Carbamation of Starch with Amine Using Dimethyl Carbonate as Coupling Agent

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Supporting Information

ABSTRACT: A one-pot coupling of starch with alkyl amine was studied using dimethyl carbonate (DMC) as the coupling agent. Although reaction occurred without a catalyst (24 h, 70 °C), different catalysts, namely, imidazole, tetramethylguanidine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and combinations thereof were investigated to improve the reaction efficiency. When 20 mol % DBU was used as a catalyst, the degree of substitution (DS) could be improved from 0.05 to 0.15 compared to the noncatalyzed reaction. When the amount of DBU was decreased to 5 mol %, catalytical activity remained, albeit with a slightly lower DS (0.09). Temperature did not have a significant effect on the DS but it could be used to alter the solubility of the product. Based on chemical analysis, the alkyl group was attached to starch by the formation of a carbamate group. As the carbonyl carbon in the carbamate originated from DMC, which, in turn, can be produced from carbon dioxide on an industrial scale, the current study provides a conventional way to utilize carbon dioxide-based chemicals in the functionalization of a natural polymer. DMC is also biodegradable and classified as a nonvolatile organic component, making it an environmentally desirable coupling agent.

INTRODUCTION

Nonrenewable resources have long been the main source for chemicals and materials utilized in science and industry. Due to concerns about the depletion of nonrenewable resources, along with their possible toxic and polluting properties, a significant amount of research has been focused on the use of renewable materials instead. Natural polymers are among the most promising renewable sources for the production of green chemicals and materials. Natural polymers, such as polysaccharides, can be utilized in their natural form, for example, in the paper and pulp industry, or they can be converted into monomeric chemicals by hydrolysis.1−4 Natural polymers can also be converted into semisynthetic polymers by chemical modification.5−7 Chemical modifications are generally intended to improve inherited properties of natural polymers, such as poor water tolerance, low solubility, and thermoformability.

As a natural polysaccharide, starch is one of the most investigated renewable raw materials to be used as a replacement for oil-based sources, for example, in films8 and composite materials.9 Similar to cellulose, starch is a glucose polymer with abundant hydroxyl groups that can be used in chemical modification to produce a bio-based material. Applications of chemically modified starch include as flocculant10 and a wet-end additive in papermaking,11,12 a carrier for drug delivery,13,14 and a tissue engineering scaffold,15 among others. Although starch is largely present in food sources and its use in nonfood applications is not entirely ethical, it is also widely available from many waste16,17 and nonedible resources.18,19 The utilization of starch from waste and nonfood materials is potentially more desirable ethically and more sustainable ecologically and environmentally.20

Starch has naturally high hygroscopicity and low thermoformability, and various chemical modifications have therefore been employed to improve these properties. For example, grafting with a long carbon chain can be used to invert the polarity of starch, and hydrophobic material has been obtained through methods such as etherification, esterification, and amidation. Although many of these methods have good efficiency, they require the use of toxic and hazardous chemicals (e.g., halogenated alkyls for etherification21 and acyl chlorides for esterification22) and multistep reactions (e.g., amidation of succinylated23 or carboxylated24 starch). Consequently, there is a demand for more environmentally friendly methods of starch alkylation.

Recently, alkyl carbonate esters have been studied for the alkylation of polysaccharides, including cellulose25,26 and starch.27 Alkyl carbonates, such as dimethyl carbonate (DMC), are formally esters of carbonic acid, although they are traditionally produced using chemicals such as phosgene. Lately, replacing the highly toxic phosgene has been investigated, and alkyl carbonates have been produced using carbon monoxide.28,29 An even more desirable route is the production of alkyl carbonates directly from carbon dioxide; DMC, for example, can be produced from carbon dioxide and methanol.

