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Advancing Paper Industry Applications with Extruded Cationic Wheat Starch as an Environmentally Friendly Biopolymer

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Abstract: Within the domain of starch modification, the study delved into cationization of wheat starch through a laboratory-scale twin-screw extruder, exploring various processing conditions. Cationic starch, a crucial component for enhancing paper attributes like dry strength and printability, took center stage. The focus shifted towards integration into papermaking, investigating the transformative potential of reactive extrusion. By contrasting it with conventional dry-process methodology, innovative strides were unveiled. The study extended to pilot-scale extrusion, bridging the gap between laboratory experimentation and potential industrial implementation. Infused with scientific rigor, the investigation navigated the benefits brought about by reactive extrusion. Empirical insights highlighted a significant reduction in the intrinsic viscosity of extruded starch, decreasing from $170 \text{ mL}\cdot\text{g}^{-1}$ (native starch) to $100 \text{ mL}\cdot\text{g}^{-1}$ at a specific mechanical energy (SME) input of $800 \text{ kWh}\cdot\text{t}^{-1}$, demonstrating remarkable stability despite increased mechanical treatment. Moreover, beyond the critical threshold of $220 \text{ kWh}\cdot\text{t}^{-1}$, retention efficiency reached a stable plateau at 78%. The study revealed that utilizing a larger extruder slightly improved the mechanical properties of the paper, emphasizing the advantage of scaling up the production process and the consistency of results across different extruder sizes.

Keywords: cationic wheat starch; twin-screw reactive extrusion; degree of substitution; papermaking; specific mechanical energy; viscosity; packaging



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1. Introduction

Starch, a crucial reserve synthesized by plants from solar energy, originates from diverse plant parts such as seeds, roots, and tubers. Modified through hydrothermal and/or chemical processes, starch serves manifold applications, acting as both a food ingredient and a biodegradable material, notably in packaging. Various treatments, including chemical modification, enzymatic modification, cross-linking, polymerization, and esterification, yielded an array of starches with varying properties [1]. Recent advances in flow simulation, coupled with kinetic equations, elucidated the effects of processing parameters on the extent of cationization [2]. The study delved into the cationization of wheat starch through twin-screw reactive extrusion [3]. Cationic starches assumed a pivotal role in the paper industry, serving as coating agents, surfacing materials, and pulp ingredients [4]. Due to their electropositive nature, cationic starches synergistically bound to cellulose fibers and negatively charged mineral fillers [5]. One objective of this endeavor lay in predicting the degree of substitution in the cationization reaction concerning processing parameters and screw profile. Flow modeling emerged as a potent tool, facilitating comprehension, analysis, optimization, and process extrapolation [6]. Emphasizing extruded product properties, the focus pivoted to elucidating the transformative potential of reactive extrusion compared to conventional dry-processing methods. This exploration sought to unveil substantial enhancements introduced via the reactive extrusion process. Additionally, the recent literature related to starch and polysaccharide materials was considered for a more comprehensive understanding of the subject.

2. Materials and Methods

2.1. Preparation of Extruded Cationic Wheat Starch

In this extensive study, we utilized wheat starch with an initial moisture content of 13 wt%, sourced from Chamtor (Bazancourt, France). The experimental complexity was heightened by subjecting the starch to a meticulous extrusion process, supplemented by the precise addition of water, encompassing a dynamic range from 29% to 40% on a dry basis. To broaden the experimental scope, we also incorporated commercial cationic starches (dry process) from Chamtor to enable comparative analysis.

At the core of our research was the catalytic transformation of starch, carefully carried out using chloride 2–3-epoxypropyl-trimethylammonium (Quab 151) as the reactive agent. Figure 1 visually illustrates the principle of cationization, where a hydroxyl group is effectively replaced by an ammonium moiety. Given the structural intricacies of anhydroglucose monomers, a notable finding emerged: each monomer possesses three theoretically accessible hydroxyl groups, establishing an upper threshold of degree of substitution (DS) at 3. The degree of substitution of cationic starch quantifies the average number of cationic groups introduced per starch unit. This metric signifies the chemical modification of starch, where positive groups are incorporated to enhance its properties. An increased value of the degree of substitution indicates a proportional augmentation of cationic groups, influencing industrial applications, particularly in areas such as packaging, agri-food, pharmaceuticals, and biomaterials. The orchestration of reagent concentrations, carefully introduced into the extruder barrel, was in harmony with the targeted DS, a critical parameter recognized to range between 0.01 and 0.1 for desired applications within the domain of paper engineering [3].

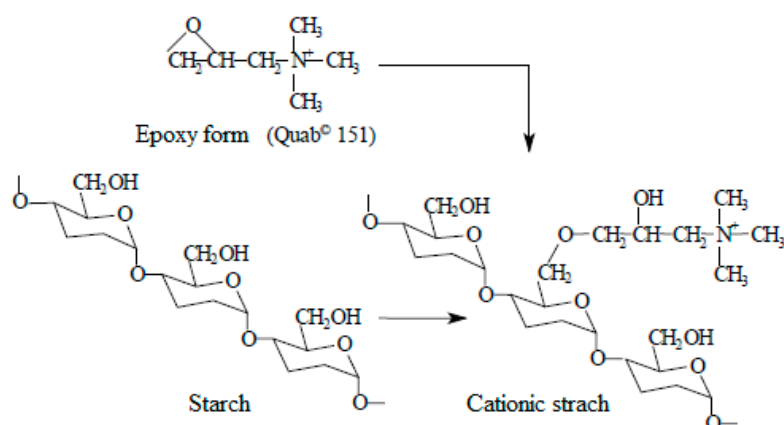


Figure 1. Starch cationisation mechanism [3].

