Fabrication and Characterization of Complex Coacervates Utilizing Gelatin and Carboxymethyl Starch

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Abstract

Background: In comparison to native polysaccharides, modified polysaccharides have greatly expanded applications due to their improved compatibility and interactions with proteins and active compounds in the realm of food-related areas. Nonetheless, there is a noticeable dearth of research concerning the utilization of carboxymethyl starch (CMS) as a microcapsule wall material in food processing despite its common use in pharmaceutical delivery. Therefore, the development of an economical and safe embedding carrier using CMS and gelatin (GE) holds immense importance within the food processing industry. In this work, the potential of innovative coacervates formed by the combination of GE and CMS as a reliable, stable, and biodegradable embedding carrier was evaluated by turbidity measurements, thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, and rheological measurements. **Results:** The results indicate that GE-CMS coacervates primarily resulted from electrostatic interactions and hydrogen bonding. The optimal coacervation was observed at pH 4.6 and a GE/CMS blend ratio of 3:1 (w/w). However, the addition of NaCl reduced coacervation and made it less sensitive to temperature changes (35–55°C). Compared to individual GE or CMS, the coacervates exhibited higher thermal stability, as shown by TGA. Importantly, XRD analysis shows that the GE-CMS coacervates maintained an amorphous structure. Rheological testing reveals that the GE-CMS coacervates exhibited shear-thinning behavior and gel-like properties. **Conclusion:** Overall, attaining electroneutrality in the mixture boosts the formation of a denser structure and enhances rheological properties, leading to promising applications in food, biomaterials, cosmetics, and pharmaceutical products.

***Keywords*:** Gelatin carboxymethyl starch coacervates; Natural Polymers; Microcapsule wall material; Polyelectrolyte complexation; Food processing; Active compounds delivery

1. Introduction

Proteins and polysaccharides, natural compounds extensively used in the food industry [1], have a natural tendency to interact due to their amphiphilic characteristics. When these two biopolymers come into contact, they can exhibit varying degrees of interaction. Typically, thermodynamic compatibility (attraction) and/or incompatibility (repulsion) emerge between biopolymers and solvents [2]. Thermodynamic incompatible interactions mainly occur at high ionic strength and concentration levels, and therefore, extensive attention has been directed towards achieving thermodynamic compatibility, characterized by low ionic strength and low concentration, resulting in the formation of soluble complexes or condensates [3].

Studies have shown that protein-polysaccharide complexes are formed under different conditions, including pH, ionic strength, temperature, the concentration of biopolymers, and the molecular characteristics of these biopolymers, like charge density and molecular weight (M_w) [4, 5]. Moreover, the polymers formed by protein and polysaccharides offer many advantages, such as high load and stability. The complexes can serve as effective delivery systems to protect bioactive compounds, such as essential oils [6], vitamins [7], and probiotics [8].

Starch is widely recognized as a highly promising material for the development of novel carriers, owing to its advantages like binding properties, cost-effectiveness, and widespread availability [9]. Despite its remarkable features, starches still have some shortcomings, such as limited solubility in cold water, which restricts its application in food delivery. In recent years, researchers have expanded the range of wall materials by using modified polysaccharides to enhance compatibility and promote interactions with proteins and active compounds, in addition to employing native polysaccharides [10]. Chemical modification of starch offers an excellent avenue to create new starch derivatives with

enhanced properties. Carboxymethyl starch (CMS), a frequently investigated modified starch, is a negatively charged polysaccharide with a wide range of promising applications owing to its pH stability, cold water solubility, renewability, and biodegradability [11]. CMS, a negatively charged ether derivative, can effectively retain hydrophilic or hydrophobic core materials within the carrier cavity through electrostatic interactions and hydrogen bonding. Previous investigations have demonstrated its potential in the oral delivery of bioactive compounds through techniques like chemical crosslinking [12]. CMS has been used to fabricate innovative delivery systems covalently crosslinked with chitosan hydrochloride [13] and polyelectrolyte complex (PEC) microparticles with chitosan for targeted drug delivery [14].

Gelatin (GE) is a protein obtained through the partial hydrolysis of collagen. It can be enzymatically degraded into various amino acids, resulting in the absence of harmful by-products. Gelatin holds a "generally recognized safe" (GRAS) status conferred by the US Food and Drug Administration (FDA) thanks to its non-toxic, non-carcinogenic, biodegradable, and environmentally friendly nature [15]. Notably, gelatin is an amphoteric protein whose molecules contain 13% positively charged amino acids (arginine and lysine) and 12% negatively charged amino acids (aspartate and glutamate) [16]. This gives gelatin a net positive charge when the pH is below its isoelectric point (pI). Gelatin-based electrostatic complexes remain the preferred choice for carriers in commercial applications, attributed to their excellent emulsifying capabilities, high stabilizing activity, water solubility, and significant crosslinking potential through their primary amino groups.