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The chemical modification of starch was performed using OA as the alkyl amine, DMC as the coupling agent, and dimethyl sulfoxide (DMSO) as the solvent. Without a catalyst, a DS of 0.05 could be obtained (Table 1). It is postulated that the reaction took place via the formation of methyl octyl carbamate between the DMC and the OA, which were used in a molar ratio of 1:1, followed by reaction with the starch to form starch alkyl carbamate (Scheme 1a). Two moles of methanol are formed as a byproduct. A similar, albeit two-step, reaction has been previously utilized in the synthesis of natural-based polyurethanes.34 Another possible reaction mechanism is the formation of starch methyl carbonate, which then reacts with the OA. Either way, nucleophilic substitution reactions of carbonate ester are catalyzed many times by the base catalyst.35,36

To improve the relatively low DS obtained without a catalyst, three different basic catalysts, namely, imidazole, TMG, and DBU, were utilized. In addition, stoichiometric mixtures of imidazole and either TMG or DBU were studied as protic ionic liquid catalysts.37,38 When using imidazole, the DS of the product could be nearly doubled from 0.05 to 0.09. Further improvement was observed using TMG (DS = 0.13), and the highest was obtained using DBU (DS = 0.15). On the other hand, the addition of imidazole together with TMG or DBU showed no increase in the DS. DS obtained with OA and DMC is similar or even slightly higher than that obtained by the alkylation of starch nanocrystals with long alkyl ch Lauran acid anhydride.39

In the literature, DBU is a well-known catalyst, for example, in the transesterification of organic carbonates. A possible catalytic mechanism in the DBU-catalyzed alkylation of starch is presented in Scheme 1b. The reaction involves the lone pair of the DBU attacking the carbonyl carbon of the DMC, resulting in the formation of a highly reactive intermediate.40,41 This activated carbonate then reacts with the amine group of the OA to produce methyl octyl carbamate. It is possible that similar activation of the methyl octyl carbamate is then repeated. Activated octyl carbamate then reacts with the starch to form starch carbamate. DBU, as a strong base, can also improve reaction efficiency by deprotonating hydroxyl groups in the starch, leading to the formation of starch alkoxide, which is highly reactive in nucleophilic reactions.42

■ RESULTS AND DISCUSSION

To investigate if the presence of nitrogen in the product was indeed due to the carbamation of the starch, the reaction was also performed catalytically (with DBU) using just DMC (sample 7 in Table 1) and just OA (sample 8), and without either chemical (sample 9). No nitrogen was observed in these cases, indicating that both DMC and OA are needed for the alkylation of starch.

The effect on the DS of the molar ratio of DBU was further investigated. A small DS decrease from 0.15 to 0.11 was observed when the catalyst loading was decreased from 20 to 15 mol%. On the other hand, DS remained at 0.11 when a catalyst loading of 10 mol% was used; a minimal decrease in nitrogen

Table 1. Catalysts and Temperatures Used During the Alkylation of Starch, and Nitrogen Content, DS of Carbamate Groups, and Mass Recovery of the Product

| sample | catalyst (mol %) | temperature (°C) | nitrogen content (%) | DS | mass recovery (g) |
|--------|----------------|----------------|---------------------|----|-----------------|
| 1      | imidazole      | 70             | 0.40 ± 0.007        | 0.05 ± 0.002 | 0.41         |
| 2      | imidazole      | 70             | 0.72 ± 0.014        | 0.09 ± 0.002 | 0.43         |
| 3      | TMG            | 70             | 0.97 ± 0.028        | 0.13 ± 0.001 | 0.43         |
| 4      | DBU            | 70             | 1.16 ± 0.028        | 0.15 ± 0.004 | 0.43         |
| 5      | DBU            | 70             | 0.99 ± 0.085        | 0.13 ± 0.004 | 0.43         |
| 6      | DBU            | 70             | 1.15 ± 0.042        | 0.15 ± 0.006 | 0.42         |
| 7      | 0              | 70             | 0                   | 0.45         |
| 8      | 0              | 70             | 0                   | 0.38         |
| 9      | 0              | 70             | 0                   | 0.4          |
| 10     | 0              | 70             | 0.89 ± 0.014        | 0.11 ± 0.002 | 0.41         |
| 11     | 0              | 70             | 0.84 ± 0.021        | 0.11 ± 0.003 | 0.47         |
| 12     | 0              | 70             | 0.72 ± 0.014        | 0.09 ± 0.002 | 0.45         |
| 13     | 0              | 100            | 0.65 ± 0.028        | 0.08 ± 0.004 | 0.43         |
| 14     | 0              | 90             | 0.74 ± 0.028        | 0.09 ± 0.004 | 0.46         |
| 15     | 0              | 80             | 0.73 ± 0.014        | 0.09 ± 0.002 | 0.44         |
| 16     | 0              | 60             | 0.72 ± 0.007        | 0.09 ± 0.001 | 0.4          |