In the realm of empirical exploration, our experimental stage was set within the laboratory-scale twin-screw extruder, Clextral BC 21 (Firminy, France). With a screw diameter of 25 mm and a length-to-diameter ratio (L/D) of 36, this intricate apparatus bore witness to the orchestrated interplay of two distinct screw profiles, meticulously depicted in Figure 2. Profile 1, characterized by its streamlined simplicity, consisted of two adjacent blocks, each housing five kneading discs strategically staggered at -45° , orchestrating a symphony of starch melting and transformation. Conversely, Profile 2 embraced a more robust constitution. Here, a third block of five kneading discs at -45° , strategically introduced after the feeding section, promised a more pronounced starch metamorphosis within barrel 7. Across all profiles, the post-feeding section maintained a constant barrel temperature of 80°C . The commencement of starch infusion took place at the hopper, while downstream, water infusion through the second barrel element was meticulously regulated by a precision pump. The experimental orchestration involved a meticulously choreographed interplay of fluctuating screw speeds (ranging from 100 to

500 rpm), synchronized with a steady feed rate (2, 2.7, and 2.9 kg/h, tailored to the specific profile) as well as a diverse range of feed rates (ranging from 1).

Profile 1 – Clextral BC 21



Profile 2 – Clextral BC 21



Profile 3 – Clextral BC 45



Figure 2. Screw profiles used for the experiments.

To substantiate and validate our findings robustly, a parallel narrative unfolded within the expansive confines of the Clextral BC 45 extruder, boasting a screw diameter of 55 mm and an L/D ratio of 23. Figure 2 provides a vivid glimpse into profile 3, distinguished by a symphony of design elements, notably featuring a left-handed screw for melting, seamlessly transitioning into a subsequent element near the die exit. This sequence was complemented by the integration of five kneading discs, strategically staggered at 45°, initiating a prelude to transformation. In harmony with our earlier endeavors, these trials resonated with a harmonious tempo, with screw speeds fluctuating between 100 and 240 rpm, all sustained by a constant feed rate of 20 kg/h. Correspondingly, feed rates danced through a spectrum from 8 to 44 kg/h, while the screw's revolutions maintained a steadfast rhythm at 240 rpm. In contrast to the laboratory extruder, the stage was set with elevated barrel temperatures of 130 °C, creating an environment characterized by heightened thermomechanical intensity. Within this domain, the measured specific mechanical energy (SME) unfolded within a spectrum spanning from 370 to 800 kWh·t^{−1}, epitomizing the dynamic essence of the process.

Various methodologies were employed to characterize and evaluate cationic starches, encompassing a range of pivotal parameters. These methodologies included determining the degree of substitution, measuring intrinsic viscosity for rheological analysis, assessing cationic demand, evaluating retention by cellulosic fibers, analyzing elongation at break, scrutinizing burst strength, and calculating specific mechanical energy. This comprehensive suite of techniques collectively provided a holistic perspective, shedding light not only on the multifaceted attributes of cationic starches, but also on the extent of starch transformation achieved through these processes.

2.2. Specific Mechanical Energy

In their native state, the wheat starch granules exhibited a round, lenticular, and flat appearance (Figure 3A). Figure 3B revealed two classes of granules: one ranging from 2 to 10 µm (minority), and the other from 20 to 35 µm (majority). This variation in size could be attributed to a mild partial hydrolysis that occurred during the wheat starch extraction process, resulting in grains breaking into subunits or small single grains. The granular form of starch seemed to completely disappear after extrusion (Figure 3C). At higher specific mechanical energy (SME) values [7], a homogeneous phase of extruded starch was obtained (Figure 3D). This complete disintegration of the granular state of starch through extrusion released amylose chains and amylopectin branches that were encapsulated in the native state, thus facilitating access to hydroxyl groups and promoting reagent grafting.

