



A New Quaternized Chitosan-Based Catalyst Obtained by an Environmentally-Friendly Synthesis Route for Green Production of Carbonated Molecules from Terminal Epoxides

Helen C. Inciarte¹ · Natalia Cortés¹ · David A. Echeverri¹ · Luis A. Rios¹

Accepted: 2 January 2025
© The Author(s) 2025

Abstract

Using CO₂ as a building block to produce monomers through carbonation (cycloaddition reaction) provides an attractive approach to carbon dioxide valorization. The design of an efficient, cheap, and reusable catalyst for epoxide carbonation remains a challenge. In this paper, a new quaternized chitosan catalyst, useful for the cycloaddition of CO₂ to epoxides, was developed. The new catalyst was obtained using a short and straightforward route, including the use of non-depolymerized chitosan and benign reactants such as succinic anhydride (a food additive), at room temperature. The catalyst allowed the carbonation of glycidyl methacrylate at 100 °C, 2 MPa, and 6 h reaction without any solvent required, with 98% epoxide conversion and 87% selectivity to the carbonated product. The catalyst was reused during 3 cycles showing stable values of conversion and selectivity to the carbonated GMA. The selectivity to the carbonated GMA remained stable at 87% during seven recycles. The use of non-depolymerized chitosan as a precursor is a key point that brought durability to the catalyst in comparison to depolymerized chitosan. The catalyst was also used in the carbonation of two di-epoxides (1,4-butanediol diglycidyl ether and bisphenol A diglycidyl ether) at 100 °C and 2 MPa affording high yields to the carbonated products.

Keywords Quaternized Chitosan · Cyclic Carbonates · Carbonation · Glycidyl Methacrylate

Introduction

There are three main strategies currently available to mitigate atmospheric CO₂: (i) emissions reduction, (ii) capture/storage, and (iii) use of CO₂ as raw material in chemical processes [1, 2]. Use of CO₂ as a building block to produce monomers provides an attractive approach to valorize this biobased, abundant, and non-toxic reagent [3]. For instance, non-isocyanate polyurethanes can be obtained from carbonated vegetable oils [4, 5].

CO₂ is thermodynamically a very stable molecule because carbon is in a highly oxidized state and requires reactive compounds and effective catalysts for its activation. However, due to the electron deficiency of the carbonyl

carbon, CO₂ has a strong affinity towards nucleophiles and electron donors [6]. Many studies show that cyclic carbonates can be successfully synthesized by the cyclo-addition reaction of CO₂ to epoxides using different homogeneous and heterogeneous acid-base catalysts [7, 8]. The most used catalytic systems for the addition of CO₂ to epoxides contain Lewis-type acidic sites for electrophilic activation of epoxide and/or CO₂ and basic Lewis-type sites that act as nucleophiles. Catalysts such as alkali metal halides, organic bases, polyoxometalates, ionic liquids, metal oxides, zeolites, titanosilicates, smectites, and metal complexes have been reported for this reaction [9–12].

Some of the aforementioned catalysts suffer from low catalyst activity and/or selectivity or low stability, and in some cases, they require a solvent. The development of a highly efficient and environmentally benign catalytic system for the chemical fixation of CO₂ on epoxides under mild conditions remains a challenge. At the same time, a major problem associated with most homogeneous catalyst systems is catalyst separation and recycling. In particular,

✉ Luis A. Rios
luis.rios@udea.edu.co

¹ Procesos Químicos Industriales, Universidad de Antioquia UdeA, Calle 70 No.52-21, Medellín, Colombia

special attention has been paid to reusable catalysts, such as inorganic materials, organic molecules grafted on inorganic supports (e.g., ionic liquids grafted on silica supports), and even on solid organic materials using continuous or batch flow reactors [6, 9, 10, 13].

Some natural biopolymers such as chitosan have recently attracted great interest as supports for catalytic reactions [14–16]. Chitosan is the N-deacetylated derivative of chitin, which is the most abundant natural amino polysaccharide. The amount of chitosan produced annually is estimated to be almost as large as that of cellulose [16]. Chitin is found widely dispersed in living organisms, including crab and lobster crustaceans. Chitosan has excellent properties such as biocompatibility, biodegradability, non-toxicity, and good adsorption properties. Specifically, chitosan can be chemically modified by alkylation, acylation, quaternization, hydroxy-alkylation, thiolation, sulfation, and phosphorylation [17].

Several papers have reported the quaternization of chitosan and its use as a catalyst for the cycloaddition of CO₂. For instance, Tharun et al. reported the synthesis of quaternized chitosan using 1-methyl-2-pyrrolidinone (NMP) and using iodomethane as a raw material [18]. Investigation of various reaction parameters in the allyl glycidyl ether (AGE) carbonation indicated that the conversion was maximum (>99%) when the reaction was carried out with 0.1 g of catalyst at 120 °C, 1.17 MPa, and 6 h. One of the major problems during synthesis of the catalyst was the solubility of chitosan in NMP which was poor even after allowing a prolonged period of 36 h at 80 °C [19]. The introduction of microwave irradiation greatly reduced the synthesis time of the catalyst and exhibited a slightly higher conversion of AGE [19]. Likewise, Besse et al. reported the use of chitosan modified with quaternary ammonium and carboxylic acid groups in the presence of KI and without the use of solvents [16]. In a first step, soluble chitosan was obtained by depolymerization with hydrogen peroxide under microwave radiation [20]. Then, allyl and trimethylammonium moieties were introduced along the chitosan backbone through epoxide-amine reactions with allyl glycidyl ether (AGE) and glycidyl trimethylammonium (GTA) chloride. The allyl-group-containing compound was then functionalized with 3-mercaptopropionic acid (3-MPA) in the presence of and 4,4'-azobis(4-cyanovaleric acid) using a thiol-ene addition. The catalyst was evaluated in the carbonation of propylene oxide and AGE as substrates at 0.7 MPa, 80 °C, and 4 h without solvent affording a complete conversion. The optimal reaction conditions were determined using AGE as a model and extended to a wide range of other epoxides.

The aforementioned methods for obtaining quaternized chitosan have some drawbacks such as long times of catalyst synthesis (typically ca. 72 h) as well the use of toxic or

irritant reactants such as NMP or 3-MPA. Likewise, there are some risks associated with the use of iodomethane as a raw material because of its high toxicity. Moreover, in all mentioned papers, chitosan was depolymerized previously to obtain it in its water-soluble form. Depolymerization is not a green process due to several issues, such as the extensive use of chemicals and energy and the requirement of several purification stages [20]. In this paper, non-depolymerized chitosan is proposed for the first time as a raw material for obtaining the quaternized derivative. The so-obtained catalyst allowed for a better recoverability of the catalyst during reusing in comparison to water-soluble chitosan. The chemical modification of chitosan was achieved in a short time using succinic anhydride (a food additive) at room temperature before quaternization. Besides, KI, which is a non-toxic substance, was used as a promoter for carbonation. The so-obtained catalytic system was used in the carbonation of glycidyl methacrylate (GMA) at 2 MPa, 100 °C and 6 h reaction without any solvent required, affording 98% conversion and 87% selectivity to the carbonated product. The catalyst was reused during 3 cycles showing stable values of conversion and selectivity to carbonated GMA. The catalytic system was also used successfully in the carbonation of more complex epoxides.

Materials and Methods

Materials

Glycidyl methacrylate (GMA, 97%) was supplied by Alfa Aesar. Glycidyl trimethylammonium chloride (GTA-Cl), bisphenol A diglycidyl ether (BADGE), succinic anhydride (SA), and chitosan (low molecular weight, ≥75% deacetylated) were purchased from Sigma Aldrich. Ethanol (≥95%), 1,4-butanediol diglycidyl ether (BDDE), and acetone (≥95%) were supplied by Merck. Hexane (≥95%), iodide potassium (99.5%), acetic acid (≥99.7%), and hydrogen peroxide (30% w/v in water) were obtained from Pan-Reac AppliChem. All reagents were used without further purification.

Synthesis of Chitosan-Based Catalyst, Q-SA-CH (Fig. 1)

First, the chitosan (1 g) and succinic anhydride (0.5 g) were mixed in deionized water (50 ml) for 7 h at room temperature with vigorous stirring. An intermediate product, succinic anhydride-chitosan adduct (SA-CH) was obtained, which was precipitated with acetone (200 ml). The supernatant and precipitate were separated by centrifugation. After

extracting the supernatant, the resulting fine white powder was washed four times with 25 ml acetone to eliminate residual succinic anhydride. The solid (SA-CH) was dried for 3 h at 40 °C. In a subsequent step, SA-CH (0.5 g) was dissolved in deionized water (8 ml) at 60 °C. Then, GTA-Cl (2.2 ml) was added with vigorous stirring. The reaction mixture was kept under these conditions for 6 h. The final catalyst (Q-SA-CH) was precipitated in acetone (30 ml), obtaining a semisolid material, which was dried in an oven at 45 °C for 24 h. The total amount of catalyst obtained was 1.779 g (ca. 75% yield).

As a comparison basis, water-soluble chitosan was also used as raw material for the synthesis of the catalyst (Q-SA-CH-Sol). Chitosan was depolymerized according to the method of Du et al. using acetic acid and H₂O₂ [21]. Then, the catalyst was obtained following the same procedure

described above. The total amount of catalyst obtained was 1.098 g (ca. 43% yield). (Fig. 1)

Synthesis of Carbonated Molecules

The carbonation reaction of GMA was performed in a 10 ml stainless-steel high-pressure batch reactor according to the following procedure [16]. GMA (4 ml), Q-SA-CH catalyst (186.5 mg, 4.8 wt % respect to the total reaction mixture) and KI (22.7 mg, 0.6 wt % respect to the total reaction mixture) were introduced into the reactor. The reactor was sealed, and the air was purged three times with CO₂. The system was pressurized with CO₂ at 2 MPa and the carbonation reaction was carried out at 100–115 °C for 6 h under constant stirring. The product was washed four times with 10 wt % NaCl-water solution at 50 °C in a separation funnel.