Numerous studies have explored the coacervation of gelatin with various biomacromolecules, including sodium carboxymethyl cellulose (CMC) [17], sodium alginate [18], and Persian gum [19]. However, while there has been extensive research on carboxymethyl starch as a pharmaceutical delivery carrier

material recently [20-22], there is a limited body of work on its application as a wall material for microcapsules in food processing. Therefore, this study established a complex coacervation system of CMS and GE to investigate the interaction mechanism between them as new wall materials. This offers valuable theoretical insights for the application of the new wall material system in the encapsulation of active compounds, particularly in the food and related industries. The influence of pH, temperature, total biopolymer concentration, ionic strength, and GE/CMS blend ratio ($R_{GE/CMS}$) on the interaction of GE-CMS mixtures was investigated through turbidity analysis. Besides, various analytical techniques were employed to characterize the physicochemical properties of GE-CMS complexes, including Fourier transform infrared (FT-IR) spectroscopy, X-ray diffractometry (XRD), and thermogravimetric analysis (TGA). Furthermore, the rheological properties of GE-CMS complexes were also measured. It is believed that this study will provide helpful information to enhance the application of starch-based delivery systems through electrostatic interactions.

2. Materials and methods

2.1. Materials

Maize starch, containing 12.8% moisture and 27.5% amylose, was sourced from National Starch Pty Ltd. Gelatin (GE, type B, Bloom 200) was supplied by Boyang Biotechnology Co., Ltd. Sodium chloroacetate was purchased from Shanghai McLin Biochemical Technology Co., Ltd. All other chemicals used were of analytical grade.

2.2. Preparation of carboxymethyl starch (CMS)

To prepare CMS, firstly, 8 g regular maize starch (RMS) and 60 mL of 80% (v/v) ethanol were added in a three-necked flask under continuous stirring, followed by a slow addition of 3.61 g sodium hydroxide. The reaction was maintained at 30 °C for 60 min. Then, 12.6 g of sodium chloroacetate

was introduced, and the mixture was stirred at 40 °C for 3 h. After completing the reaction, any unreacted sodium hydroxide was neutralized using glacial acetic acid. The resulting mixture was filtered, and the slurry was washed with an 80% ethanol aqueous solution until no chloride ions were detected (confirmed with 0.2 M $AgNO_3$). The resulting precipitate was dried in an oven at 40 °C for 24 h and subsequently ground into a fine powder, passing through a 100-mesh sieve. The degree of substitution (DS) of the prepared CMS was 0.76.

2.3. Preparation of biopolymer solution

A certain quantity of gelatin was dissolved in deionized water and allowed to soak for 2 h to achieve full swell. Then, it was heated at 60 °C for 30 min. The CMS solution was stirred using magnetic force at room temperature for 4 h and then refrigerated overnight at 4 °C to ensure complete hydration.

2.4. ζ-Potential measurement

A zetasizer (Nano-ZS, Malvern Instruments Ltd, Malvern, Worcestershire, UK) was used to measure the ζ-potentials of samples at a concentration of 0.1% (w/v) under different pH conditions.

2.5. Turbidity measurement

Turbidity measurements were utilized to study the GE-CMS interaction behavior. The pH of the solutions was adjusted using acetic acid (10%, v/v) through an injector. The mass mixing ratio ($R_{GE/CMS}$) was varied from 1:1 to 5:1 at a total concentration of 0.1% (w/v). The total concentration in this study ranged from 0.05% to 0.1% at a constant $R_{GE/CMS}$ of 3:1. Temperature was varied in the range of 35–50 °C, and ionic strength was adjusted from 0 to 10 mM. Turbidity analysis was performed using a UV-vis spectrophotometer (UV-3802, Unico Instruments Corporation, Shanghai, China) at 600 nm. Deionized water was used as a blank for all tests.

2.6. FT-IR spectroscopy

The FT-IR spectra of RMS, GE, CMS, and GE-CMS complex coacervates were acquired using FT-IR spectroscopy (VERTEX 70, BRUKER, Germany). Each sample was mixed with KBr powder. The frequency range was set from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.7. X-ray diffraction (XRD)

The powder was characterized using a Rigaku Ultima IV X-ray diffractometer operating at 40 kV and 40 mA. Diffractograms were collected in reflection mode within a range of 4° to 50° at a scanning speed of 2 °/min.

2.8. Thermogravimetric analysis (TGA)

The thermal stability of GE, CMS, and GE-CMS coacervates was determined using a TGA instrument (TG 209 F1 Libra, German). The parameters for the analysis were as follows: The temperature range was set from 35 °C to 500 °C with a heating rate of 20 °C/min, and a nitrogen flow rate of 20 mL/min was maintained.

2.9. Rheological measurement

Dynamic rheological properties of GE-CMS complexes were assessed using a HAAKE MARS 60 rheometer (Thermo Fisher Scientific, USA). The GE-CMS coacervates were loaded onto the plate and allowed to equilibrate for 3 min. Strain sweep tests were first carried out to determine the linear viscoelastic region of the samples, and a constant strain value of 1% was selected for the subsequent frequency sweep tests. Dynamic viscoelastic properties of GE-CMS coacervates were measured over a frequency range from 0.1 to 10 Hz. Viscosity was measured using a steady shear rate sweep, and the temperature was set at 25°C.