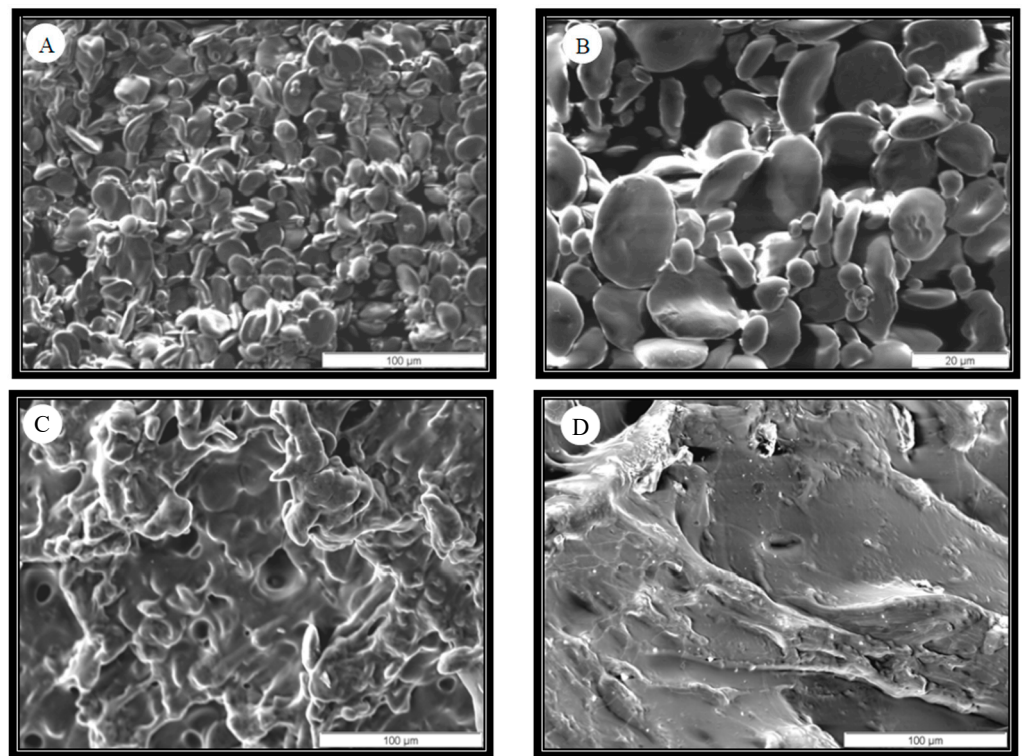


Figure 3. Scanning electron microscopy (Jeol Ltd., Tokyo, Japan; JSM-5400LV with LaB6 filament, at 10 kV) of native wheat starch ((A): 100 μm and (B): 20 μm) and extruded cationic wheat starch ((C): 301 $\text{kWh}\cdot\text{t}^{-1}$ and (D): 861 $\text{kWh}\cdot\text{t}^{-1}$).

The degree of thermomechanical treatment intensity applied to the extruded products exhibits variability contingent upon the interplay of flow rate (Q) and screw speed (N). As depicted in Figure 4, the evolution of specific mechanical energy (SME) concerning the N/Q ratio for both screw profiles remained consistent across diverse experimental conditions. Notably, a linear correlation between SME and N/Q materialized for each screw profile, enabling the direct control of the extent of starch transformation (and concomitant viscosity alteration) through the manipulation of the processing parameters: screw speed and flow rate. It is noteworthy that at a fixed N/Q ratio, the second, more restrictive profile bestows heightened SME upon the product, amplifying the potential for starch transformation, as previously highlighted.

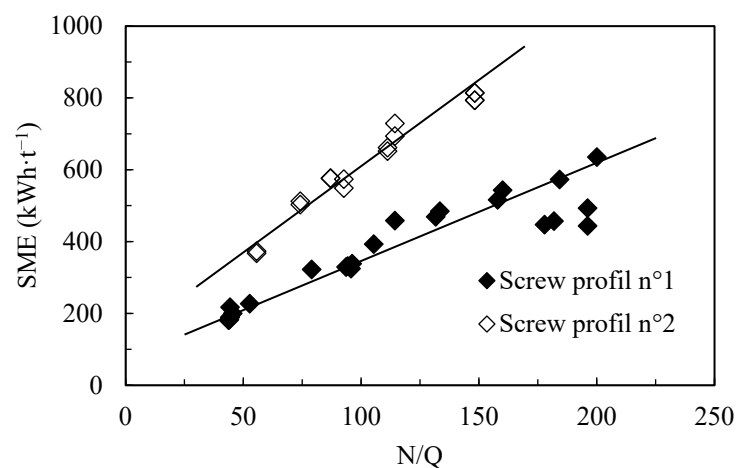


Figure 4. Specific mechanical energy variation as a function flow ratio of screw speed (both with and without reaction).

2.3. Degree of Substitution

For the quantification of the degree of substitution, we employed the Kjeldahl method [8,9]. This method facilitated the determination of the percentage of nitrogen content within the grafted groups attached to liberated starch hydroxyls after reactive extrusion. The procedure involves a dual-phase process consisting of mineralization and distillation. In the mineralization phase, the organic nitrogen content is converted into ammonium ions with the catalytic effect of titanium dioxide (TiO_2) under the influence of hot concentrated sulfuric acid. Using dedicated apparatus (Gerhardt, Kjeldatherm), an excess of sodium hydroxide is introduced, followed by the subsequent distillation stage.

Within the distillation stage, water vapor generated ammonia, which was subsequently condensed using a refrigerant and captured within boric acid. Boric acid acts as a molecular trap for ammonia, liberating borate ions. Quantification of borate is performed through titration using sulfuric acid ($0.05 \text{ mol}\cdot\text{L}^{-1}$), thereby restoring the initial pH of boric acid. The mole count of sulfuric acid aligns with the mole count of borate, which in turn corresponds to the quantity of liberated ammonia (equating to the nitrogen moles within the sample). This crucial nitrogen content measurement is pivotal in determining the extent of substitution, providing insightful information into the grafting phenomena stemming from the reactive extrusion process.

