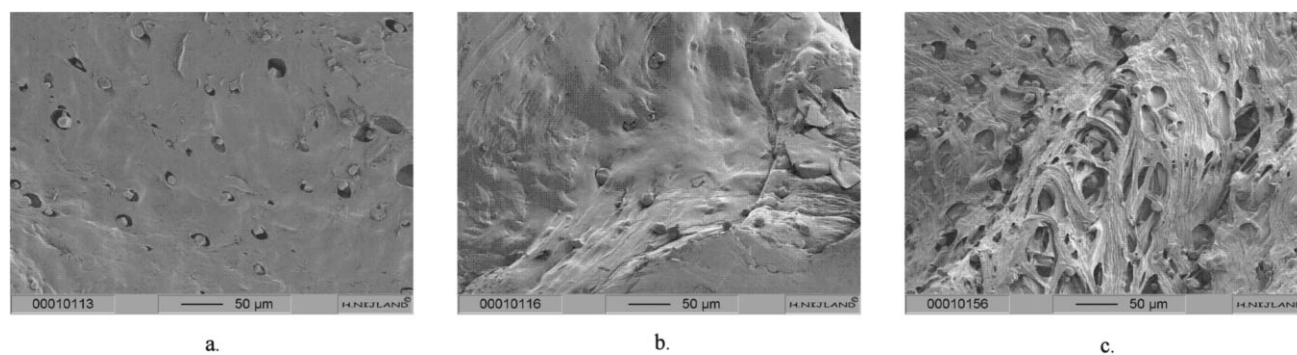


Figure 11 Morphology of ternary blends S/PCL/PCL-g-GMA. (a) S/PCL/PCL-g-GMA 20/80/1, (b) S/PCL/PCL-g-GMA 20/80/2, (c) S/PCL/PCL-g-GMA 20/80/3.

reaction of PCL-g-GMA with one of the -OH groups on the surface of the starch particles will render the remaining GMA groups less accessible for further reaction with other starch -OH groups.

PCL-g-DEM has a lower amount of reactive groups (lower FD) available for reaction than PCL-g-GMA (right of Fig. 12). However, as DEM is preferentially present as a graft with one DEM unit, the distribution of the reactive group along the PCL backbone is more "homogeneous". As a consequence, once PCL-g-DEM has reacted with a starch -OH group, other DEM groups will presumably remain available (arrows in Fig. 12) for further reaction.

The proposed explanation implies that at relatively higher starch contents (>20 wt %) the segregation of the poly(GMA) chains in "isolated" spot along the PCL backbone would be less important. At higher starch contents more -OH groups are available for reaction with the GMA groups, thus attenuating the effect discussed earlier. To check this hypothesis, blends with the same intake of PCL-g-GMA (2 wt %) but with different starch intakes (10, 20, and 30 wt % respectively) were prepared and the properties were compared. When considering the thermal behavior (Table III), it is observed that the T_c decreases compared to the corresponding binary blends while all other properties (T_m and enthalpies) remain virtually unchanged. Moreover, for all starch intakes, the stress and strain at break decrease. The modulus is constant at low starch contents and increases signifi-

cantly for starch-PCL blends with 30 wt % starch. The latter clearly indicates that the efficiency of the PCL-g-GMA as a compatibilizer is improved considerably at higher starch intakes (>30 %).²⁵ This is in agreement with the hypothesis made above (Fig. 12) which relates 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 adjusting the blend composition.

Conclusions and outlook

A systematic study, including statistical modeling, has been performed on the synthesis of two reactive compatibilizers, PCL-g-GMA and PCL-g-DEM. A statistical model has been developed which quantifies the effects of process variables (monomer and initiator intake) and the type of reactive compatibilizer on the FD adequately ($R^2 = 0.957$, P -value $\leq 10^{-9}$). The most important variable for the product FD is the interaction between the amount of monomer and initiator used. This represents an unreported mathematical confirmation that these 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 than virgin PCL.

The reactive compatibilizers were used in blends of starch and PCL. At a fixed starch content (20 wt %) PCL-g-DEM seems to have a better compatibilizing effect than PCL-g-GMA as shown by blend morphologies and the elasticity modulus. This is in contrast with the chemical reactivity and the amount of chemical groups along the PCL backbone, which are both favorable for GMA. The results may be explained on the basis of the distribution of the reactive groups along the reactive compatibilizer backbone, which is less uniform for GMA. The

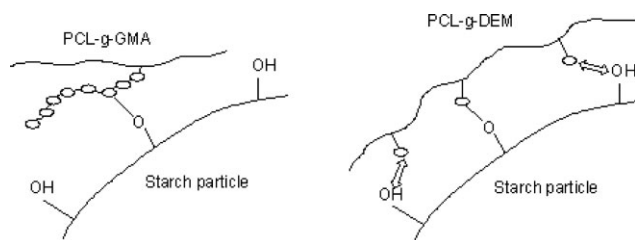


Figure 12 Schematic representation of the reaction between functionalized PCL and starch.

hypothesis is indirectly confirmed by the observation that PCL-g-GMA becomes more efficient as a compatibilizer at relatively higher starch intakes. From a more practical point of view it can be concluded that the novel PCL-g-DEM compatibilizer can replace PCL-g-GMA as compatibilizer at relatively low starch contents.

Blends of PCL and starch are known to have application potential as biodegradable material in the packaging industry. Examples are for the production of sheets and films (with end products such as shopping bags, wrapping films and paper lamination) and for agricultural purposes (for instance mulch films).^{30,31} The results presented in this article imply that reactive compatibilizers in general and PCL-g-DEM in particular have potential to improve the product properties of starch-PCL blends. However, further research activities are required to assess the full potential of these compatibilizers. From a purely scientific point of view, a better knowledge of the influence of the topological features of the compatibilizers (distribution of reactive groups) on product properties is of prime importance for a better understanding and tuning of reactive compatibilization processes. From an application point of view, an economic assessment on the costs of the reactive compatibilizers and advanced product testing (including the use of common plasticizers and other additives) are required before its commercial value can be estimated.

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