2.10. Statistical analysis

The experimental data were presented as the mean ± standard deviation (SD) based on at least triplicate measurements. Statistical analysis was performed using Origin 2021 and SPSS 26.0 software. Duncan's HSD test ($p < 0.05$) was used to determine significant differences.

3. Results and discussions

3.1. Effect of pH on the ζ-potential of gelatin and carboxymethyl starch

The pH plays a crucial role in complex coacervation, impacting the charge interactions between proteins and polysaccharides [23]. **Fig. 1** illustrates the pH-dependent ζ-potential of 0.1% GE and CMS. CMS showed a negative zeta potential, decreasing from −15 to −39 mV as the pH increased due to carboxylic group deprotonation. In contrast, GE showed a decreasing trend as pH gradually increased, shifting from positive to negative at pH 5.25, which is the pI of gelatin. At pH < pI (5.25), gelatin becomes positively charged due to the protonation of amino groups and the neutralization of carboxylate groups. These measurements show that GE and CMS carry opposite charges within the pH range of 5.25 to 3, suggesting potential electrostatic complexation between these biopolymers in this pH range.

3.2. Turbidity measurement: Factors influencing the complex coacervation of gelatin and carboxymethyl starch

3.2.1 Effects of biopolymer concentration and mass ratio

Turbidity measurement provides valuable insights into the coacervation progress. **Fig. 2A** shows the effect of varying the total biopolymer concentration on GE-CMS complexes under different pH conditions. The total biopolymer concentrations, ranging from 0.05 to 0.1% (w/w), were measured at

a fixed 3:1 biopolymer mixing ratio in the absence of NaCl. The maximum turbidity values increased as the total biopolymer concentration rose. Specifically, a higher concentration of total biopolymer in the solution means that more positively charged protein fragments can interact with the anionic sites on CMS chains.

Furthermore, all these curves presented a similar trend, with maximum turbidity occurring at nearly 4.6 **(Fig. 2B)**, indicating that pH-absorbance behavior is independent of the total biopolymer concentration. These results align with previous research on casein/gum tragacanth mixtures [24]. Previous reports have revealed that at higher total biological concentrations, an increased presence of counter ions in the solution can effectively shield the charged sites on the surface of biological macromolecules [25, 26]. Therefore, the 0.1% total biopolymer concentration was selected for further investigations into the factors influencing the turbidity of GE-CMS coacervates.

The impact of mass ratio ($R_{GE/CMS}$ = 1:1–5:1) on complex coacervation was studied at a 0.1% total biopolymer concentration without the addition of sodium chloride. As shown in **Fig. 2C**, the turbidity curve shifted towards a higher pH value with an increase in the mixing ratio. With $R_{GE/CMS}$ > 4, the pH of the soluble complex formed was higher than the pI of GE (Fig. 2D). As $R_{GE/CMS}$ decreased, the acidity of the solution gradually increased, indicating a greater requirement for GE's positive ions to neutralize the excess negative charge ($–COO^-$) of CMS. When the mixing ratio was 3:1, the maximum turbidity was attained. Hence, it can be inferred that CMS chains became saturated and adsorbed by gelatin, showing the strongest electrostatic interaction.

The critical pH values (the pH value at which the slope of the turbidity curve first changes, pH_c; the pH value corresponding to a sudden increase in the slope of the turbidity curve, $pH_{\varphi 1}$; and the pH value corresponding to the maximum turbidity, pH_{opt}) shifted to higher pH values as the mixing ratio

189 increased from 1:1 to 5:1**(Fig. 2D)**, confirming that an increased mixing ratio enhanced the formation
190 of GE-CMS coacervates. Actually, polysaccharides may not require a large number of positive charges
191 to form complexes, and their stability reached a plateau with a further increase in biopolymer mixing
192 ratio [27].
193
194 **3.2.2. Effects of NaCl concentration (C_{NaCl}) and temperatures**
195 **Fig. 3A** presents the turbidity curves of GE-CMS coacervates at different C_{NaCl}. The maximum
196 turbidity was observed at pH 4.6 in the absence of NaCl. However, as C_{NaCl} increased, the turbidity
197 decreased, consistent with findings on ovalbumin and propylene glycol alginate coacervates [28]. The
198 consistent reduction in the turbidity with increasing C_{NaCl} can be explained by a competition
199 mechanism. The addition of NaCl introduced Na^+ ions to compete with the positively charged sites of
200 GE for binding with CMS, while Cl^- ions competed with the negatively charged sites of CMS to bind
201 to GE. As a result, the binding affinity between gelatin and carboxymethyl starch gradually diminished.
202 A shift toward lower pH in critical pH was observed with increasing C_{NaCl} **(Fig. 3B)**, indicating a
203 lower degree of electrostatic attraction and a greater need for acidity for complex coacervation.
204 However, $pH_{\varphi 2}$, the pH value corresponding to the stable slope of the turbidity curve, shifted to higher
205 pH values, and the range between $pH_{\varphi 1}$ and $pH_{\varphi 2}$ for biopolymer interactions reduced. Another study
206 suggested that the reduction in pH range between $pH_{\varphi 1}$ and $pH_{\varphi 2}$ was attributed to ion screening of the
207 protein-polysaccharide charges [29].
208 The relationship between turbidity and pH was also examined at critical temperatures (35–55°C).
209 As shown in **Fig. 3C**, the turbidity of the GE-CMS complexes increased as the temperature reached
210 40 °C, possibly due to the higher solubility of gelatin. This leads to the exposure of more hydrophobic