2.4. Paper Application Assessment

The cationic exchange capacity allows for the quantification of cationic starch retention within paper pulp, assessed through cationic demand determination. This determination involves measuring the zeta potential using the $\mu\text{M}\ddot{\text{u}}\text{t}\ddot{\text{e}}\text{k}$ Analytic apparatus (PCD 02) and Poly-Damac reagent (0.001 N). A suspension of 50 g of corrugated brown paperboard pulp in distilled water ($10 \text{ g}\cdot\text{L}^{-1}$) at 40°C is prepared. A titration of 10 mL of the resulting solution is conducted using Poly-Damac (initially at 0% cationic starch). Subsequently, extruded cationic starch is introduced into the mother solution in varying percentages (0.5 to 2 wt.%). Comparative analysis of these tests facilitates the evaluation of cationic retention by the cellulosic fibers. Burst strength assessment is performed using an Adamel Lhomargy EC.053 burst tester, introducing air into the paper until a notch initiates rupture. Tensile strength is conventionally measured in both the machine's longitudinal and transverse directions using a dynamometer. The ratio between transverse and longitudinal values serves as an indicator of paper anisotropy, reflecting fiber orientation. Additionally, the paper sheet's self-weight-induced rupture yields the elongation at break measurement.

2.5. Intrinsic Viscosity

Intrinsic viscosity measurements were conducted using circulating solutions at varying concentrations within a thermostated Ubbelohde viscometer set at 25°C . An aqueous solution containing potassium hydroxide, with a flow time of 97.3 s, served as the solvent. The experimental procedure commenced with the preparation of a parent solution, comprising 47 mL of water, 2.8 g of potassium hydroxide, and 0.5% (0.25 g) of pre-crushed starch. This solution was agitated for 3 h. Subsequently, four solutions ranging from 0.1% to 0.4% starch concentrations were prepared. Intrinsic viscosity was determined through the extrapolation to zero concentration of reduced viscosity. This intrinsic viscosity metric offers comprehensive insights into starch transformation, serving as a discerning indicator of macromolecular degradation. A reduction in intrinsic viscosity, compared to native starch, signifies a decline in the average molecular weight.

3. Results and Discussion

3.1. Specific Mechanical Energy

Table 1 displays a comprehensive array of 20 distinct extruded starch samples, systematically evaluated under both QUAB-present and QUAB-absent conditions. These samples represent the outcome of meticulous experimentation, spanning a wide range of specific mechanical energy (SME) conditions. The SME magnitudes varied in accordance with

the specifications of the two differently sized extruders utilized. To facilitate comparative analysis, the study also includes commercial cationic starches, labeled Samples A, B, and C.

Table 1. Starches' characteristics.

Samples	Extruder	T (°C)	Profile	SME (kWh·t ⁻¹)	QUAB	[η] (mL·g ⁻¹)	DS
1	BC 21	80	1	252	Without	138	-
2	BC 21	80	1	370	Without	132	-
3	BC 21	80	1	560	Without	121	-
4	BC 21	80	1	254	With	137	0.024
5	BC 21	80	1	376	With	131	0.031
6	BC 21	80	1	555	With	123	0.04
7	BC 21	130	2	205	Without	130	-
8	BC 21	130	2	271	Without	124	-
9	BC 21	130	2	402	Without	116	-
10	BC 21	130	2	652	Without	98	-
11	BC 21	130	2	203	With	129	0.038
12	BC 21	130	2	262	With	125	0.05
13	BC 21	130	2	398	With	116	0.058
14	BC 21	130	2	656	With	98	0.066
15	BC 45	130	3	188	Without	138	-
16	BC 45	130	3	219	Without	133	-
17	BC 45	130	3	303	Without	125	-
18	BC 45	130	3	181	With	138	0.052
19	BC 45	130	3	220	With	134	0.057
20	BC 45	130	3	297	With	124	0.062
A	Cationic wheat starch (dry process)					170	0.035
B	Cationic wheat starch (dry process)					170	0.05
C	Cationic potato starch (dry process)					-	0.2

The trend we observed, wherein SME values escalated, aligns with a corresponding reduction in intrinsic viscosity, underlining a clear indication of starch degradation. To delve deeper into the dynamics of intrinsic viscosity, we meticulously conducted measurements, at specific intervals, on the array of extruded starch samples. Noteworthy is the observation that only those samples extruded at lower SME levels (SME < 400 kWh·t⁻¹) exhibited stability over an extended period. This intriguing behavior can be attributed to the complex interplay between recrystallization phenomena and the magnitude of SME. It is important to underscore that the extrusion process bestows a significant advantage upon starch by notably enhancing its solubility profile, thus accentuating the transformative potential of this process [10]. This transformative capacity holds promise for revolutionizing various applications within the starch modification domain.

Moreover, a thorough comparison was conducted between samples that underwent cationization induced by QUAB and their non-cationized counterparts, all processed under comparable operational conditions. This comparison revealed a significant finding: the specific mechanical energy (SME) demonstrated notable resistance to the cationization reaction. This finding is consistent with prior research wherein we analyzed the rheological behavior of starch in the context of cationization, concluding that this chemical transformation had a minimal impact on the inherent rheological properties of starch [11].