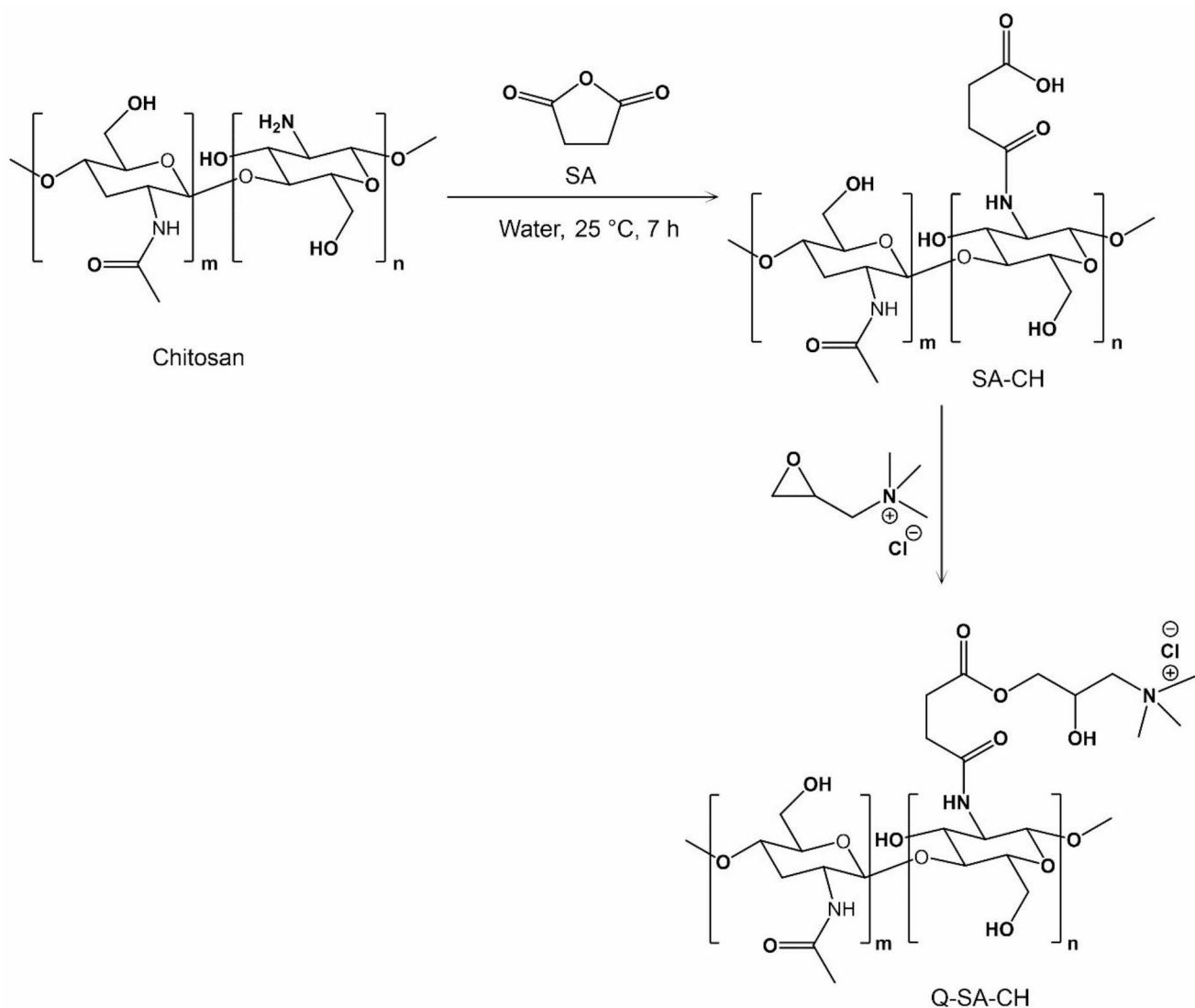


Fig. 1 Synthesis of Q-SA-CH catalyst

Then, the product was diluted with diethyl ether and poured into a beaker with anhydrous sodium sulfate to completely remove water. Finally, it was filtered, and the solvent was removed by evaporation. The carbonations of BDDE and BAGE were performed at the best reaction conditions found for GMA (Fig. 2b-c).

Carbonated GMA was obtained as colorless liquid product with 85% yield. $^1\text{H NMR}$ [CDCl_3 , δ (ppm)]: 6.15 (m, $\text{CH}_2=\text{CH}$), 5.66 (m, $\text{CH}_2=\text{CH}$), 4.99 (m, $\text{CH}-\text{CH}_2$, from carbonate ring), 4.59 and 4.42 (m, CH_2-COO), 4.34 (m, $\text{CH}-\text{CH}_2$, from carbonate ring), 1.95 (t, CH_3). $^{13}\text{C NMR}$ [CDCl_3 , δ (ppm)]: 167.1 (C=O), 155.6 (C=O, from carbonate ring), 135.3 ($\text{CH}_2=\text{C}$), 127.5 ($\text{CH}_2=\text{C}$), 73.4 (CH_2-CH , from carbonate ring), 66.5 (CH_2-COO), 63.4 (CH_2-CH , from carbonate ring), 18.2 (CH_3).

Carbonated BDDE was obtained as white, solid product with 93% yield. $^1\text{H NMR}$ [CDCl_3 , δ (ppm)]: 4.81 (m, $\text{CH}-\text{CH}_2$, from carbonate ring), 4.30–4.50 (m, $\text{CH}-\text{CH}_2$, from carbonate ring), 3.55–3.70 (m, CH_2-CH), 3.53 (m, $\text{CH}_2-\text{CH}_2-\text{O}-$), 1.64 (m, $\text{CH}_2-\text{CH}_2-\text{O}$). $^{13}\text{C NMR}$ [CDCl_3 , δ (ppm)]: 154.9 (C=O, from carbonate ring), 75.1 (CH_2-CH), 71.5 ($\text{CH}-\text{CH}_2$, from carbonate ring), 70.1 ($\text{CH}_2-\text{CH}_2-\text{O}-$), 66.5 ($\text{CH}-\text{CH}_2$, from carbonate ring), 25.7 ($\text{CH}_2-\text{CH}_2-\text{O}$).

Carbonated BADGE was obtained as white, solid product with 79% yield. $^1\text{H NMR}$ [CDCl_3 , δ (ppm)]: 7.14 and 6.82 (m, $\text{CH}=\text{CH}$), 5.01 (m, CH_2-CH , from carbonate

ring), 4.60 and 4.52 (m, CH_2-CH), 4.21 and 4.12 (m, CH_2-CH , from carbonate ring), 1.64 (t, CH_3). $^{13}\text{C NMR}$ [CDCl_3 , δ (ppm)]: 156.9 (C–O, from aromatic ring), 155.6 (C=O, from carbonate ring), 146.3 (C–CH, from aromatic ring), 127.7 and 114.9 ($\text{CH}=\text{CH}$, from aromatic ring), 72.4 (CH_2-CH), 71.5 ($\text{CH}-\text{CH}_2$, from carbonate ring), 62.6 ($\text{CH}-\text{CH}_2$, from carbonate ring), 42.4 (C– CH_3), 30.9 (CH_3).

Reusability Tests

After the carbonation reaction, the catalyst was separated from the product by decantation. Before use, the catalyst was washed with CH_2Cl_2 and dried in an oven at 45 °C for 24 h. The weight of the dry catalyst was measured after each use as reported in Table S1 [22].

Quantification of the Reaction Products

$$\text{Epoxide conversion (\%)} = \frac{A_{(\text{CH ox})} \text{ in epoxide} - A_{(\text{CH ox})} \text{ in product}}{A_{(\text{CH ox})} \text{ in epoxide}} \times 100$$

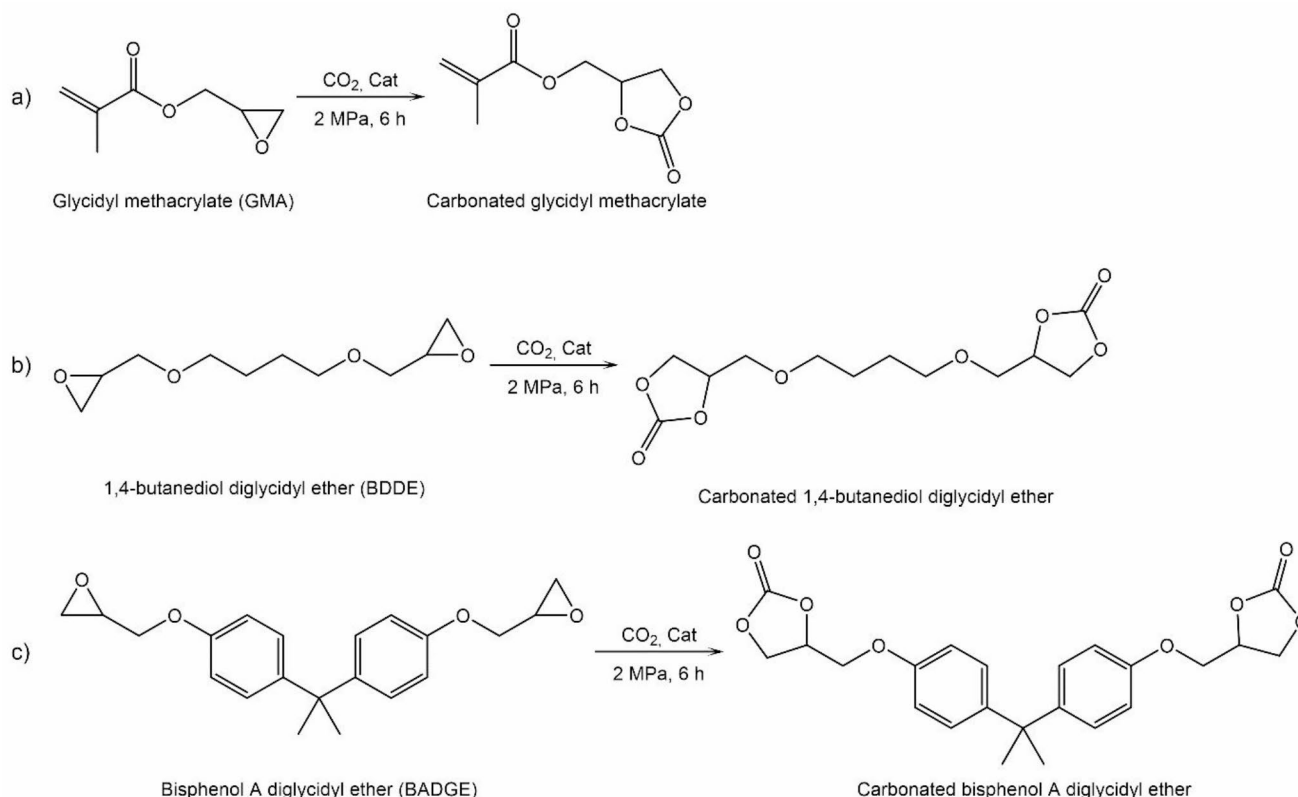


Fig. 2 Synthesis of carbonated molecules from GMA (a), BDDE (b), and BADGE (c)

$$\text{Selectivity to carbonate group (\%)} = \frac{A_{(CH\ carb)} \text{ in product}}{A_{(CH\ ox)} \text{ in epoxide} - A_{(CH\ ox)} \text{ in product}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{Weight of product obtained (g)}}{\text{Theoretical weight of product obtained (g)}} \times 100$$

Where, $A_{CH\ ox}$ corresponds to the methine protons of the oxirane group at 3.25 ppm in the $^1\text{H NMR}$ spectra of epoxide molecules or carbonated products.

$A_{CH\ carb}$ corresponds to the methine protons of the cyclic carbonate group at 4.94 ppm in the carbonated products.

For GMA carbonation, the integral of CH_3 proton (3 protons) at 1.95 ppm was taken as a reference. For BADGE carbonation, the integral of CH_3 proton (6 protons) at 1.65 ppm was taken as a reference. For BDDE carbonation, the CH_2 proton (4 protons) adjacent to the epoxide group at 3.35 ppm was taken as a reference.