"Reaction time in all of the samples was 24 h. 6S 5 wt % starch solution in DMSO with 6 times molar excess of both OA and DMC compared to starch. 70.5 g of starch was used as the starting material. 8Without OA. 9Without DMC. 10Without OA and DMC."
content was observed at 10 mol % compared to that at 15 mol %. In addition, the DS at a catalyst loading of 5 mol % was still higher compared to the reaction without a catalyst (0.09 vs 0.05).

Temperature had a minimal effect on the DS, and only a slightly lower DS was obtained when the reaction temperature was increased from 70 to 90 °C, decreasing from 0.11 to 0.09. A further increase in temperature to 100 °C resulted in a decrease of the DS from 0.09 to 0.08. At the high temperature, DMC is present in the gas phase of the reaction system, leading to lower reaction efficiency at high temperature. The reaction temperature, however, had an effect on the reaction mixture; at temperatures of 70 °C and lower, a gel-like material was obtained after the reaction, most likely due to the poor solubility of the product in the reaction mixture. In contrast, when a reaction temperature of 80 °C or higher was used, the reaction mixture was a clear, colorless solution. This difference resulted in slightly different dissolution behavior of the product as the sample obtained at 80 °C was slightly soluble in pure DMSO, whereas other samples remained nonsoluble. This difference in solubility might be due to the different substitution patterns of the product obtained at 80 °C compared to that of other samples. However, further studies are requested to confirm this.

Diffusion reflectance infrared Fourier transform (DRIFT) spectroscopy provided further insight into the reaction mechanism. When the reaction was performed in the absence of both OA and DMC, no apparent chemical changes were observed (Figure 1). In addition, in the presence of OA but in the absence of DMC, the product spectrum remained similar to that of pristine starch. On the other hand, with DMC but without OA, a strong carbonyl vibration band was observed at a wavenumber of 1760 cm$^{-1}$. This band is between cyclic (1790 cm$^{-1}$) and linear (1745 cm$^{-1}$) carbonate esters,$^{43}$ indicating that both are formed by the reaction of DMC with starch (Scheme 1c). This is in contrast with previous results where methylation of the starch has been observed after its reaction with DMC.$^{27,33}$ However, linear carbonate esters of cellulose have been produced in homo-$^{25}$ and heterogeneous$^{44}$ reactions of DMC and other acyclic carbonates. The results here indicate that DMC is the main requisite for a chemical reaction to take place.

Scheme 1. Schematic Illustration of a Possible Reaction Mechanism in the Alkylation of Starch with OA by DMC (a), the Catalytic Activation of DMC with DBU (b), Formation of Acyclic and Cyclic Starch Carbonate in the Absence of OA
In the presence of both OA and DMC, two new distinct peaks were observed at 1702 and 1534 cm$^{-1}$. These peaks are assigned to the carbonyl stretching and the NH deformation bands of the carbamate group, respectively.$^{45,46}$ The DRIFT results strongly indicate that the alkylation of starch took place via DMC-mediated amine coupling to form carbamate linkage between the OA and the starch.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to further support the observations based on DRIFT. Only the peaks relating to carbon (Figure 2) and oxygen (Figure S1 in the Supporting Information) were observed in the pristine starch. Carbon peaks at binding energies of 286.4 and 287.7 eV are associated with the C–O and O–C–O bonds, respectively. The C–C/C–H bond peak was observed at a binding energy of 284.8 eV. When starch was allowed to react with OA in the absence of DMC, no nitrogen was observed in the XPS spectrum. In addition, the only observable change in the XPS spectra was a decrease in the intensity of the C–C/C–H bond peak at 284.8 eV. This can be attributed to the removal of impurities that exist in natural starch.$^{47}$