groups in the aqueous solution, facilitating the participation of phenolic hydroxyl groups in the reaction. However, as the temperature continued to rise, the turbidity values decreased, and critical pH values shifted to lower pH values (**Fig. 3D**), potentially related to a decrease in hydrogen bonding [30]. Liu et al. [31] also observed a correlation between critical pH values and temperature, which decreased with increasing temperature. Changes in temperature had a minimal effect on the turbidity curve of the GE-CMS complexes, indicating that hydrophobic interaction is not the primary driving force behind the GE-CMS complexes.

3.3. Fourier-transform infrared (FT-IR) spectroscopy analysis of the complex coacervation of gelatin and carboxymethyl starch

Fig. 4A displays the infrared spectra of RMS, GE, CMS, and GE-CMS coacervates. Compared to RMS, the spectrum of CMS showed a new absorption peak in the range of 1300–1600 cm^{-1}. The absorption peaks at 1590 cm^{-1} and 1409 cm^{-1} could be attributed to carbonyl functional groups, confirming the occurrence of starch carboxymethylation. Similar results were observed in carboxymethylated kudzu starch [32]. The infrared absorption peaks of gelatin induced a characteristic band at 3407 cm^{-1} resulting from N-H and O-H vibrations [33]. Additionally, the peaks at 1629 cm^{-1} (C=O band vibration of amide I), 1526 cm^{-1}, and 1229 cm^{-1} represented amide II and amide III, respectively [34]. The spectrum of GE-CMS coacervate closely resembled that of gelatin, with some absorption peaks shifting. Notably, the N-H bands of GE (3270 cm^{-1}) shifted to 3294 cm^{-1}, indicating that the amide group of GE might have formed strong hydrogen bonds with the hydroxyl group of CMS during the coacervation process. These results align with previous research [35].

Furthermore, the amide II band in gelatin exhibited a shift from 1526 cm^{-1} to 1540 cm^{-1},

corresponding to the disappearance of the -NH_3 vibration peak in gelatin. The most significant change occurred in the amide I band, shifting from 1629 cm^{-1} to 1640 cm^{-1}. This change is attributed to the electrostatic interaction between the carboxyl groups of CMS and the amino groups of GE, indicating the occurrence of complex coacervation. This change may be related to the transformation of the protein from the α-helical structure to more organized β-sheet and amorphous structures [36], indicating the occurrence of complex coacervation. A similar slight shift has also been observed in egg proteins-xanthan gum mixtures [37].

In addition, the absorption peak representing the symmetric and asymmetric stretching vibrations of carboxyl groups (1590 cm^{-1} and 1409 cm^{-1}) disappeared upon the forming of GE-CMS coacervates. This suggests that in the presence of proteins, carbohydrate molecules have a reduced ability to form intermolecular hydrogen bonds [38]. Therefore, it can be concluded that GE-CMS coacervates formed mainly through hydrogen bonding and electrostatic interaction.

3.4. X-ray diffraction (XRD) analysis of the complex coacervation of gelatin and carboxymethyl starch

Assessing whether a substance is in an amorphous or crystalline state is important for evaluating the stability of dried products. The XRD patterns of gelatin, CMS, and their coacervates are shown in **Fig. 4B**. Gelatin showed distinct broad peaks at 20.92° and 7.75°, which correspond to the triple helical crystal structure of collagen [39].

Notably, both GE and GE-CMS coacervates share similar XRD patterns, highlighting the high compatibility between gelatin and CMS. However, there is a reduction in the intensity of XRD peaks at 20.92° and 7.75° for the GE-CMS complexes. Interactions with polysaccharides can induce

structural changes in proteins. Previous studies have shown that the formation of xanthan gum–gelatin coacervates could change protein structures by disrupting the compact molecular arrangement of gelatin chains [40]. Ghobadi et al. [35] also observed a decrease in diffraction peak intensity when Alyssum homolocarpum seed gum was added to Grass pea (Lathyrus sativus) protein isolates due to the formation of hydrogen bonds between these two biopolymers.

Importantly, the GE-CMS coacervates maintain their amorphous structures. Amorphous structures are known for their higher soluble and hygroscopic properties. Furthermore, they promote the efficient release of core materials within capsules.

