

Improving the mechanical properties of fatty acid starch esters

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The novel use of sago starch and vinyl laurate in densified carbon dioxide increases the reactivity of esterification and produces final products that have higher degrees of substitution.

As the global demand for plastics continues to grow, it is becoming increasingly important to produce biodegradable plastics, particularly from sustainable and renewable resources. Although starch—a natural biopolymer—is an abundant raw material, its use for the production of biodegradable plastics is limited^{1,2} because of its brittleness, low hydrophobicity, and low mechanical strength.^{3–5} These problems can be overcome, however, through chemical modification of the starches (i.e., to obtain a thermoplastic). For example, fatty acid starch esters are thought to be viable candidates as biodegradable and renewable thermoplastic materials.⁶ These materials are commonly synthesized by reacting starch with various fatty acid ester precursors, including fatty acid chlorides, fatty acid vinyl esters (FAVEs), or fatty acid methyl esters (FAMEs) in a variety of organic solvents (e.g., toluene, pyridine, or dimethyl sulfoxide).^{1,6–8} There are, however, some problems associated with this process. That is, the use of the organic solvents has a detrimental environmental impact and the product work-up is often cumbersome.^{1,9}

As an alternative to the use of organic solvents, for the past 12 years, we have been investigating the application of supercritical carbon dioxide (CO₂) in the starch modification process. CO₂ is a ‘green’ solvent with several desirable properties, i.e., it is non-flammable, relatively non-toxic, inert, and can be easily separated from reaction mixtures by simple depressurization (thus simplifying the product work-up).⁹ In addition, CO₂ has a plasticizing effect on starch matrices. Swelling, and then gelatinization of the starch, are thus induced, which helps the diffusion of the reagent within the starch granules upon reaction.^{9,10} We have previously demonstrated successful transesterification of potato starch with FAVE, FAME, and fatty acid anhydride using various alkaline base salts as the catalyst in densified CO₂ (i.e., CO₂ in a range of conditions, from subcritical to supercritical).⁹ Our products, however,

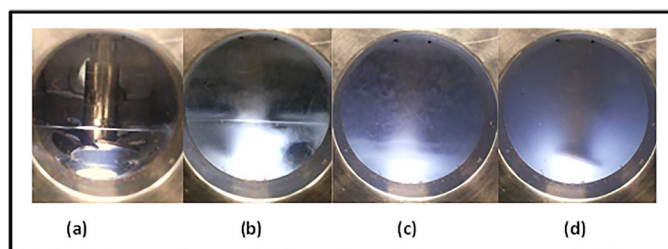


Figure 1. Photographs of the high-pressure view-cell reactor containing vinyl laurate–carbon dioxide (VL–CO₂) mixtures at 100°C and at pressures of (a) 16MPa, (b) 20MPa, (c) 22MPa, and (d) 23MPa. The mixture changes from a gas/liquid (a, b) to a monophasic phase (c, d) with increasing pressure.

had a relatively low degree of substitution, DS (0.01–0.3), which gave rise to non-optimal mechanical properties.⁹

In this work,¹¹ we have thus explored the use of sago starch and vinyl laurate as novel starch esters and reagents, respectively. In particular, we aimed to increase the reactivity of our esterification process and we targeted higher-DS final products.¹¹ Indeed, we chose sago starch for this work because it has been shown to have a higher reactivity with FAME than potato starch.¹² In our systematic study we have examined the influence of several process variables on the DS of our products and we have performed a number of experiments, at different temperatures and pressures, to understand the phase behavior of the ester–solvent mixture during the reaction.¹¹

In the first part of our phase behavior study, we used a high-pressure view-cell reactor to determine the critical point of our VL–CO₂ mixtures. As illustrated in Figure 1, we observed phase changes in the mixture (at a temperature of 100°C) as the pressure increased. Indeed, with increasing pressure, the mixture changed from a gas/liquid VL–CO₂ phase—see Figure 1(a) and (b)—to a monophasic (supercritical) phase: see Figure 1(c) and (d). At this temperature, we find that the critical pressure occurs at about 22MPa. In addition, the critical parameters (i.e., temperature and pressure) of the binary VL–CO₂ mixtures

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Table 1. The effect of pressure (*P*) on the degree of substitution (*DS*) for three final products. These results were obtained at a temperature (*T*) of 100°C and with VL and potassium carbonate (catalyst) intakes of 5 and 0.1 mol/mol anhydroglucose unit, respectively.

T (°C)	P (MPa)	Reaction time (hours)	DS
100	8	3	0.88
100	10	3	0.97
100	20	3	0.74

are higher than those of pure CO₂ (which has a critical temperature and pressure of 31°C and 7.38MPa, respectively). Our determination of the critical point at different temperatures (50 and 120°C) also reveals an increase in the critical pressure with temperature.

In our experiments we also evaluated the influence of important process variables on the DS of our final products (which ranged from 0.06 to 0.97).¹¹ Specifically, we examined the role of pressure, temperature, the particular alkaline catalyst (sodium acetate, sodium sulfate, or potassium carbonate), and the catalyst intake. We conducted these tests under a range of conditions, to include both the subcritical and near-critical regimes (8–20MPa). In particular, to determine the effect of pressure on the DS, we performed the tests at a constant temperature of 100°C, a VL intake of 5mol/mol anhydroglucose unit (AGU), and a potassium carbonate intake of 0.1mol/mol AGU. From our results (see Table 1), it is clear than the optimum DS (0.97) occurred at 10MPa, which is in the subcritical region and is in agreement with previous results.⁹ We can explain these findings by the presence of opposite, i.e., plasticizing and compressive, effects at elevated pressure.^{9,13}

In summary, we have demonstrated the potential application of sago starch and VL for the esterification reaction of CO₂. In this way, it is possible to produce fatty acid starch esters with higher DS values than has previously been possible. Indeed, by fine-tuning the experimental conditions, we have obtained final products with relatively high DS values (up to 0.97). We have also examined how substantial changes to important properties (including morphology and thermal characteristics) influence the final products. In our future work we plan to make an in-depth process and product study of this esterification reaction, and to thus provide the necessary overview of the whole process–product relationship.

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