When starch was allowed to react with DMC in the absence of OA, a new peak was observed in both carbon and oxygen XPS spectra. The peaks at binding energies of 290.7 eV$^{44}$ (Figure 2) and 534.2 eV$^{48}$ (Figure S1) are related to the carbonate ester moiety. This further confirms the formation of starch carbonate when starch reacts with DMC in the absence of amine.

When both DMC and OA are presented in the reaction, no carbon peaks relating to carbonate ester were observed. Instead, new carbon peaks were seen at a binding energy of 289.6 eV, relating to the carbonyl carbon in the carbamate group (O–CO–N).$^{49,50}$ The intensity of the peak relating to the C–C/C–H bond was observed to be higher compared to that of the sample prepared without DMC (i.e., regenerated starch), indicating the presence of an alkyl chain. Most importantly, and in contrast to other XPS spectra, a nitrogen peak was observed at a binding energy of 400.0 eV (Figure S2). The presence of these peaks supports the observations from the elemental analysis and DRIFT measurements that OA is coupled with starch via carbamate formation. Based on XPS, nitrogen content was found to be slightly lower compared to elemental analysis (0.8 vs 1.12 mmol/g). This difference is most likely due to the measurement techniques as the elemental analysis is a bulk method, whereas XPS only analyzes the surface of a sample.

Due to the partial solubility of the sample produced at 80 °C (Table 1, sample 15, DS 0.09) in DMSO-$d_6$, it was characterized using $^1$H and $^{13}$C NMR (Figure 3). The proton assignment of a starch moiety corresponds to the previous assignments.$^{51}$ The signals of OH protons at positions 2, 3, and 6 together with proton H-1 can be seen between 4.57 and 5.49 ppm. Also, the characteristic peaks of protons H-3 and H-5 can be clearly found at 3.65 and 3.58 ppm, respectively. The signals of protons H-2,
H-4, and H-6 cannot be assigned due to overlapping H2O signal. The successful attachment of an octyl carbamate to the starch was also confirmed by the nuclear magnetic resonance (NMR) spectra. The signal at 0.86 ppm in 1H NMR (a peak in Figure 3A) relates to a CH3 group in the octyl chain, and the signals at 1.24 and 1.39 ppm (peaks b and c) can be assigned to six CH2 groups within the octyl chain. The CH2 group closest to the nitrogen atom (peak d) is observed at 2.95 ppm, and most
importantly, a weak amide proton signal can be seen at around 7 ppm.52 The degree of substitution (DS) was determined using the following equation:

\[
DS = \frac{4A}{3B + A}
\]

where \(A\) is the integral value of methyl protons of the octyl chain and \(B\) is the integral value of proton H-1 and OH protons at positions 2, 3, and 6. Based on the integration of the \(^1\)H NMR spectrum, the DS of sample 15 is 0.090, which corresponds to the DS value received from elemental analysis (Table 1). The assignment of carbon atoms (C1–6) of the starch backbone (Figure 3B) corresponds to the previous assignments.53 The assignment of carbon atoms (C1′–8′) of octyl chain is also presented in Figure 3B. However, the signal of carbon atom C8′ next to the nitrogen stands underneath the DMSO peak.52 The signal of the carbonyl carbon could not be observed, most likely due to its long relaxation time.53