Characterization

The catalyst and the reaction products were characterized by $^1\text{H NMR}$ and $^{13}\text{C NMR}$ using a Bruker Advance II (600 MHz), D_2O or CDCl_3 as a solvent, and TMS as an internal standard. FTIR analyses were carried out with a Prestige 21 Shimadzu IR spectrometer using an ATR accessory. All FTIR spectra were acquired at room temperature in the range of 400 to 4000 cm^{-1} with a spectral resolution of 2 cm^{-1} . The thermal stability of the catalyst was performed by Thermogravimetric analysis (TGA) with 15 mg of sample and 20 ml/min of N_2 as carrier gas. A TA Instruments Q600 equipment was used. The sample was heated from $25\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The surface morphology and the surface composition analyses of the catalyst were obtained by SEM and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) with a JSM5910LV microscope and an Oxford Instruments INCA energy analyzer respectively. Specimens were gold-coated by low vacuum sputter coating before analysis.

Results and Discussion

Synthesis of Chitosan-Based Catalyst

The FTIR spectrum of chitosan, SA-CH, and Q-SA-CH are shown in Fig. 3. In the chitosan spectra (Fig. 3a), the characteristic absorptions at 1570 cm^{-1} , 1645 cm^{-1} are related to the bending vibration of the N–H bond and the carbonyl group of residual acetyl amides, respectively [15]. The peaks at $3200\text{--}3500\text{ cm}^{-1}$ are related to the stretching vibrations

of O–H and N–H bonds. The peaks around 896 cm^{-1} and 1153 cm^{-1} correspond to the saccharide structure of chitosan. The stretching vibrations of C–O bonds appear at 1065 and 1030 cm^{-1} [23]. The reaction between the amino groups of chitosan and succinic anhydride was confirmed by the appearance of a band at 1549 cm^{-1} corresponding to the –NH bending of the amide group (Fig. 3b). On the other hand, the FTIR spectrum of Q-SA-CH (Fig. 3c) shows the band at 3283 cm^{-1} of hydroxyl group resultant of the GTA-Cl epoxide opening with carboxylic acid groups. Also, the carbonyl of the ester group formed is observed at 1698 cm^{-1} [24]. The absorption bands in the IR spectra of Q-SA-CH (Fig. 3d) after seven reaction cycles did not show important differences with respect to fresh catalyst. This suggests that the structure of the catalyst did not suffer changes after reusing.

Figure 4a–d shows the SEM spectra of pristine chitosan, SA-CH, Q-SA-CH, and the used catalyst. As shown, pristine chitosan (Fig. 4a) shows a non-porous layered surface. After the reaction with succinic anhydride, the surface undergoes a visible change likely due to the formation of acid moieties (Fig. 4b). After the reaction with GTA-Cl, the surface became more homogeneous with some protuberances (Fig. 4c). A marked change is observed in the catalyst used after the carbonation reaction since the surface was partially covered by iodine and potassium, as shown in SEM-EDX analyses (Fig. 5). This suggests that KI has a good affinity by the quaternized surface of Q-SA-CH forming an effective catalytic system

In Fig. 6a–c are shown the $^1\text{H NMR}$ spectra of non-depolymerized chitosan, SA-CH, and Q-SA-CH. As shown, in pristine chitosan (Fig. 6a), the peaks 1–6 correspond to the protons of the glucosamine unit while the CH_3 protons of the acetylated group are observed at 1.97 ppm. The main evidence of modification with succinic anhydride is the peak corresponding to the CH_2 protons at 2.4–2.6 ppm from the succinate structure (Fig. 6b). After quaternization, the peaks corresponding to the formation of CH_2 and CH protons formed from the epoxide ring-opening of GTA-Cl with SA appear at 3.56 and 4.17 ppm respectively (Fig. 6c). The methyl protons joined to the N atom are observed at 3.13 ppm. According to $^1\text{H NMR}$ spectra of water-soluble chitosan and the corresponding derivatives obtained thereof (Fig. S1) no changes were observed in the characteristic shifts in comparison to non-depolymerized chitosan and their derivatives. The $^{13}\text{C NMR}$ spectra of non-depolymerized chitosan and derivatives obtained thereof are shown in Fig.

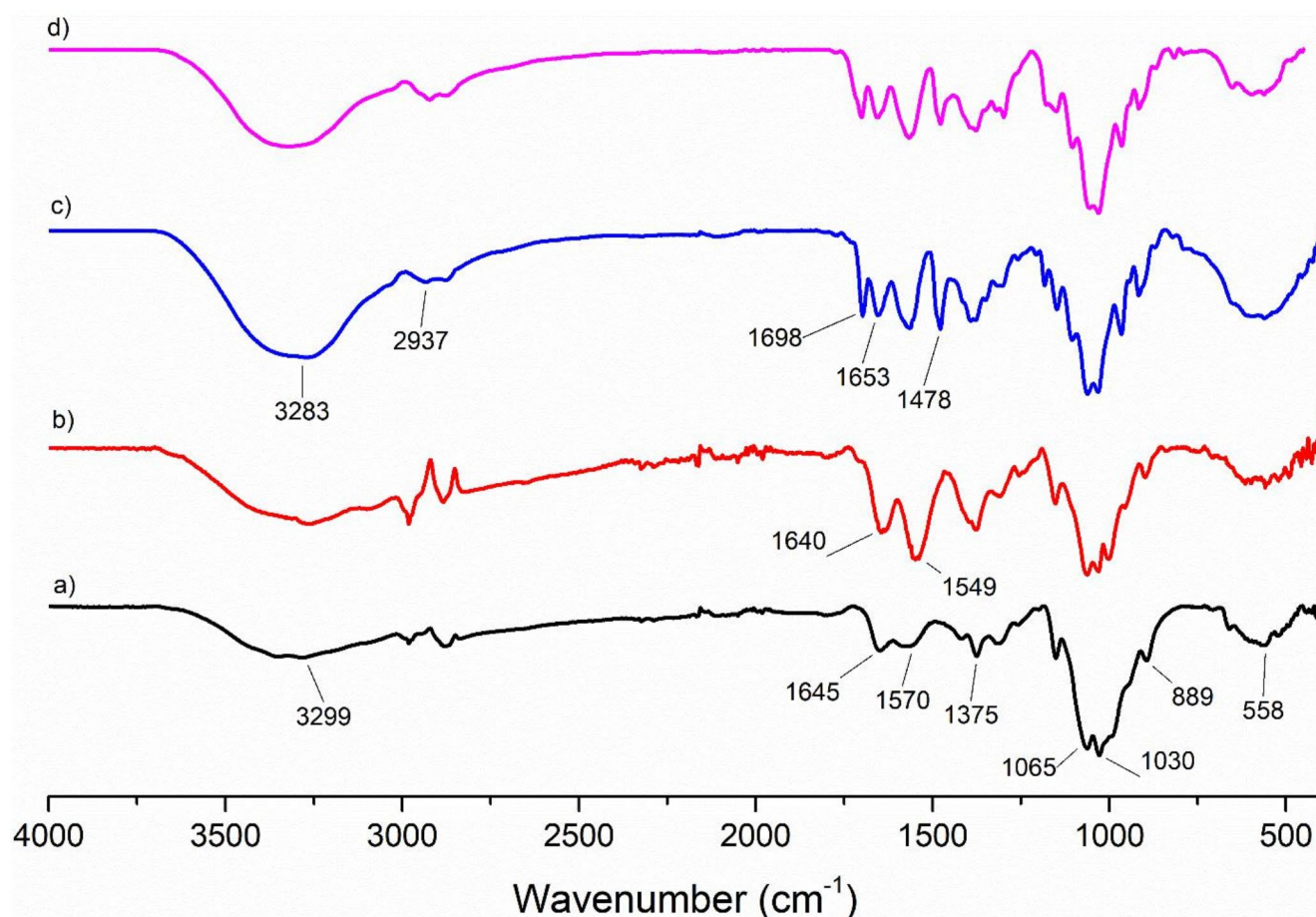


Fig. 3 FTIR spectra of chitosan (a), SA-CH (b), Q-SA-CH (c), and the catalyst after seven reaction cycles (d)

S2-S4 and described in the results and discussion section of SI. The ^1H NMR spectrum of Q-SA-CH after seven reaction cycles (Fig. S12) did not show differences with respect to fresh catalyst, in line with the FTIR analysis shown above.

Figure 7 and Table 1 show the TGA analyses of pristine chitosan, SA-CH, and Q-SA-CH. Pristine chitosan showed an initial weight loss at 25–119 °C, which can be attributed to the removal of adsorbed water molecules and accounts for $T_{5\%}$ losses. The pristine chitosan undergoes a non-oxidative thermal degradation in two steps in the range of 240–577 °C with maximum degradation temperatures of 274 and 490 °C in each stage. According to other authors, these stages possibly correspond to the deacetylation of chitosan, vaporization, and elimination of volatile products [18]. The degradation of SA-CH showed an initial weight loss of 25% below 275 °C. The succeeding degradation behavior was closer to this one of pristine chitosan. Probably the first step corresponds to the degradation of the succinate component. As reported by Govindaraj et al., the pure succinic acid decomposes entirely in the range of 170–240 °C [25]. The temperatures for maximum weight loss of Q-SA-CH were 257 °C and 447 °C, which were lower than pristine chitosan,

as shown in Table 1. Thus, the thermal stability of chitosan decreased after succinylation and quaternization. It has been reported by several authors that the quaternized derivatives are less thermally stable than the parent chitosan, whose stability seems to depend on their quaternization degree [18, 26]. The explanation for the decrease in thermal stability has been attributed to the breakage of the intramolecular hydrogen bonding after quaternization, i.e. the destruction of the crystalline structure of chitosan.