3.2. Cationic Demand (Degree of Substitution)

Figure 5 depicted a clear relationship between the cationic demand and the experimental degree of substitution. This correlation became noticeable as the surrounding environment became enriched with cationic charges, resulting in a reduction in the activation of cationic demand, particularly evident in the comparison between DS values of 0.05 and 0.2. An intriguing observation was that cellulosic fibers showed similar affinities for extruded samples 13 and 18, as well as for sample B (with DS approximately 0.05).

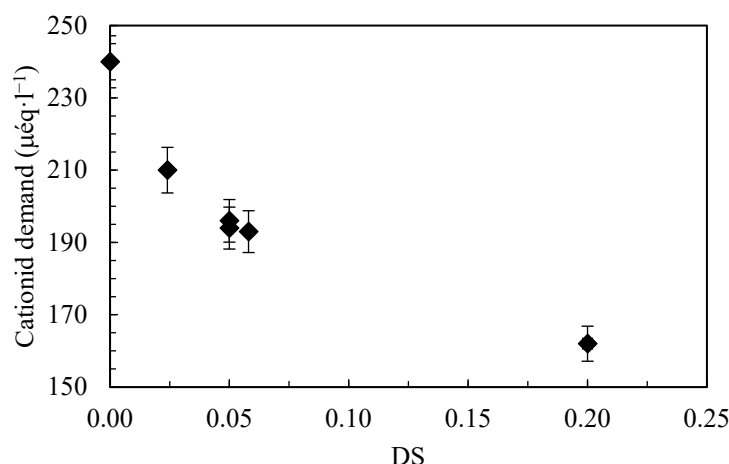


Figure 5. Cationic fiber demand in the presence of various cationic starches.

In aqueous systems, a ubiquitous acquisition of surface charge occurs on most interfaces. This charge intricately modulates the mobility of diffusing tracer particles in proximity to the interface. The electrophoretic mobility or zeta potential, contingent upon both the sample surface characteristics and the embedding medium, plays a pivotal role. Through the measurement of zeta potential of tracer beads as a function of their distance from the investigative surface, we can discern the surface zeta potential, which can fluctuate significantly, often within the range of 20 to -30 mV. This variance is attributed to factors such as botanical origin, mineral load suspensions, chemical composition, and the extent of cellulose aqueous suspension refining. Understanding these dynamics provides critical insights into the behavior of particles and their interactions with the surrounding medium, shedding light on fundamental processes in aqueous environments.

The negative charges, which induce repulsion, serve as a deterrent against flocculation and sedimentation, in direct relation to the absolute magnitude of the zeta potential. These repulsive forces acting between fibers and fillers can be nullified by introducing positively charged entities on their surfaces, underscoring the pronounced utility of cationic starches in such contexts. Understanding and manipulation of the electrokinetic properties, particularly zeta potential, enable tailored solutions for improving interactions and performance in various applications, from papermaking to colloidal stabilization.

3.3. Enhanced Retention Efficacy

Intriguing insights into the influence of cationic starches, subject to transformative reactive extrusion, are unveiled through the prism of retention dynamics, as illustrated in Figure 6. A comparative assessment of starches synthesized via the conventional “dry process” was conducted. Notably, a profound revelation arises from the investigation: the retention performance of sample 19 (DS = 0.057), characterized by a modest additive content of QUAB, parallels that of sample C (DS = 0.2). This juxtaposition underscores the remarkable potential of judiciously modified cationic starches, particularly when orchestrated through reactive extrusion, to effectuate retention enhancement. The findings open a promising avenue for tailoring cationic starch properties, ensuring optimal performance in diverse applications like paper manufacturing. The strategic integration of reactive extrusion techniques offers a dynamic toolkit for optimizing retention performance, ultimately revolutionizing how cationic starches augment efficiency and sustainability in paper production.

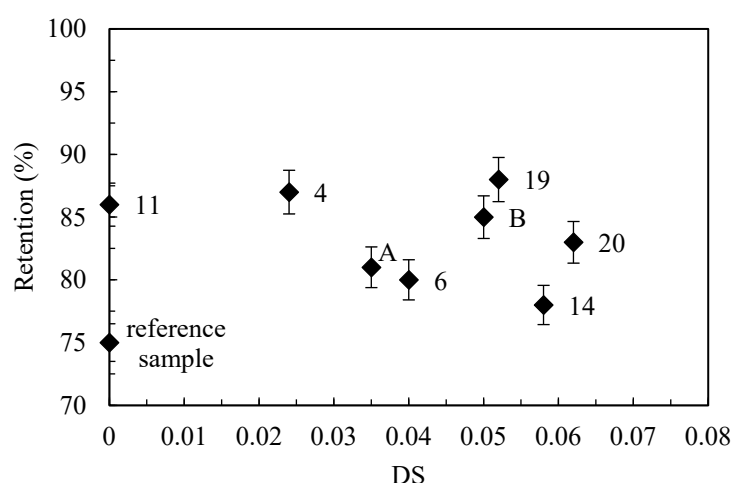


Figure 6. Comparative analysis of retention measurements across varied cationic starch formulations.