Previously, very high DS (around 3) of short carbon chain carbamate has been obtained.56 However, previous studies have utilized very hazardous isocyanates as reagents.56,57 Thus, the current study can be seen as a sustainable method to obtain starch carbamate when low DS is desired. The low DS in the current study might originate from the low solubility of octyl carbamate starch in the reaction mixture. In addition, cross-linking of starch with DMC might take place. However, as the reaction mixture remained clear (no formation of gel) when the DMC was used without OA, the amount of cross-linking might be negligible. It is notable that DS obtained here is higher than alkyl starch having carbon chain lengths of 6 and 10 produced using alkyl epoxide.58

The hydrophobization of starch due to the addition of a long alkyl chain is apparent in Figure 4. Directly after mixing with water, the starch became a cloudy suspension, while starch octyl carbamate remained on the water’s surface. After intensively mixing at 90 °C for 1 h, the starch suspension became more gel-like; starch is known to gelatinize or even dissolve in water. On the other hand, the starch octyl carbamate could not be efficiently dispersed in water as some of the material remained on the surface of the liquid, while the rest sank to the bottom of the container. In this case, the water layer remained more or less clear. This indicates that the introduction of long alkyl chains on starch significantly alters the hydrophilicity of the material and, therefore, its interaction with water.

The starch octyl carbamate produced here could only be dissolved in DMSO. Although the low solubility of products can restrict their usability in many applications, hydrophobized starch particles could, for example, be used to produce a Pickering emulsion. Hydrophobized microcrystalline cellulose has been studied for the production of an emulsion between water and toluene.59 Moreover, it is also envisioned that further optimization of reaction efficiency could be used to improve the DS, which could then lead to better dissolution of the product.

In addition to the use of DMC as a coupling agent, carbon dioxide could be an even more sustainable reagent for starch carbamation. Several studies have been conducted for the direct use of carbon dioxide for the synthesis of alkyl carboxylates from amines. However, instead of the use of alcohols, titanium60,61 or silicate62–64 esters have been used in these reactions.

## CONCLUSIONS

Starch was alkylated with long-chain alkyl amine using DMC as a coupling reagent. The use of basic catalysts improved the DS, and the highest reaction efficiency was obtained using DBU as the catalyst. Reaction temperature did not have a significant effect on the DS of alkylated starch; however, the use of different temperatures could be used to alter the dissolution of the product. The alkylation of the starch method introduced here can be seen as environmentally friendly because DMC is biodegradable and not classified as a volatile organic component. Furthermore, DMC can be produced from carbon dioxide, and this method could therefore be seen as a way to utilize waste carbon dioxide-based chemical for the modification of natural polymers. Further studies should be conducted to improve the DS of the product and to investigate the possible applications of starch carbamate.

## MATERIALS AND METHODS

**Materials.** Starch from wheat, OA (99%), TMG (99%), DBU (98%), and deuterated dimethyl sulfoxide (DMSO-d_6; 99.9 atom % D) were obtained from Sigma-Aldrich (Germany); dimethyl sulfoxide (DMSO; ≥99.5%) and ethanol from VWR (Finland); and DMC (>98.0%) and imidazole (>98.0%) from TCI (Belgium). All chemicals were used as received, without further purification.

**Chemical Modification of Starch.** A reaction bottle was charged with 0.5 g of starch, 9.5 g of DMSO, 1.56 mL (18 mmol) of DMC, 3.06 mL (18 mmol) of OA, the desired amount (0–0.15 mol %) of a catalyst (imidazole, TMG, or DBU), and a magnetic stirring bar. The reaction vessel was closed with a Teflon cap, placed in a heating block at a predetermined temperature (60–100 °C), and allowed to react for 24 h under stirring in a closed system. After reaction, the mixture was poured into 100 mL of ethanol under vigorous stirring. The precipitated product was filtrated and washed with 500 mL of ethanol in 100 mL portion and, finally, dried in a 60 °C oven overnight. Reference reaction was conducted using both DMC or OA alone and without either of them. All of the used reaction conditions are presented in Table 1.