GMA Carbonatation

The carbonated GMA product was characterized by ^1H NMR and ^{13}C NMR (Fig. S5-S6). The ^1H NMR spectrum of the carbonated product (Fig. S5) shows that the signals of protons attached at oxirane groups at 2.67, 2.85, and 3.25 ppm disappeared. Besides, the new signals of the methylene and methine protons from the cyclic carbonates appear at 4.99 and 4.34 ppm [27]. The ^{13}C NMR spectrum of the carbonated GMA (Fig. S6) showed the signal of carbonyl carbon from the ester group at 167.1 ppm, the signal of carbonyl ester from the carbonate ring at 155.6 ppm as well as the

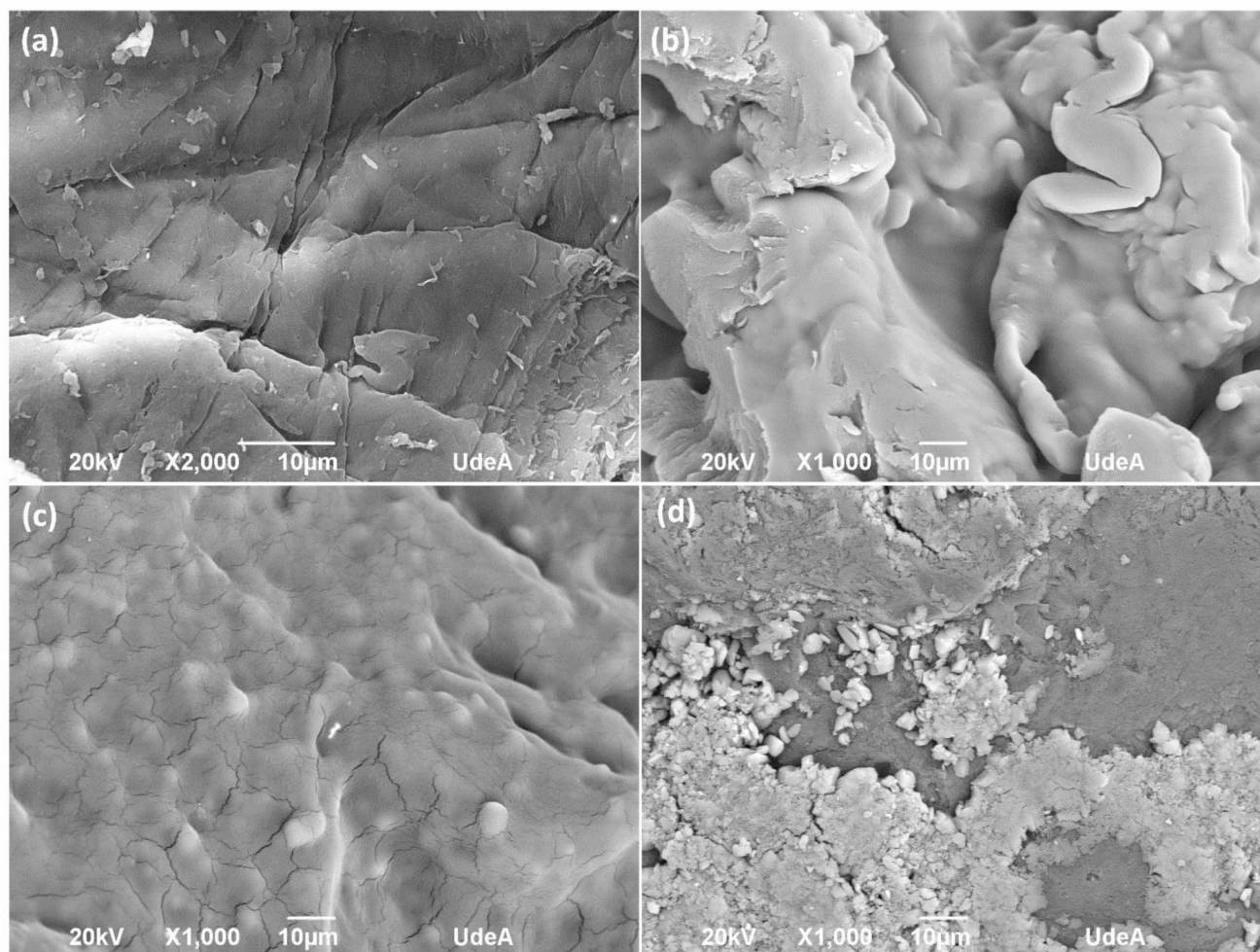


Fig. 4 SEM of pristine chitosan (a), SA-CH (b), Q-SA-CH (c), and the catalyst after seven reaction cycles (d)

methine carbon and methylene carbon from methacrylate group at 135.3 ppm and 127.5 ppm respectively. Besides, the peak of methine carbon from the carbonate ring appears at 73.4 ppm [10].

Two reference experiments were performed, the first using only KI and the second, using the catalyst Q-SA-CH without KI at 100 °C and 2 MPa CO₂ during 6 h. As expected, in the first experiment, the epoxide conversion was insignificant (0.82%), while in the second experiment, the epoxide conversion was 1.03%. As reported by Besse et al., the use of quaternized chitosan without KI during AGE carbonation results in low yield (15%) [16]. This fact was explained by the presence of chlorine anions, which are known to show a lower activity compared to iodide for the synthesis of cyclic carbonates. Chloride anions are present in the catalytic system as the initial counter-ions of the ammonium groups. Cl⁻ and I⁻ act as competitors.

The carbonation of GMA was carried out at two temperatures (100 °C and 115 °C) at 2 MPa CO₂ without solvent and using Q-SA-CH as a catalyst. The levels of pressure and

amount of catalyst were fixed according to literature and previous experiments [18, 28–30]. Further increases in these variables above these levels had no significant effect on the conversion of epoxides or selectivity to cyclic carbonates. Regarding the effect of catalyst amount and CO₂ pressure, Tharun et al. analyzed the effect of reaction parameters on the carbonation of allyl glycidyl ether (AGE), which is structurally very similar to GMA, using quaternized chitosan [18]. Specifically, the authors observed that the conversion increased with the amount of catalyst up to 0.1 g (4.71 wt % catalyst) [18]. Further increases in the amount of catalyst did not produce any significant increase in the conversion. Regarding pressure effect, AGE conversion increased from 20 to 67% when the CO₂ pressure increased from 0.34 MPa to 0.97 MPa. This can be explained by higher solubility CO₂ in AGE and thus results in an acceleration of the cyclic carbonate formation. After a further increase in the pressure, to 1.17 MPa, the conversion increased to its maximum, 91%. Other authors have observed similar effects

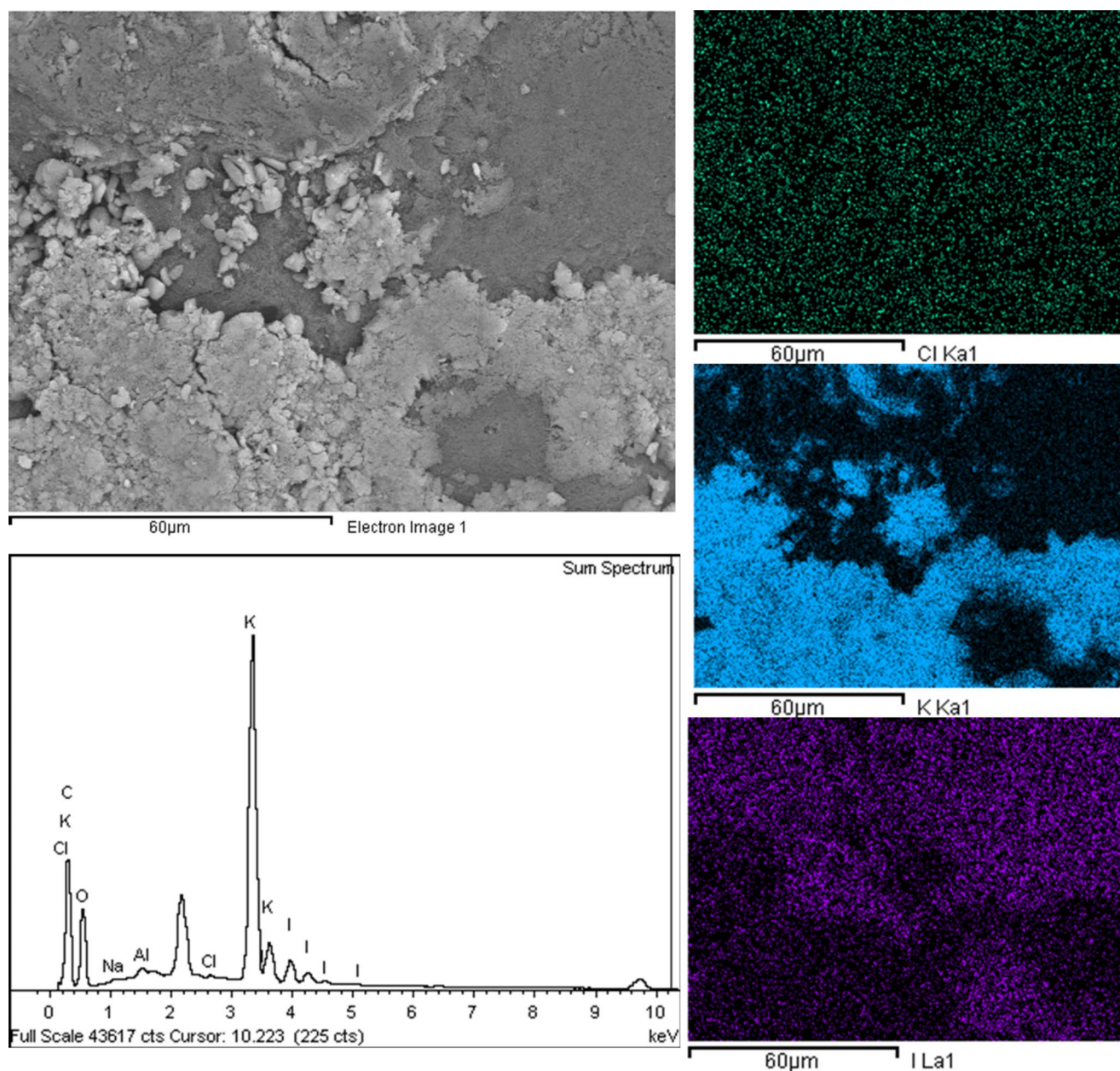


Fig. 5 SEM-EDX of Q-SA-CH

of the CO_2 pressure and the catalyst amount on the carbonation reaction [28–30].

Concerning the activation mechanism for CO_2 cycloaddition, the hydrogen atom from the OH group of Q-SA-CH forms a hydrogen bond with the oxygen atom of the oxirane group of the epoxide molecule (Fig. S11). The halide anion formed between Q-SA-CH and the iodide ion of KI acts as a nucleophilic group and attacks the less sterically hindered β -carbon atom of the epoxide, causing the opening of the oxirane ring. Subsequently, this intermediate reacts with CO_2 to form the corresponding cyclic carbonate and the catalyst is regenerated.