Deeper interpretation of our findings elucidates a conspicuous phenomenon: the augmentation of SME beyond the critical threshold of $220 \text{ kWh} \cdot \text{t}^{-1}$ precipitates a counterproductive influence on retention efficiency. This perceptible pattern reaches its zenith in the form of a stabilized plateau, where the retention prowess attains a commendable pinnacle of 78%, meticulously documented in Table 2. This keen observation imparts a pivotal guiding principle, encapsulating the intricate equilibrium between the impelled infusion of transformative energy and the resultant capacity for retention.

Table 2. Effect of specific mechanical energy on retention performance.

Samples	Extruder	SME ($\text{kWh} \cdot \text{t}^{-1}$)	DS	Retention (%)
4	BC 21	254	0.024	87
6	BC 21	555	0.04	80
11	BC 21	203	0.038	86
14	BC 21	656	0.066	78
19	BC 45	220	0.057	88
20	BC 45	297	0.062	83

In doing so, it casts an illuminating spotlight upon a seminal facet of cationic starch functionality within the intricate realm of papermaking processes. This unexpected parity underscores the nuanced interplay of factors shaping the retention dynamics. Delving further, a pivotal discovery takes center stage: the escalation of SME beyond the discernible threshold of $220 \text{ kWh} \cdot \text{t}^{-1}$ has a detrimental effect on the retention performance, eventually culminating in a remarkable stabilization plateau at the commendable pinnacle of 78%, meticulously corroborated by the data enshrined in Table 2. This intriguing revelation ushers in a new era of understanding, offering a pivotal vantage point for optimizing the interplay of mechanical treatment and retention efficacy in industrial paper production.

3.4. Elongation at Break and Burst Strength Analysis

Extruded cationic starches exhibit a heightened capacity to enhance both inter-fiber connections and internal cohesion. This influence on mechanical properties offers a distinct advantage by concurrently elevating elongation at break while maintaining a lower specific mechanical energy (SME), as depicted in Figure 7. Furthermore, these starches contribute to the augmentation of burst strength, a critical attribute intended to be maximized, notably evident in the case of sample 20. This augmentation in burst strength is particularly pronounced when correlated with elevated SME values, as indicated in Figure 8.

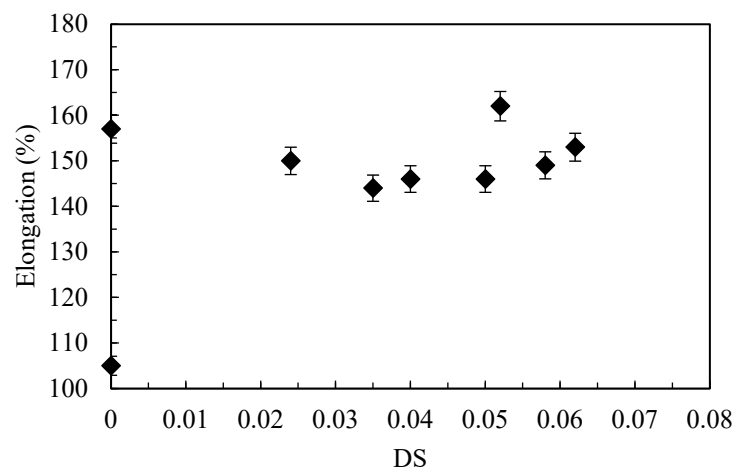


Figure 7. Elongation at break comparison among different cationic starches.

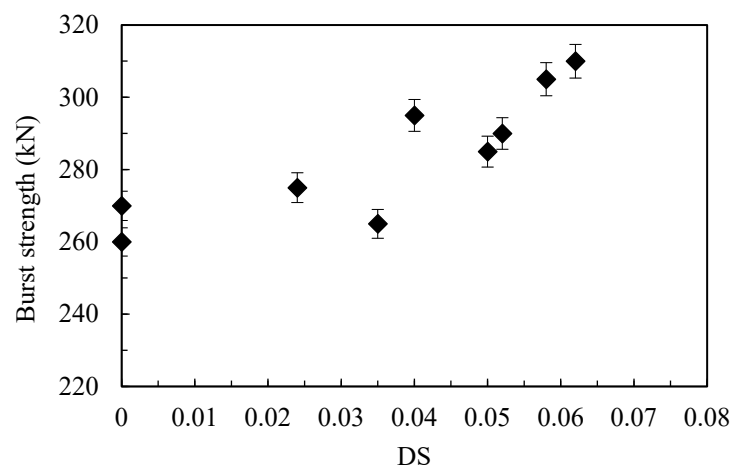


Figure 8. Burst strength variation for different cationic starches.

Interestingly, it is noteworthy that the botanical origin of the starch significantly modulates burst strength. Sample C, derived from potato starch, displays a marked reduction in burst strength, even under the influence of higher degrees of substitution (DS = 0.2). This observation underscores the intricate interplay between starch origins and resultant mechanical traits.

The transition to a larger extruder, specifically BC 45, yields a minor yet discernible enhancement in the mechanical characteristics of the paper. This enhancement is especially pronounced in Samples 14 and 20, both characterized by a degree of substitution (DS) of 0.06. It is essential to highlight that the outcomes obtained from the application of BC 45 exhibit a commendable level of consistency when juxtaposed with those generated via BC 21.