3.5. Thermogravimetric analysis (TGA) analysis of the complex coacervation of gelatin and carboxymethyl starch

As depicted in **Fig. 5**, all samples exhibited a two-step weight loss pattern during thermal analysis. The first minor mass reduction, occurring at approximately 100 °C, was primarily due to water evaporation from the biopolymers. Subsequently, the second step in weight loss is associated with the decomposition of these biopolymers.

Specifically, CMS started to undergo a substantial weight reduction in the temperature range of 225-314 °C due to the degradation of the backbone, involving processes such as carbonization and ash formation. Previous studies have indicated that CMS showed relatively low thermal stability, particularly when it had a high DS [41]. When heated to 500 °C, CMS retains only about 50% of its initial weight.

In contrast, gelatin demonstrated high-temperature stability and underwent significant weight loss at temperatures ranging from 267 to 374 °C, with a derivative thermogravimetric (DTG) curve peak at

342 °C (**Fig. 5B**), which corresponds to degradation temperature (T_d). This weight loss can be attributed to the cleavage of covalent peptide bonds in the gelatin structure [42]. Gelatin residue accounts for about 28% of its initial weight when heated to 500 °C, aligning with previous findings [43].

In contrast to CMS and gelatin, the GE-CMS coacervates showed a more gradual weight loss profile and retained about 34% of their weight even at 500 °C. The decomposition temperature of coacervates was 44 °C higher than CMS, and this enhanced thermal stability can be attributed to the effective molecular interactions between CMS and GE within the coacervates. Notably, the coacervates did not undergo thermal decomposition until reaching temperatures as high as 251 °C, indicating significantly improved thermal stability compared to their individual components.

3.6. Rheological properties of the complex coacervation of gelatin and carboxymethyl starch at different conditions

3.6.1 Effect of pH

The apparent viscosity of GE-CMS coacervates at different coacervation pH levels is presented in **Fig. 6A**. The coacervates exhibit relatively high viscosity, exceeding 100 Pa/s at low shear rates. Furthermore, they displayed shear-thinning behavior, likely attributed to the structural relaxation within the polysaccharides [44]. Notably, the coacervates reached their highest viscosity at pH 4.6, mainly due to the enhanced interactions between GE and CMS.

Oscillatory measurements provided information about the viscoelastic behavior of the coacervates. As can be seen from **Fig. 6B**, the elastic modulus was higher than the viscous modulus ($G' > G''$), indicating a gel-like character. This gel-like network structure aligns with previous findings in sodium caseinate-gum tragacanth coacervates [45]. In contrast, whey protein–puka gum exhibited a

more viscous behavior [46]. Therefore, a rheological study of different coacervates is instrumental in understanding their internal structure. Notably, the values of G' and G'' reached their maxima at pH 4.6, in line with previous research [47] suggesting that coacervates collected at their pH_{max} exhibit the highest gel strength as a result of the tighter structures resulting from stronger electrostatic attraction.

3.6.2 Effect of C_{NaCl}

The apparent viscosity of GE-CMS coacervates at different C_{NaCl} is shown in **Fig. 6C**. The shear-thinning behavior remained unchanged with the addition of NaCl, but the apparent viscosity decreased as C_{NaCl} increased. This phenomenon can be attributed to salt ions shielding the charges of the biopolymer, leading to a more relaxed coacervate structure and reduced viscosity. Moreover, the presence of sodium chloride tended to increase the water content in the coacervates, further contributing to their looser structure.

The modulus (G' and G'') of the coacervates increased with frequency and remained roughly parallel, indicating weak gel-like characteristics in the binding of gelatin to CMS. Interestingly, these modulus values decreased with increasing C_{NaCl} from 0 to 10 mM, indicating that the presence of salt ions shields the biopolymer charges, weakening the electrostatic interaction between protein and polysaccharide. It has been observed that low concentrations of salt ions can shield the repulsive forces between proteins and polysaccharides, facilitating molecular binding and enhancing the modulus of the composite condensate [48]. Ovalbumin-carboxymethylcellulose coacervates, for instance, showed the maximum values of G' and G'' values at a salt ion concentration of 20 mM [49]. Therefore, it can be inferred that the rheological properties of a colloidal system are often closely related to its internal structure.

4. Conclusion

In this study, the complex coacervates based on gelatin and CMS were prepared and thoroughly characterized, including turbidity analysis, TGA, XRD, FT-IR, and rheology, to elucidate the interaction mechanism between these two biopolymers. The FT-IR analysis reveals that GE-CMS coacervates were primarily formed through electrostatic interactions and hydrogen bonding under specific conditions. Notably, the strongest electrostatic interaction of GE-CMS coacervation was observed at a $R_{GE/CMS}$ of 3:1 (w/w) and pH 4.6. Additionally, the coacervates exhibited the highest viscosity at pH 4.6, mainly due to the stronger interactions between GE and CMS, which aligns with the results of turbidity measurements. Compared to individual GE and CMS, the GE-CMS coacervates showcased greater thermodynamic stability according to TGA. Moreover, XRD analysis reveals that the GE-CMS coacervates maintained their amorphous structure. These findings hold significant implications, providing valuable theoretical support for the utilization of GE and CMS interactions in various applications, such as foods, biomaterials, cosmetics, and pharmaceutical products.