**Elemental Analysis.** The degree of substitution (DS) of the products was determined by analyzing their nitrogen content with an elemental analyzer (PerkinElmer 2400 Series II CHNS/O). The DS was calculated using the following equation

\[
DS = \frac{4A}{3B + A}
\]
where N is the percentage of nitrogen, 162.15 is the molecular weight of the anhydroglucose unit of starch, 157.24 is the molecular weight of the octyl carbamate group, and 1401 is the atomic weight of nitrogen multiplied by 100.

Chemical Characterization. Chemical characterization of the starch and the alkylated starch was performed using diffusion reflectance Fourier transform (DRIFT) infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR) spectroscopy. DRIFT spectra were collected from the dried samples with a Bruker Vertex 80v spectrometer. The spectra were obtained in the 600–4000 cm⁻¹ range, and 40 scans were taken from each sample at a resolution of 2 cm⁻¹.

XPS was performed using a Thermo Fisher Scientific ESCALAB 250Xi (U.K.) equipped with a monochromatic Al Kα X-ray source, operated at 300 W with a combination of electron flood gun and ion bombarding for charge compensation. The take-off angle was 45° in relation to the sample surface. The low-resolution survey scans were taken with a 1 eV step and a 100 eV analyzer pass energy, and high-resolution spectra were taken with a 0.1 eV step and a 20 eV analyzer pass energy. All measurements were performed in an ultrahigh vacuum chamber (5·10⁻⁶ mbar). Prior to measurement, each dry sample was pressed onto indium film.

Prior to the NMR measurements, samples were dissolved in DMSO-d₆ at 90 °C. The samples were placed in 5 and 10 mm NMR tubes, and the ¹H and ¹³C NMR spectra were recorded using a Bruker Ascend 400 MHz spectrometer at ambient temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02350.