This observed marginal improvement in mechanical properties, attributed to the adoption of a larger extruder, underscores the advantages of scaling up the production process. This phenomenon is a direct result of optimized processing conditions and enhanced control within the context of a larger-scale extrusion setup. Consequently, the limited variance between the results achieved from BC 21 and BC 45 serves to underscore the reproducibility and reliability of the findings, validating the robustness of the reactive extrusion technique across varying scales.

In summation, the implementation of extruded cationic starches imparts heightened inter-fiber linkages and internal cohesion, thereby enhancing mechanical properties. The profound effect on elongation at break, coupled with the correlation between burst strength

and SME, substantiates the advantageous role of these starches. The interplay between botanical origin and burst strength underscores the intricacies of starch contributions. Furthermore, the transition to a larger extruder showcases the potential for improvement in mechanical attributes, notably for specific DS values, while maintaining a commendable level of consistency across different extruder scales. This confluence of results underscores the multifaceted potential of extruded cationic starches in advancing paper's mechanical attributes.

3.5. Rheology

Figure 9 illustrates a direct relationship between the degree of starch degradation and the magnitude of a specific mechanical energy input. Across both scenarios with the presence and absence of the reaction, and throughout the series, the intrinsic viscosity of extruded starch experiences a decline from $170 \text{ mL}\cdot\text{g}^{-1}$ (in its native state) to $100 \text{ mL}\cdot\text{g}^{-1}$ at an energy input of $800 \text{ kWh}\cdot\text{t}^{-1}$, demonstrating stability despite increasing mechanical treatment. This observed stability is attributed to the inherent molecular structure constraint of starch post-chain cleavage. Remarkably, this level of transformation remains unaffected by the type of reagent (QUAB 151 or QUAB 188) or the chosen concentrations (DS ranging from 0.01 to 0.1).

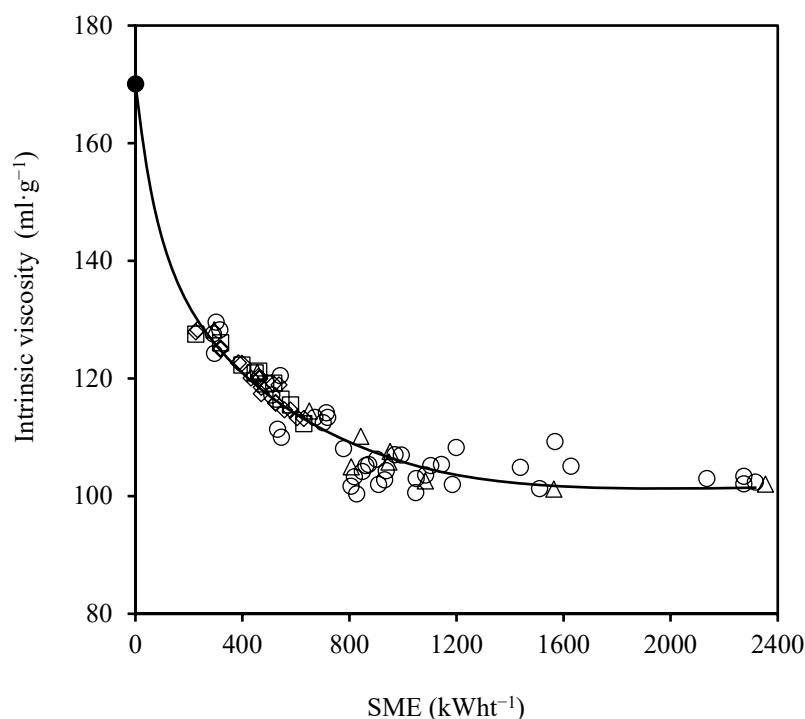


Figure 9. Intrinsic viscosity variation with SME: native starch (●), Series I (○/△: with/without QUAB), and Series II (◇/□/: with/without QUAB)—Profile 2—Die temperature = 80°C . DS = 0.04 and 0.1.

Starch products encompass both linear amylose and branched amylopectin molecules; thus, intrinsic viscosity serves as an aggregate measure reflecting degradation's influence on each constituent. Colonna et al. [12] revealed that the intrinsic viscosity of wheat flour-derived products, whether through extrusion or conventional thermal processes, offers a comprehensive insight into starch degradation. Even earlier, Colonna and Mercier [13] proposed intrinsic viscosity as a gauge for molecular degradation estimation. This perspective extends to polymolecular samples, where intrinsic viscosity characterizes an average molecular state. Relative to native starch, it serves as a sensitive indicator of macromolecular depolymerization, as any decrease in intrinsic viscosity signals a reduction in average molecular weight.

This comprehensive view from intrinsic viscosity is nuanced, as evidenced by Kowalski et al. [14], who revealed that amylopectin's intrinsic viscosity is more responsive to mechanical treatment intensity compared to amylose, despite retaining its original branched structure. The authors propose that this sensitivity arises from amylopectin's larger molecular masses rather than its branching. Consequently, Della Valle et al. [15] recommend adapting the Mark–Houwink equation to align with chain architecture and conformation in solution. Despite providing a holistic view of starch degradation, this measurement's ease of execution has led to its widespread adoption.