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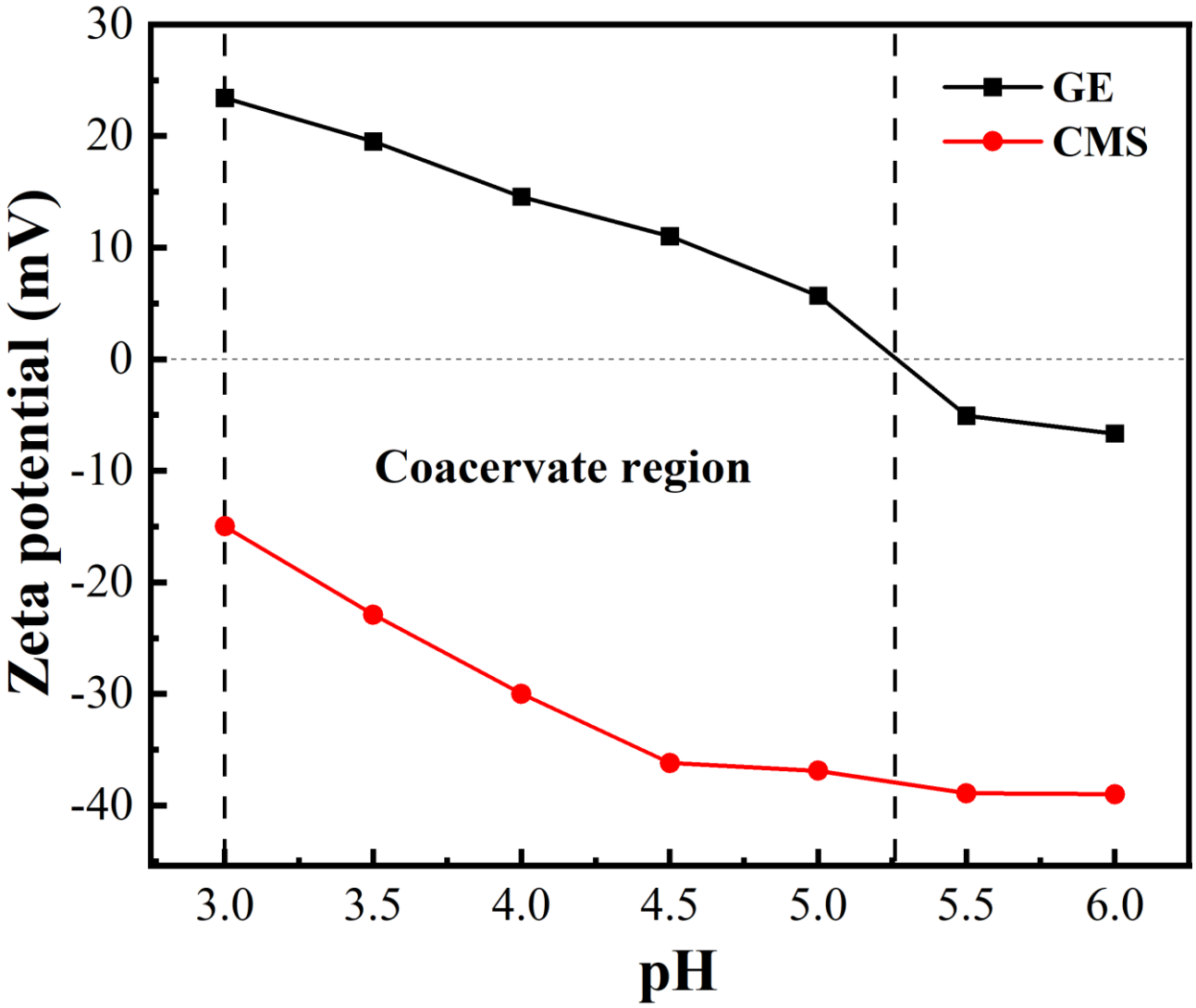

Fig. 1. ζ-potential of GE and CMS at different pH values.