The epoxide conversion and the selectivity to carbonate groups at both temperatures are shown in Fig. 8. At 115°C the epoxide conversion afforded values near to 98%. At 100°C the reaction was quite slower. However, at 6 h the conversion values were similar at both temperatures. The selectivity to the carbonate group at 100°C and 115°C kept around 87% and 75% respectively. The non-complete selectivity values obtained can be explained by the side reaction of the carbonate ring with the alkoxide (from epoxides) with the subsequent decarboxylation which could yield ether linkages [31, 32]. Guerdener et al. have reported the consumption after 1 h of reaction of the formed cyclic

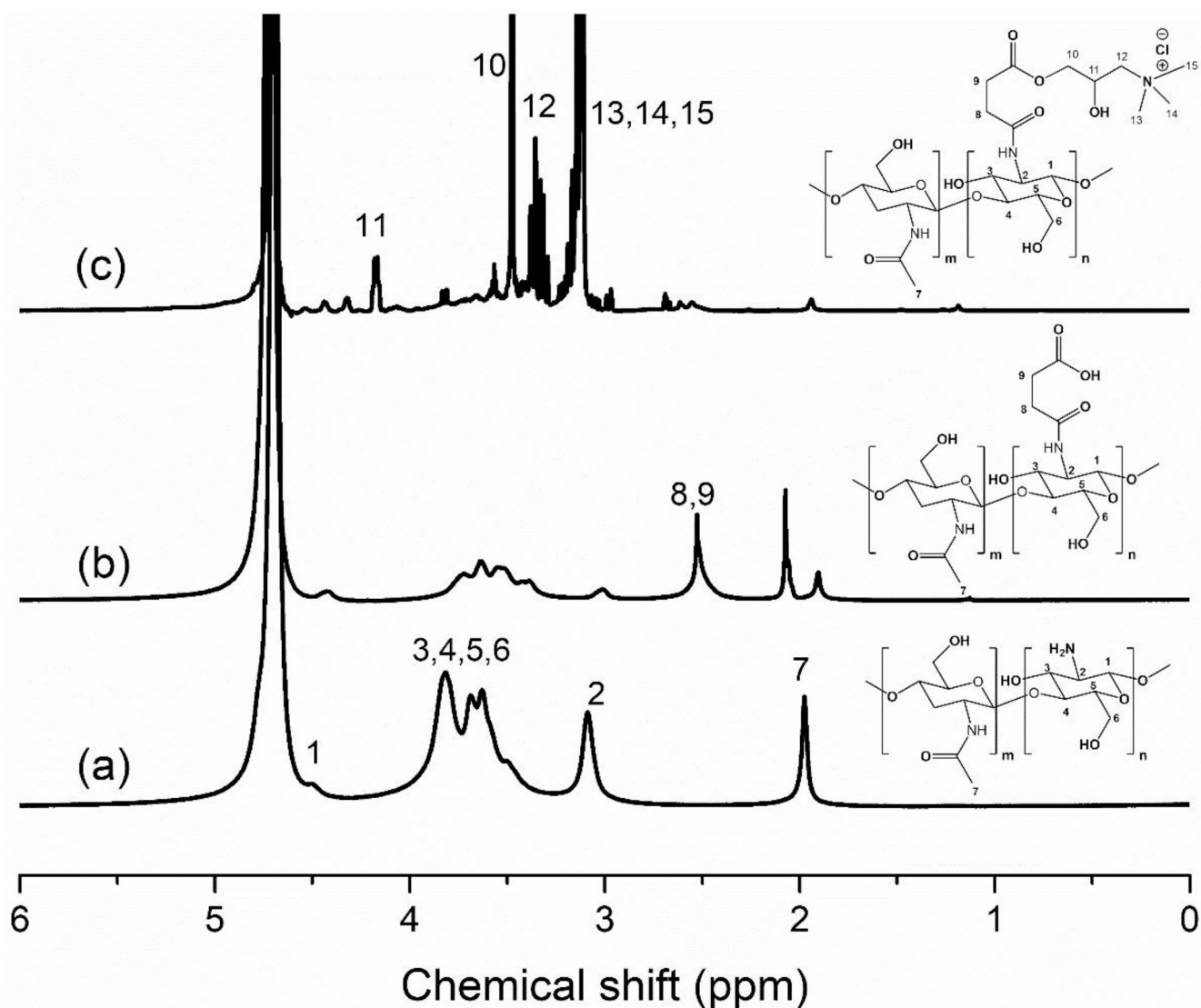


Fig. 6 ^1H NMR spectra of non-depolymerized chitosan (a), SA-CH (b), and Q-SA-CH (c) obtained thereof

carbonates obtained from the carbonation of [ethylene-glycidyl methacrylate]-based copolymers with CO_2 [32]. The reaction conditions were 110 °C and tetrabutylammonium chloride as catalyst. However, after 5 h, an increase in the temperature from 110 °C to 130 °C led to a decrease in the yield from 99% to 45%. This fact was attributed to the formation of a polyether structure at the expense of the formed cyclic carbonate via the mentioned mechanism. The signals of the methylene protons attached to carbon next to ether linkages appeared around 3.8 ppm in the ^1H NMR spectra of carbonated GMA (Fig. S5). The signals of the carbons joined to ether linkages appear around 70.1 ppm in the ^{13}C NMR spectrum (Fig. S6). The carbonation reaction was also evaluated at 100 °C using the catalyst obtained from soluble chitosan (Q-SA-CH-Sol), as shown in Fig. 8. This catalyst allowed a better dispersion in the reaction media

possibly due to the lower molecular weight of chitosan, achieving slightly higher conversion values during the first hours of reaction in comparison to the catalyst based in non-depolymerized chitosan. However, the selectivity values to carbonated products were not significantly affected by the chitosan pretreatment.

The reusability of the chitosan catalyst for the carbonation of GMA during seven cycles is shown in Fig. 9. The selectivity of the carbonated product remained stable at 87% during all recycles. The conversion remained stable at ca. 98% during the first three uses. However, after the fourth use, the conversion gradually decreased to 78% on the seventh use. The cause of the decrease in epoxide conversion could not be attributed to changes in the catalyst structure, according to the characterization of the used catalyst by FTIR and ^1H NMR. However, the mentioned effect

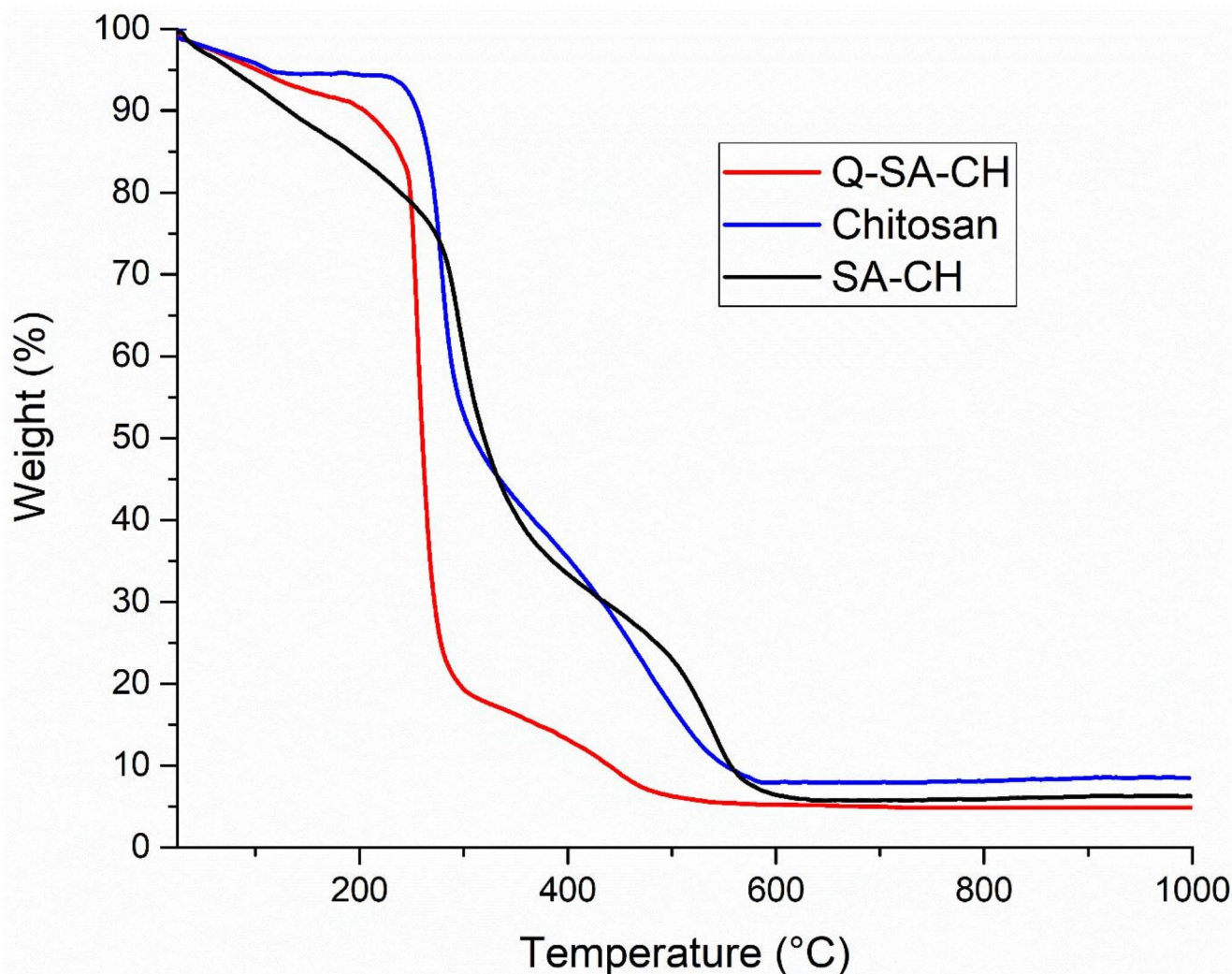


Fig. 7 TGA traces of non-depolymerized chitosan, SA-CH, and Q-SA-CH obtained thereof

Table 1 Thermal degradation temperatures of non-depolymerized chitosan, SA-CH, and Q-SA-CH obtained thereof

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{\max}^a (°C)
Non-depolymerized chitosan	113	310	274; 490
SA-CH	77	319.5	294; 545
Q-SA-CH	101	260	257; 447

^aTemperature at which the maximum rate of degradation occurred in each degradation step

could be explained by the losses of catalyst during washing which were 1% during cycles 1–3 (Table S1). However, at 4–7 cycles the catalyst loss increased to ca. 9% due to repeated cycles of reaction-washing. This fact was observed more dramatically with the catalyst based on water-soluble chitosan since it could not be recovered from the reaction product after the first use. This proves that use of non-depolymerized chitosan is a key point which brings durability to the catalyst.

Di-epoxide Carbonation

Q-SA-CH was used in the carbonation of two di-epoxides: BDDE and BADGE at 100 °C and 2 MPa. The carbonated BADGE and BDDE products were characterized by ¹HNMR and ¹³CNMR (See Fig. S7-S10 and the corresponding results and discussion). The carbonation of BADGE (Fig. 10) evidenced a high selectivity (ca. 90%) to the carbonated product at the beginning of the reaction which decreased to 85% after 6 h while the conversion increased slowly to reach the maximum value of 93% at 8 h reaction. In a similar fashion to BADGE, carbonation of BDDE (Fig. 11) showed 100% selectivity at zero time which decreased to ca. 93% at 6 h, while the conversion was 100% at 8 h reaction. A possible explanation of the decreasing of the selectivity to carbonated products from BADGE and BDDE is the direct nucleophilic attack of the alkoxide (from epoxides) on the carbonate ring with the subsequent