High-resolution spectra of O 1s regions: starch, starch treated with OA, starch treated with DMC, and starch treated with OA and DMC (Figure S1); and high-resolution spectra of N 1s region of starch treated with OA and DMC (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Ruppert, A. M.; Weinberg, K.; Palkovits, R. Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals. Angew. Chem., Int. Ed. 2012, 51, 2564–2601.
(2) Sun, Y.; Cheng, J. Hydrolysis of Lignocellulosic Materials for Ethanol Production: A Review. Bioresour. Technol. 2002, 83, 1–11.
(3) Pandey, M. P.; Kim, C. S. Lignin Depolymerization and Conversion: A Review of thermochemical Methods. Chem. Eng. Technol. 2011, 34, 29–41.
(4) Hu, L.; Lin, L.; Wu, Z.; Zhou, S.; Liu, S. Chemocatalytic Hydrolysis of Cellulose into Glucose over Solid Acid Catalysts. Appl. Catal., B 2015, 174–175, 225–243.
(5) O’Connell, D. W.; Birkinshaw, C.; O’Dwyer, T. F. Heavy Metal Adsorbents Prepared from the Modification of Cellulose: A Review. Bioresour. Technol. 2008, 99, 6709–6724.
(6) Li, X.; Tabl, L. G.; Panigrahi, S. Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. J. Polym. Environ. 2007, 15, 25–33.
(7) Masina, N.; Choonara, Y. E.; Kumar, P.; du Toit, L. C.; Govender, M.; Indermun, S.; Pillay, V. A. Review of the Chemical Modification Techniques of Starch. Carbohydr. Polym. 2017, 157, 1226–1236.
(8) Luchese, C. L.; Spada, J. C.; Tessaro, I. C. Starch Content Affects Physicochemical Properties of Corn and Cassava Starch-Based Films. Ind. Crops Prod. 2017, 109, 619–626.
(9) Adamus, J.; Spychaj, T.; Zdanowicz, M.; Jędrezejewski, R. Thermoplastic Starch with Deep Eutectic Solvents and Montmorillonite as a Base for Composite Materials. Ind. Crops Prod. 2018, 123, 278–284.
(10) Pal, S.; Mal, D.; Singh, R. P. Cationic Starch: An Effective Flocculating Agent. Carbohydr. Polym. 2005, 59, 417–423.
(11) Nachtegaele, W. The Benefits of Cationic Starches for the Paper Industry. Starch 1989, 41, 27–31.
(12) Chen, X.; Souvannhthong, B.; Wang, H.; Zheng, H.; Wang, X.; Huo, M. Polyoxometalate-Based Ionic Liquid as Thermoregulated and Environmentally Friendly Catalyst for Starch Oxidation. Appl. Catal., B 2013, 138–139, 161–166.
(13) Tuovinen, L.; Peltonen, S.; Liikola, M.; Hotakainen, M.; Lahtela-Kakkonen, M.; Poso, A.; Järvinen, K. Drug Release from Starch-Acetate Microparticles and Films with and without Incorporated α-Amylese. Biomaterials 2004, 25, 4355–4362.
(14) Paleos, C. M.; Sideratou, Z.; Tsiorvias, D. Drug Delivery Systems Based on Hydroxyethyl Starch. Bioconjugate Chem. 2017, 28, 1611–1624.
(15) Malafaya, P. B.; Silva, G. A.; Reis, R. L. Natural–Origin Polymers as Carriers and Scaffolds for Biomolecules and Cell Delivery in Tissue Engineering Applications. Adv. Drug Deliver. Rev. 2007, 59, 207–233.
(16) Wu, D. Recycle Technology for Waste Residue in Potato Starch Processing: A Review. Procedia Environ. Sci. 2016, 31, 108–112.
(17) Lappalainen, K.; Kärkkäinen, J.; Joensuu, P.; Lajunen, M. Modification of Potato Peel Waste with Base Hydrolysis and Subsequent Cationization. Carbohydr. Polym. 2015, 132, 97–103.
(18) Patil, N. V.; Ntrakvalli, A. N. Microfibrillated Cellulose-Reinforced Nonedible Starch-Based ThermoSET Biocomposites. J. Appl. Polym. Sci. 2016, 133, No. 43803.
(19) Patil, N. V.; Ntrakvalli, A. N. Nonedible Starch Based “Green” ThermoSET Resin Obtained via Esterification Using a Green Catalyst. ACS Sustainable Chem. Eng. 2016, 4, 1756–1764.
(20) Hernoux-Villière, A.; Lassi, U.; Hu, T.; Paquet, A.; Rinaldi, L.; Cravotto, G.; Molina-Boisseau, S.; Marais, M-F.; Lévêque, J-M. Simultaneous Microwave/Ultrasonic-Assisted Hydrolysis of Starch-Based Industrial Waste into Reducing Sugars. ACS Sustainable Chem. Eng. 2013, 1, 995–1002.
(21) Teramoto, N.; Motoyama, T.; Yosomiya, R.; Shibata, M. Synthesis, Thermal Properties, and Biodegradability of Propyl-Etherified Starch. Eur. Polym. J. 2003, 39, 255–261.
(22) Winkler, H.; Vorwerk, W.; Wetzel, H. Synthesis and Properties of Fatty Acid Starch Esters. Carbohydr. Polym. 2013, 98, 208–216.
(23) Ferrutti, P.; Tani, M. C.; Vaccaroni, F. Synthesis and Exchange Reactions of Biodegradable Drug-Binding Matrices. Makromol. Chem. 1979, 180, 375–382.
(24) Sroková, I.; Sasinová, V.; Ebringerová, A. Biodegradable Polymeric Surfactants from O-(Carboxymethyl) Starch. Fibres Text. East. Eur. 2007, 15, 118–120.
(65) Liesiene, J.; Kazlauske, J. Functionalization of Cellulose: Synthesis of Water-Soluble Cationic Cellulose Derivatives. Cellul. Chem. Technol. 2013, 47, 515–525.