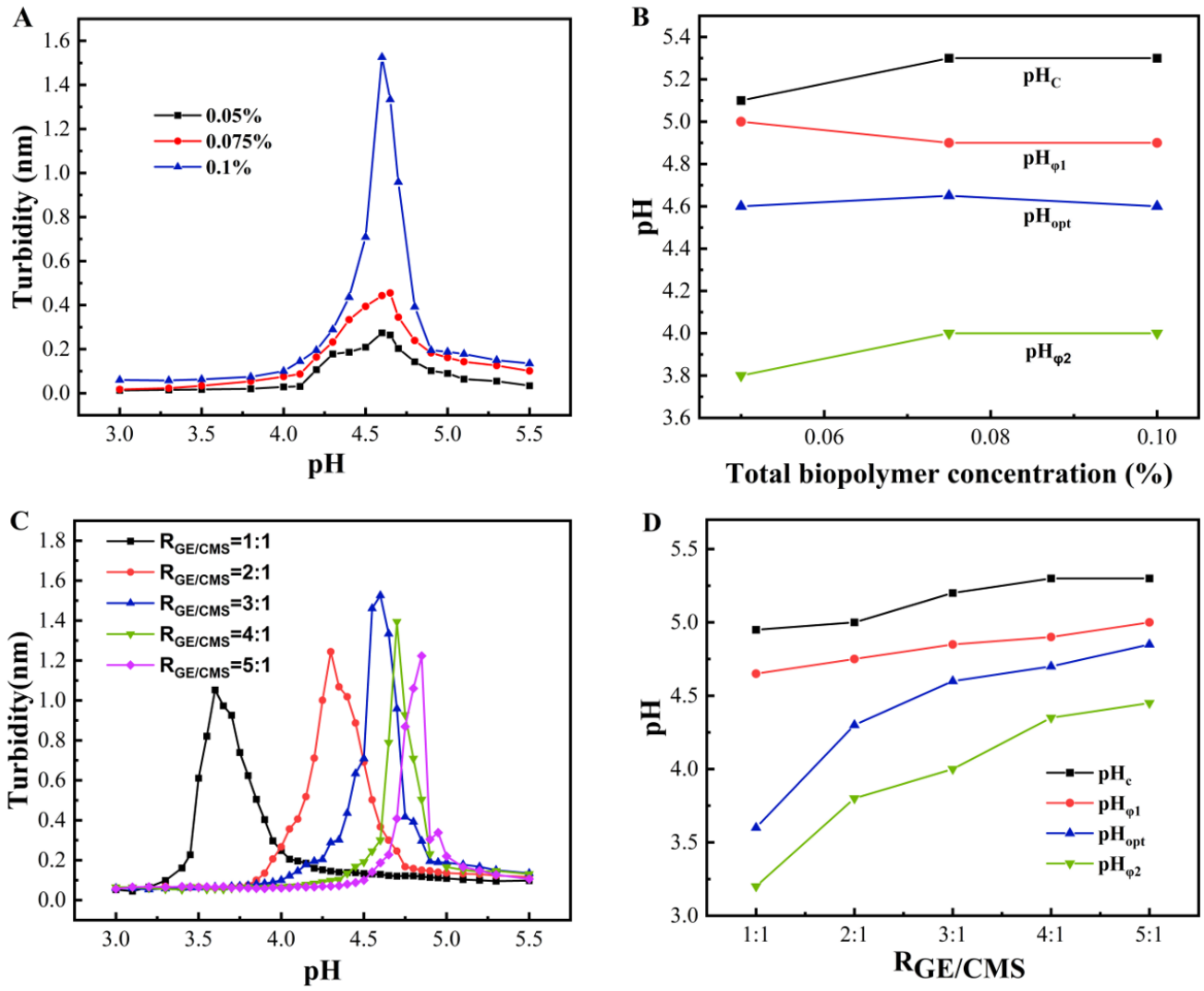

Fig. 2. Turbidity results of GE-CMS mixtures at different biopolymer concentration (A) and different mass ratios (C); critical pH values according to the biopolymer concentration (B) and the mass ratio (D) of GE-CMS mixtures.