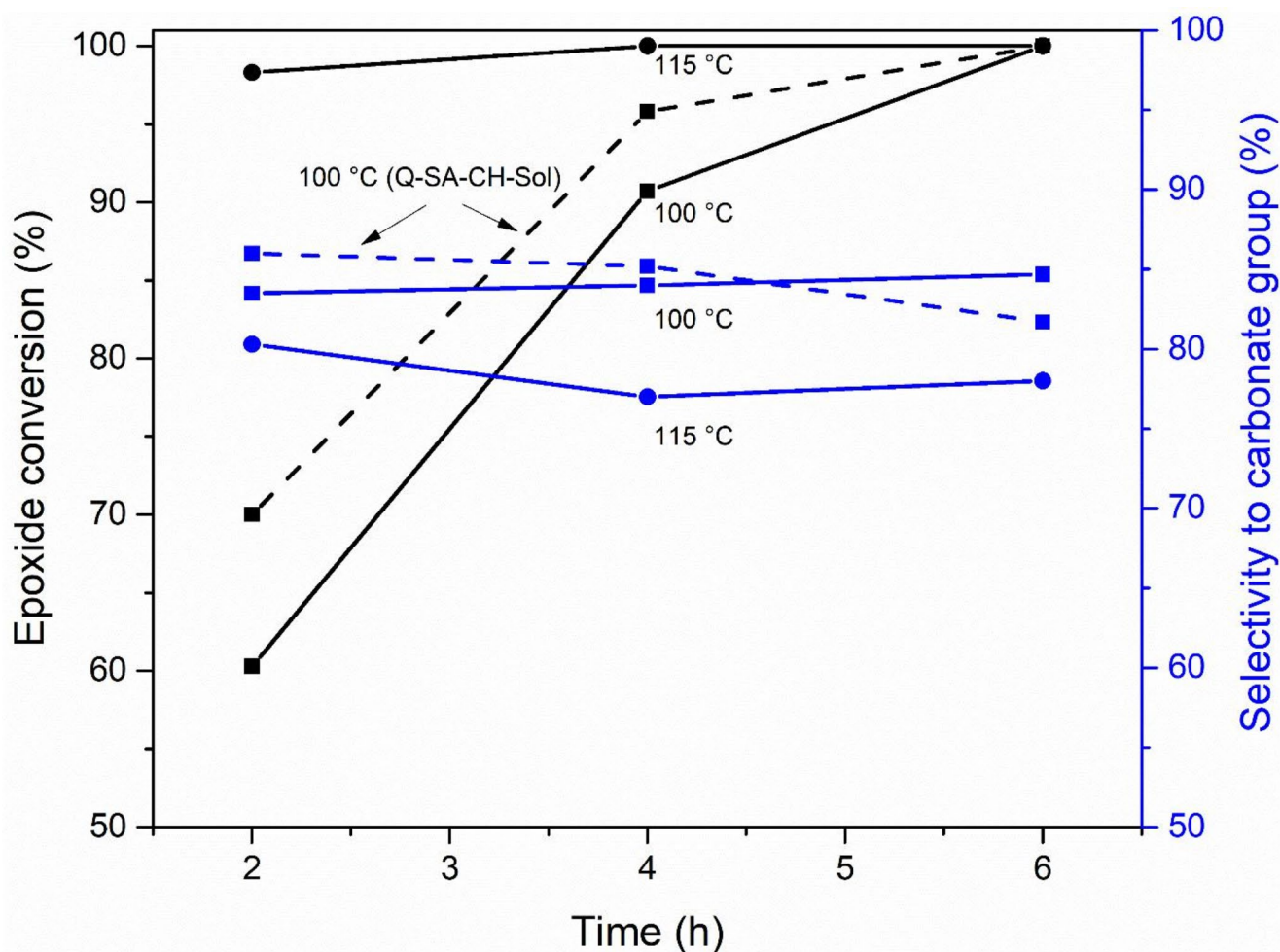


Fig. 8 Epoxide conversion (black lines) and selectivity to carbonate groups (blue lines) at 100 °C and 115 °C as function of the reaction time during the carbonation of GMA with Q-SA-CH (solid lines) and Q-SA-CH-Sol (dashed lines)

decarboxylation which could yield several ether linkages, as explained before for GMA carbonation. This is supported by the ^1H NMR and ^{13}C NMR spectra of carbonated BDDE (Fig S9-S10). In the ^1H NMR spectrum, the protons joined to the carbon next to ether linkages are observed at 3.7–3.8 ppm while the respective carbon signals appear around 70.46 ppm in the ^{13}C NMR spectrum. For the carbonation of BADGE, the corresponding signals appear at 3.6–3.8 ppm and around 70.08 ppm in Fig S7 and S8 respectively.

In this work, special epoxides (GMA, BDDE, BADGE) were used as substrates for carbonation. These molecules have high reactivity due to the presence of terminal epoxides. Therefore, high temperatures and long times could increase secondary reactions of labile groups, as mentioned above. The Q-SA-CH/KI system is suitable for the carbonation of these epoxides because it allows to perform the reaction in shorter times than most other heterogeneous catalysts and in some cases lower temperatures, as compared with the literature in Table 2. In the case of GMA

carbonation, metal halides/quaternary ammonium halide-based ionic liquids have been used, affording almost total conversion at 24 h, although the selectivity to the carbonated product was not reported [33]. During the reuse of the catalyst, the authors reported some losses of material at each cycle. The catalytic performance slightly dropped after each cycle and, in particular, between the third and fourth cycle. The GMA conversion in the fifth cycle dropped to 72% for $\text{ZnCl}_2(1.99)\text{-IL-I}$ whereas it was 78% with $\text{SnCl}_4(0.66)\text{-IL-Br}$ in the fifth cycle. On the other hand, BDDE carbonation has been reported over $\text{Fe}(\text{BPMCDAC})/\text{TBABr}$ with high conversion, although this is a homogeneous system that cannot be reused [34]. Likewise, B-carbon nitride has reported high conversion and selectivity at 20 h reaction as well as good stability during five reuses [35]. In the case of BADGE carbonation, high conversions have been reported with a homogeneous catalyst (TBABr) and a heterogeneous catalyst (CaI_2/BTP), however, the selectivity data were not reported [36, 37]. Specifically, the system of CaI_2 with

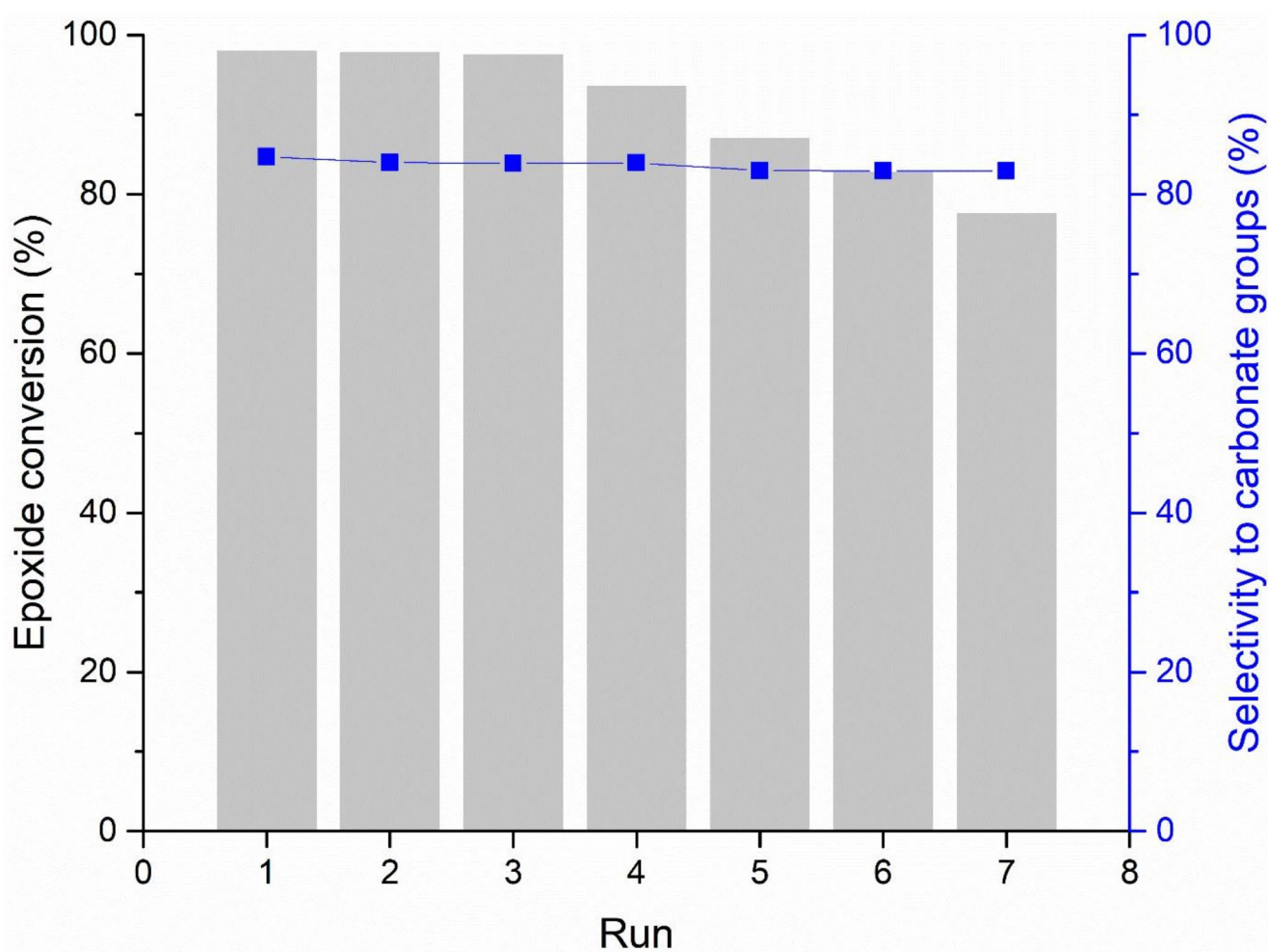


Fig. 9 Reusability of Q-SA-CH catalyst during the carbonation of GMA at 100 °C, 2 MPa CO₂, and 6 h

3-bis[tris(hydroxymethyl)-methylamino]-propane (BTP) as ligand afforded high conversion in 24 h using DMSO as a solvent and atmospheric CO₂. The epoxide conversion kept stable during three cycles. Despite the high conversions achieved with the catalytic systems of Table 2, the selectivity values were not reported in most of them. Probably, the selectivity values to carbonated products were low due to the high reaction times usually required (> 20 h). Long times imply increasing of secondary reactions of carbonates and epoxides, as explained before.

The main advantage of Q-SA-CH/KI lies in the easy and environmental synthesis route. This includes the use of pristine chitosan (non-depolymerized form). A water-soluble chitosan (depolymerized form) is required for the solubilization with the other reactants in the studies performed so far. The depolymerization of chitosan requires extensive use of chemicals such as H₂O₂, NaOH, acetic acid, methanol as well as high energy input: thermal or microwave treatment and stirring during long times (≥ 24 h). In contrast, the synthesis of Q-SA-CH was performed in a short time (7 h)

using succinic anhydride (a food additive) at room temperature before quaternization during 6 h at 60 °C. Besides, KI, which is a non-toxic substance, was used as a promoter for carbonation. In comparison, most of the catalysts in Table 2 were obtained through long times (16–24 h), or higher temperatures (450 °C in the case of Melem catalyst and B-carbon nitride) and/or extensive use of solvents such as dichloromethane, diethyl ether, acetonitrile, and toluene (in the case of ZnCl₂-IL-I, SnCl₄-IL-Br catalysts).