4. Conclusions

This study delved into the realm of cationic starches and their production using reactive extrusion. Beyond enhanced solubility, these extruded cationic starches exhibited compelling advantages compared to their conventionally produced commercial counterparts. These benefits often equaled or surpassed those obtained through traditional means, contingent upon the targeted degree of substitution (DS). A critical consideration for paper applications was specific mechanical energy (SME), the values of which were effectively managed through the new technique.

By addressing the crystallization tendencies seen in extruded starches, which induce instability, this method ensured suitability for paper-related applications. Reactive extrusion, operating without solvents, brought about enhancements in the physicochemical attributes of cationic starches, going beyond mere solubility. Parameters like elongation, impacting tensile strength and durability, were favorably influenced. Moreover, the technique significantly bolstered retention properties, a pivotal factor in paper production.

Demonstrating its robustness, this method successfully scaled up to larger extruders (BC 45) from laboratory scale (BC 21), highlighting its reliability and adaptability in producing consistent cationic starch attributes. In essence, the transformative potential of reactive extrusion extended well beyond solubility, offering improvements in critical paper-related properties. It therefore presents a promising pathway for leveraging modified cationic starches optimally within the paper and packaging industry.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ashogbon, A.O. Dual modification of various starches: Synthesis, properties and applications. *Food Chem.* **2021**, *342*, 128325. [CrossRef]
2. Xin-Ru, C.; Yu-Sheng, W.; Yan, C.; Hong-Yan, M.; Hai-Hua, C. Understanding the digestibility of wheat starch-caffeic acid complexes prepared by hot-extrusion 3D printing technology. *Food Hydrocoll.* **2023**, *141*, 108692. [CrossRef]
3. Tara, A.; Berzin, F.; Tighzert, L.; Vergnes, B. Preparation of cationic wheat starch by twin screw reactive extrusion. *J. Appl. Polym. Sci.* **2004**, *93*, 201. [CrossRef]
4. Miladinov, V.D.; Hanna, M.A. Starch esterification by reactive extrusion. *Ind. Crops Prod.* **2000**, *11*, 51. [CrossRef]
5. Matsushita, Y.; Suzuki, A.; Sekiguchi, T.; Saito, K.; Imai, T.; Fukushima, K. Mapping of the cationic starch adsorbed on pulp fibers by ToF-SIMS. *App. Surf. Sci.* **2008**, *255*, 1022–1024. [CrossRef]
6. Berzin, F.; Tara, A.; Vergnes, V. Optimization and scale-up of starch cationization in a twin screw extruder. *Polym. Eng. Sci.* **2007**, *47*, 814. [CrossRef]
7. Della Valle, G.; Koslowski, A.; Colonna, P.; Tayeb, J. Starch transformation estimated by the energy balance of a twin-screw extruder. *Lebensm. Wiss. u-Technol.* **1989**, *22*, 279. Available online: <http://pascal-francis.inist.fr/vibad/index.php?action=getRecordDetail&idt=7363314> (accessed on 3 September 2023).
8. Della Valle, G.; Colonna, P.; Tayeb, J. Use of twin-screw extruder as a chemical reactor for starch cationisation. *Stärke* **1991**, *43*, 300. [CrossRef]

9. Murúa-Pagola, B.; Beristain-Guevara, C.I.; Martínez-Bustos, F. Preparation of starch derivatives using reactive extrusion and evaluation of modified starches as shell materials for encapsulation of flavoring agents by spray drying. *J. Food Eng.* **2009**, *91*, 380. [CrossRef]
10. Guy, R.C.E.; Horne, A.W. Extrusion and coextrusion of cereals. In *Food Structure: Its Creation and Evaluation*; Blanshard, J.M.V., Mitchell, J.R., Eds.; Butterworths: London, UK, 1988; pp. 331–349. [CrossRef]
11. Jie, M.; Fujita, K.; Lei, M.; Mengnan, G.; Chunxia, D.; Jiamin, W.; Guangzhong, L. The effects of extruded black rice flour on rheological and structural properties of wheat-based dough and bread quality. *J. Food Sci. Technol.* **2019**, *54*, 1729. [CrossRef]
12. Colonna, P.; Doublier, J.L.; Melcion, J.P.; De Monredon, F.; Mercier, C. Extrusion-Cooking and Drum-Drying of Wheat Starch. *Phys. Macromol. Modif. Cereal Chem.* **1984**, *61*, 538. Available online: https://www.cerealsgrains.org/publications/cc/backissues/1984/documents/chem61_538.pdf (accessed on 3 September 2023).
13. Colonna, P.; Mercier, C. Macromolecular Structure of Wrinkled and Smooth Pea Starch Components. *Carbohydr. Res.* **1984**, *126*, 233. [CrossRef]
14. Kowalski, R.J.; Hause, J.P.; Joyner, H.; Ganjyal, G.M. Waxy flour degradation—Impact of screw geometry and specific mechanical energy in a co-rotating twin screw extruder. *Food Chem.* **2018**, *239*, 688. [CrossRef]
15. Della Valle, G.; Barrès, C.; Plewa, J.; Tayeb, J.; Vergnes, B. Computer Simulation of Starchy Products Transformation by Twin Screw Extrusion. *J. Food Eng.* **1993**, *19*, 1–31. [CrossRef]

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