The reaction temperatures used in this study were within the typical range of the other works, while the reaction time was considerably short (6 h) in comparison to most of the other studies, i.e., 20–48 h. The exception was the catalyst Fe(BPMCDAC) which afforded high conversion in 4 h, although it requires TBABr as co-catalyst. The reusability of some catalysts of Table 2 was not studied (e.g. Melem and Fe(BPMCDAC)). The most of works reported that the catalytic performance dropped after each cycle. The exception was B-carbon nitride which showed an insignificant decrease in conversion and selectivity after five cycles. In

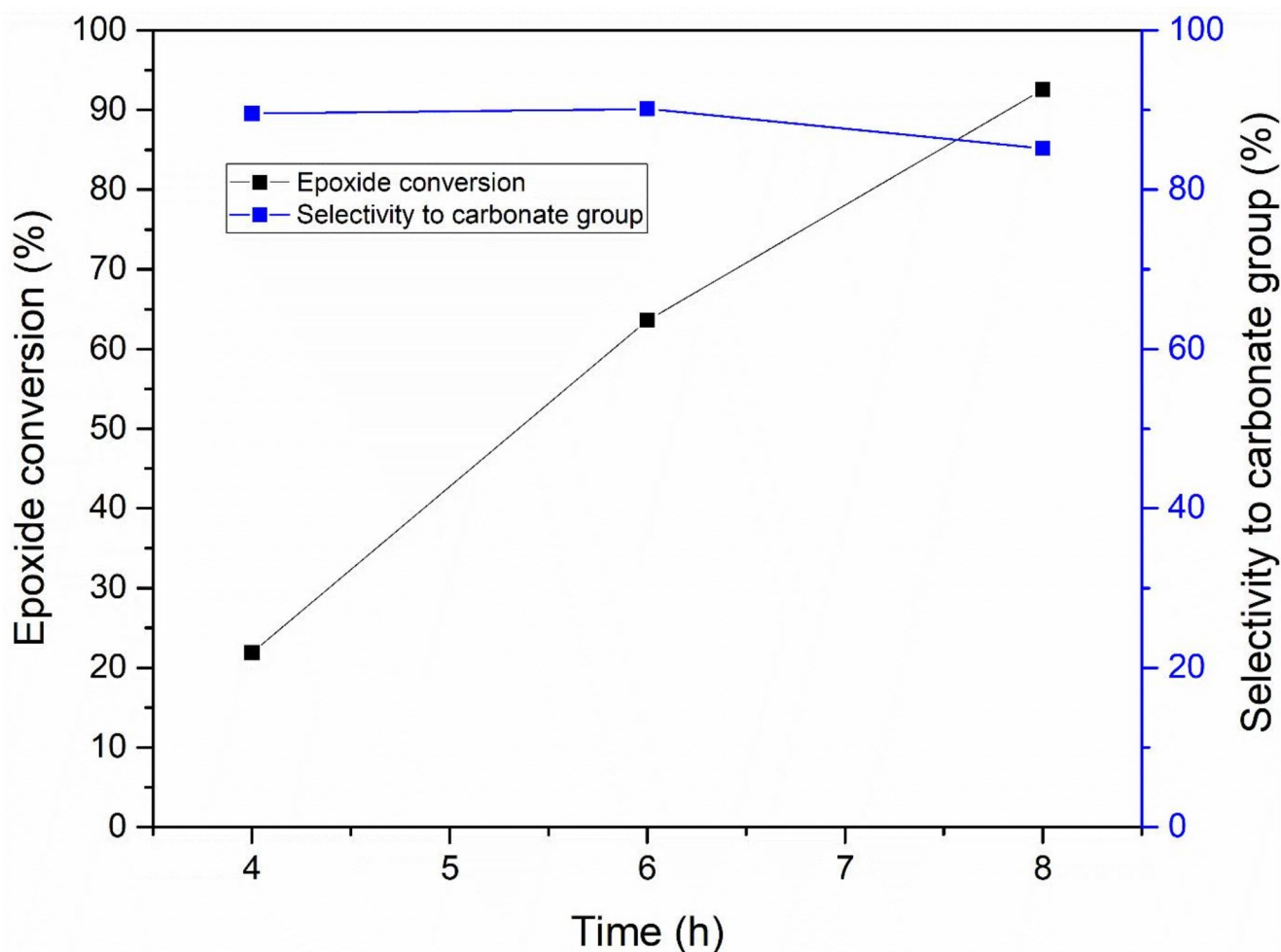


Fig. 10 Conversion of epoxide and selectivity to carbonate groups as a function of the reaction time for the carbonation of BADGE at 100 °C and 2 MPa CO₂

the case of Q-SA-CH/KI selectivity remained stable after seven cycles while the conversion dropped after the third use possibly due to losses of catalyst.

Conclusions

A new catalyst based on non-depolymerized chitosan for the carbonation of epoxides was developed. The use of this raw material is advantageous from the industrial viewpoint because depolymerization implies a large use of chemicals and energy as well as several purification stages. In addition, the catalyst obtained from non-depolymerized chitosan demonstrated better recyclability with respect to soluble chitosan, which could not be recovered from the reaction product. The catalyst was thermally stable below 210 °C and showed faster degradation than the original chitosan because of the breakage of the intramolecular hydrogen bonding after quaternization. The carbonation of GMA

yields 98% conversion and 87% selectivity to the carbonated product at 2 MPa, 100 °C and 6 h reaction without any solvent required. The catalyst was reused during 3 cycles showing stable values of conversion and selectivity to carbonated GMA. After the fourth use, the conversion decreased gradually to 78% at the seventh use while the selectivity to carbonated GMA remained stable. The use of non-depolymerized chitosan as a precursor is a key point that brings durability to the catalyst. The chemical structure of the catalyst was preserved along reaction cycles, even though some of the catalyst was lost in the product, which explains the conversion drop after recycling. The catalyst was used in the carbonation of di-epoxides (BDDE and BADGE) at 100 °C and 2 MPa yielding conversion values of 100% and 93% respectively at 8 h. The selectivity to carbonated products of BDDE and BADGE reached values of 92% and 85% respectively at 8 h. The secondary reaction of the carbonate ring with alkoxide moieties to produce ether

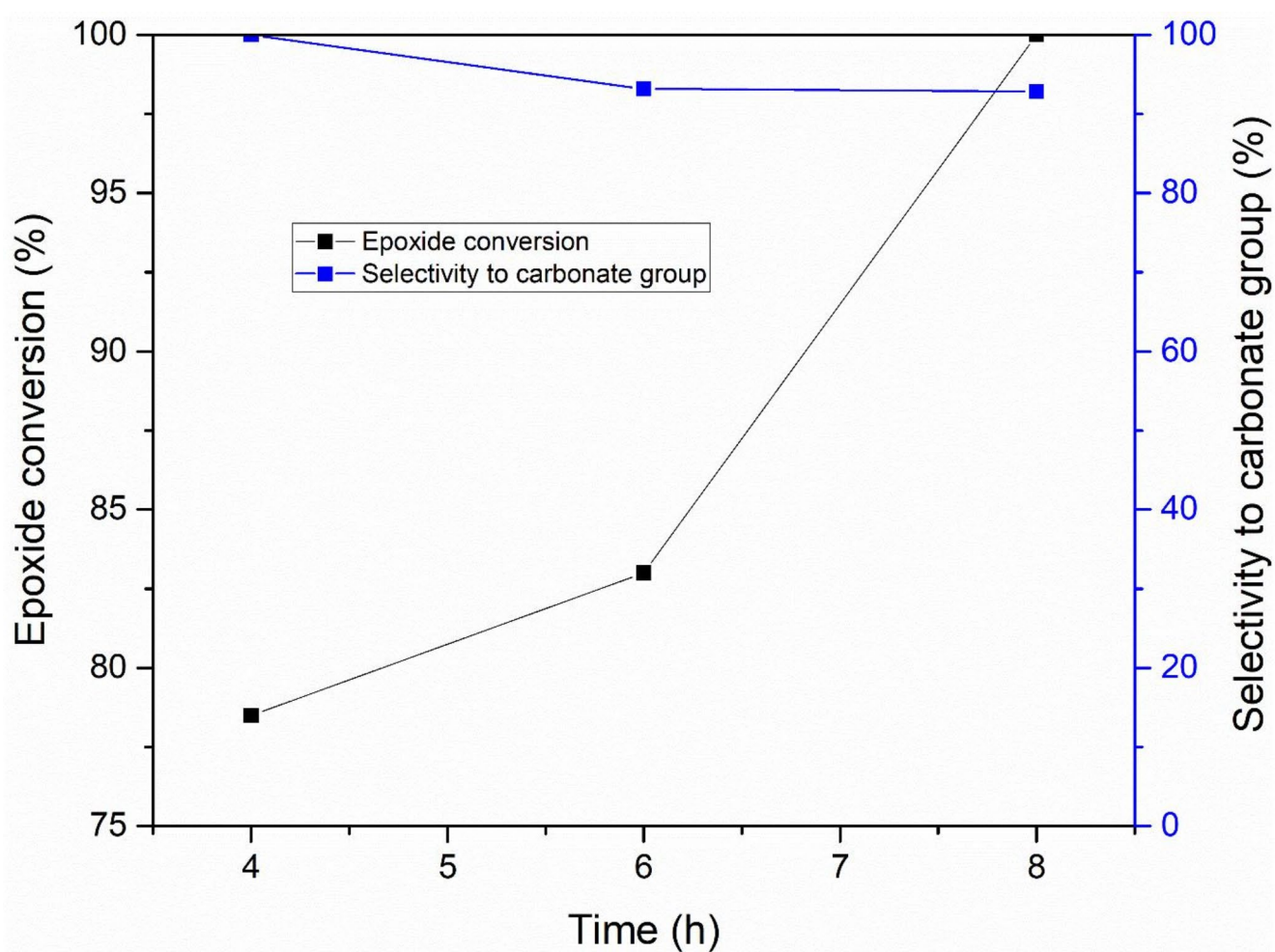


Fig. 11 Conversion of epoxide and selectivity to carbonate groups as a function of the reaction time for the carbonation of BDDE at 100 °C and 2 MPa CO₂

linkages could explain the decrease of the selectivity over time.

Table 2 Comparison of the activity of different catalysts for the carbonation of GMA, BDDE, and BADGE

Epoxide	Catalyst	Conditions	Conversion (%)	Selectivity (%)	Reference
GMA	ZnCl ₂ -IL-I	40 °C, 0.1 MPa, 24 h	>99	-	[33]
	SnCl ₄ -IL-Br	40 °C, 0.1 MPa, 24 h	>99	-	[33]
	Q-SA-CH/KI	100 °C, 2 MPa, 6 h	98	85	This work
BDDE	Fe(BPMCDAC) TBABr as co-catalyst	100 °C, 3 MPa, 4 h	97	-	[34]
	B-carbon nitride	130 °C, 2 MPa, 20 h	99.8	99.2	[35]
	Melem catalyst	130 °C, 2 MPa, 20 h	99.7	99.5	[38]
	Q-SA-CH/KI	100 °C, 2 MPa, 8 h	100	92	This work
BADGE	TBABr	110 °C, atmospheric CO ₂ , 48 h	96	-	[36]
	Ca ₂ /BTP	60 °C, atmospheric CO ₂ , 24 h Solvent: DMSO	99	-	[37]
	Q-SA-CH/KI	100 °C, 2 MPa, 8 h	93	85	This work

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10924-025-03493-9>.

Acknowledgements The authors gratefully acknowledge the financial support provided by “Ministerio de Ciencia Tecnología e Innovación de Colombia, Minciencias” within the framework of the call No. 914–2022 (Contract No. 80740-098-2022) and “Comité para el Desarrollo de la Investigación”, CODI (Project 2022–52130).

Author Contributions Conceptualization: Helen Inciarte, Natalia Cortés, David A. Echeverri, and Luis A. Rios; Methodology: Helen Inciarte, Natalia Cortés, and David A. Echeverri; Formal analysis and investigation: Helen Inciarte, Natalia Cortés, and David A. Echeverri; Writing-original draft preparation: Helen Inciarte, Natalia Cortés, David A. Echeverri, and Luis A. Rios. Writing-review and editing: David A. Echeverri and Luis A. Rios; Supervision: David A. Echeverri and Luis A. Rios.

Funding Open Access funding provided by Colombia Consortium

Data Availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing Interests The authors declare no competing interests.

Funding This work was supported by “Ministerio de Ciencia Tecnología e Innovación de Colombia, Minciencias” within the frame-

work of the call No. 914–2022 (Contract No. 80740-098-2022) and “Comité para el Desarrollo de la Investigación”, CODI (Project 2022–52130).

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Saeidi S, Amin NAS, Rahimpour MR (2014) Hydrogenation of CO₂ to value-added products—A review and potential future developments. *J CO₂ Utilization* 5:66–81. <https://doi.org/10.1016/J.JCOU.2013.12.005>
- Xiaoding X, Moulajn JA (1996) Mitigation of CO₂ by Chemical Conversion: plausible chemical reactions and Promising products. *Energy Fuels* 10:305–325. <https://doi.org/10.1021/EF9501511>
- Inciarte HC, Cortés N, Echeverri DA, Rios LA (2024) A fully bio-based monomer derived from undecylenic acid, glycerol, and CO₂ useful for the synthesis of polyhydroxyurethanes. *J Appl Polym Sci* 141:e54831. <https://doi.org/10.1002/APP.54831>
- Maheshwari P, Mistry · Mansi, Dholakiya BZ (2024) Non-traditional vegetable oil-based isocyanate-free polyurethane: a short review. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-024-05369-9>
- Gartia Y, Moore J, Felton C et al (2013) Total replacement of solvent in polyurethane synthesis using carbon dioxide soluble 1,3-dichlorodistannoxane catalysts. *J Appl Polym Sci* 128:3522–3527. <https://doi.org/10.1002/APP.38546>
- Omae I (2012) Recent developments in carbon dioxide utilization for the production of organic chemicals. *Coord Chem Rev* 256:1384–1405. <https://doi.org/10.1016/j.ccr.2012.03.017>
- Li J, Yue C, Ji W et al (2023) Recent advances in cycloaddition of CO₂ with epoxides: halogen-free catalysis and mechanistic insights. *Front Chem Sci Eng* 17:1879–1894. <https://doi.org/10.1007/s11705-023-2354-4>
- Kiatkittipong K, Mohamad Shukri MAA, Kiatkittipong W et al (2020) Green Pathway in utilizing CO₂ via Cycloaddition reaction with Epoxide—A. *Mini Rev Processes* 8:548. <https://doi.org/10.3390/pr8050548>
- Dai W-L, Luo S-L, Yin S-F, Au C-T (2009) The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts. *Appl Catal Gen* 366:2–12. <https://doi.org/10.1016/j.apcata.2009.06.045>
- North M, Pasquale R, Young C (2010) Synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem* 12:1514–1539. <https://doi.org/10.1039/C0GC00065E>
- Ramidi P, Sullivan SZ, Gartia Y et al (2011) Catalytic cyclic carbonate synthesis using epoxide and carbon dioxide: combined catalytic effect of both cation and anion of an ionic CrV(O) amido macrocyclic complex. *Ind Eng Chem Res* 50:7800–7807. <https://doi.org/10.1021/ie2003939>

12. Ramidi P, Munshi P, Gartia Y et al (2011) Synergistic effect of alkali halide and Lewis base on the catalytic synthesis of cyclic carbonate from CO₂ and epoxide. *Chem Phys Lett* 512:273–277. <https://doi.org/10.1016/J.CPLETT.2011.07.035>
13. Masahiro Y, Masataka I (2004) Novel methodologies for the synthesis of cyclic carbonates. *Chem–Eur J* 10:2886–2893. <https://doi.org/10.1002/chem.200305583>
14. Taheri M, Ghiaci M, Shchukarev A (2018) Cross-linked chitosan with a dicationic ionic liquid as a recyclable biopolymer-supported catalyst for cycloaddition of carbon dioxide with epoxides into cyclic carbonates. *New J Chem* 42:587–597. <https://doi.org/10.1039/c7nj03665e>
15. Kumar S, Wani MY, Koh J et al (2017) Carbon dioxide adsorption and cycloaddition reaction of epoxides using chitosan-graphene oxide nanocomposite as a catalyst. *J Environ Sci* 69:77–84. <https://doi.org/10.1016/j.jes.2017.04.013>
16. Besse V, Illy N, Ghislain D et al (2016) A Chitosan Derivative containing both carboxylic acid and quaternary ammonium moieties for the synthesis of cyclic carbonates. *Chemosuschem* 9:2167–2173. <https://doi.org/10.1002/cssc.201600499>
17. Pan D, Ganguly J (2019) Assessment of Chitosan Based Catalyst and their Mode of Action. *Curr Organocatal* 6:106–138. <https://doi.org/10.2174/2213337206666190327174103>
18. Tharun J, Hwang Y, Roshan R et al (2012) A novel approach of utilizing quaternized chitosan as a catalyst for the eco-friendly cycloaddition of epoxides with CO₂. *Catal Sci Technol* 2:1674–1680. <https://doi.org/10.1039/c2cy20137b>
19. Tharun J, Kim DW, Roshan R et al (2013) Microwave assisted preparation of quaternized chitosan catalyst for the cycloaddition of CO₂ and epoxides. *Catal Commun* 31:62–65. <https://doi.org/10.1016/j.catcom.2012.11.018>
20. Illy N, Robitzer M, Auvergne R et al (2014) Synthesis of water-soluble allyl-functionalized oligochitosan and its modification by thiol-ene addition in water. *J Polym Sci Polym Chem* 52:39–48. <https://doi.org/10.1002/POLA.26967>
21. Du Y, Zhao Y, Dai S, Yang B (2009) Preparation of water-soluble chitosan from shrimp shell and its antibacterial activity. *Innovative Food Sci Emerg Technol* 10:103–107. <https://doi.org/10.1016/j.ifset.2008.07.004>
22. Motokucho S, Takenouchi Y, Satoh R et al (2020) Novel polyurethane-catalyzed cyclic carbonate synthesis using CO₂ and Epoxide. *ACS Sustain Chem Eng* 8:4337–4340. <https://doi.org/10.1021/acssuschemeng.9b07752>
23. Xi X, Antonio P, Lei H et al (2022) Environmentally friendly chitosan adhesives for plywood bonding. *Int J Adhes Adhes* 112:103027. <https://doi.org/10.1016/j.ijadhadh.2021.103027>
24. Palacio J, Monsalve Y, Ramírez-Rodríguez F, López B (2020) Study of encapsulation of polyphenols on succinyl-chitosan nanoparticles. *J Drug Deliv Sci Technol* 57:101610. <https://doi.org/10.1016/j.jddst.2020.101610>
25. Govindaraj P, Abathodharanan N, Ravishankar K, Raghavachari D (2019) Facile preparation of biocompatible macroporous chitosan hydrogel by hydrothermal reaction of a mixture of chitosan-succinic acid-urea. *Mater Sci Engineering: C* 104:109845. <https://doi.org/10.1016/J.MSEC.2019.109845>
26. De Britto D, Campana-Filho SP (2004) A kinetic study on the thermal degradation of N,N,N-trimethylchitosan. *Polym Degrad Stab* 84:353–361. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2004.02.005>
27. Farkhondehnia M, Maric M (2023) Design of crosslinked networks with hydroxyurethane linkages via bio-based alkyl methacrylates and diamines. *J Appl Polym Sci* 140. <https://doi.org/10.1002/app.54039>
28. Sun J, Wang J, Cheng W et al (2012) Chitosan functionalized ionic liquid as a recyclable biopolymer-supported catalyst for cycloaddition of CO₂. *Green Chem* 14:654–660. <https://doi.org/10.1039/c2gc16335g>
29. Liu M, Lan J, Liang L et al (2017) Heterogeneous catalytic conversion of CO₂ and epoxides to cyclic carbonates over multifunctional tri-s-triazine terminal-linked ionic liquids. *J Catal* 347:138–147. <https://doi.org/10.1016/j.jcat.2016.11.038>
30. Vieira MO, Monteiro WF, Neto BS et al (2018) Surface active ionic liquids as Catalyst for CO₂ Conversion to Propylene Carbonate. *Catal Lett* 148:108–118. <https://doi.org/10.1007/s10562-017-2212-4>
31. Clements JH (2003) Reactive applications of cyclic alkylene carbonates. *Ind Eng Chem Res* 42:663–674. <https://doi.org/10.1021/IE020678I>
32. Guerdener B, Ayzac V, Norsic S et al (2023) Carbonation of -based copolymers with carbon dioxide as a reagent: from batch to solvent-free reactive extrusion. *Green Chem* 25:6355–6364. <https://doi.org/10.1039/D3GC01127E>
33. Sodpiban O, Phungpanya C, Del Gobbo S et al (2021) Rational engineering of single-component heterogeneous catalysts based on abundant metal centers for the mild conversion of pure and impure CO₂ to cyclic carbonates. *Chem Eng J* 422:129930. <https://doi.org/10.1016/j.cej.2021.129930>
34. Sheng X, Ren G, Qin Y et al (2015) Quantitative synthesis of bis(cyclic carbonate)s by iron catalyst for non-isocyanate polyurethane synthesis. *Green Chem* 17:373–379. <https://doi.org/10.1039/C4GC01294A>
35. Zhang Y, Wang Q, Chen Q et al (2024) A new boron modified carbon nitride metal-free catalyst for the cycloaddition of CO₂ and bisepoxides. *Appl Catal Gen* 675:119615. <https://doi.org/10.1016/j.apcata.2024.119615>
36. Ghasemi S, Ghezelsoufloo M, Naeimi M et al (2024) Non-isocyanate epoxy vinyl ester urethane prepolymer based on diglycidyl ether of bisphenol-A. *Iran Polym J* 33:757–772. <https://doi.org/10.1007/s13726-024-01289-7>
37. Liu K-T, Chuang J-Y, Jeng R-J, Leung M (2021) Sustainable synthesis of cyclic carbonates from terminal epoxides by a highly efficient CaI 2 /1,3-Bis[tris(hydroxymethyl)-methylamino]-propane Catalyst. *ACS Omega* 6:27279–27287. <https://doi.org/10.1021/acsomega.1c04086>
38. Zhang Y, Liang H, Li X et al (2022) Melem based mesoporous metal-free catalyst for cycloaddition of CO₂ to cyclic carbonate. *J CO2 Utilization* 64:102173. <https://doi.org/10.1016/j.jcou.2022.102173>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.