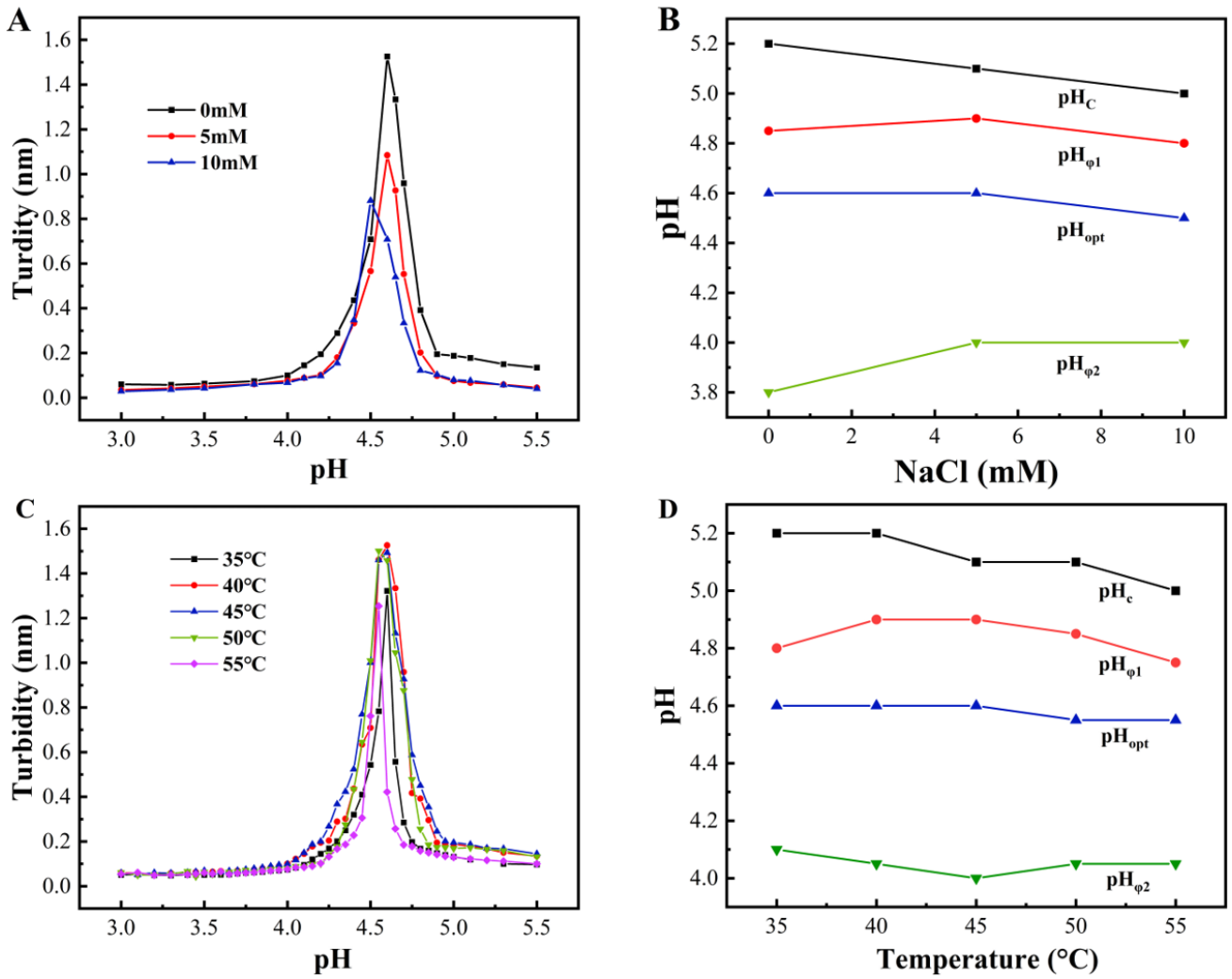

Fig. 3. Turbidity results of GE-CMS mixtures at different C_{NaCl} (A) and different temperatures (C); critical pH values according to the sodium chloride concentration (B) and the temperature (D) of GE-CMS mixtures.

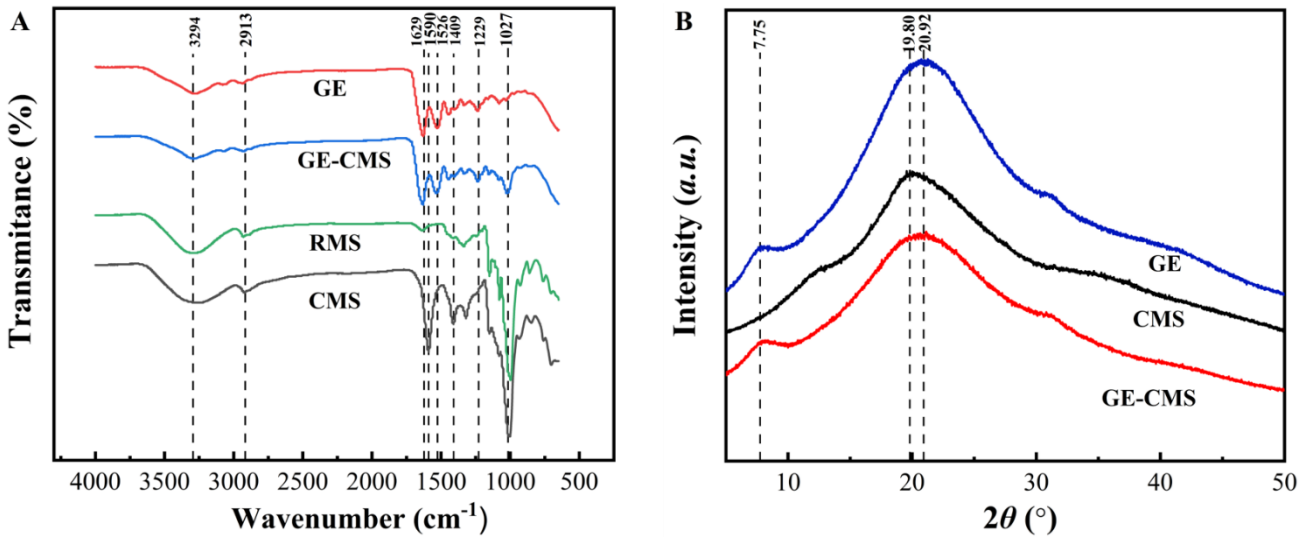

Fig. 4. FT-IR spectra of RMS, CMS, GE, and GE-CMS coacervates (A); and XRD patterns of GE, CMS, and GE-CMS coacervates (B).

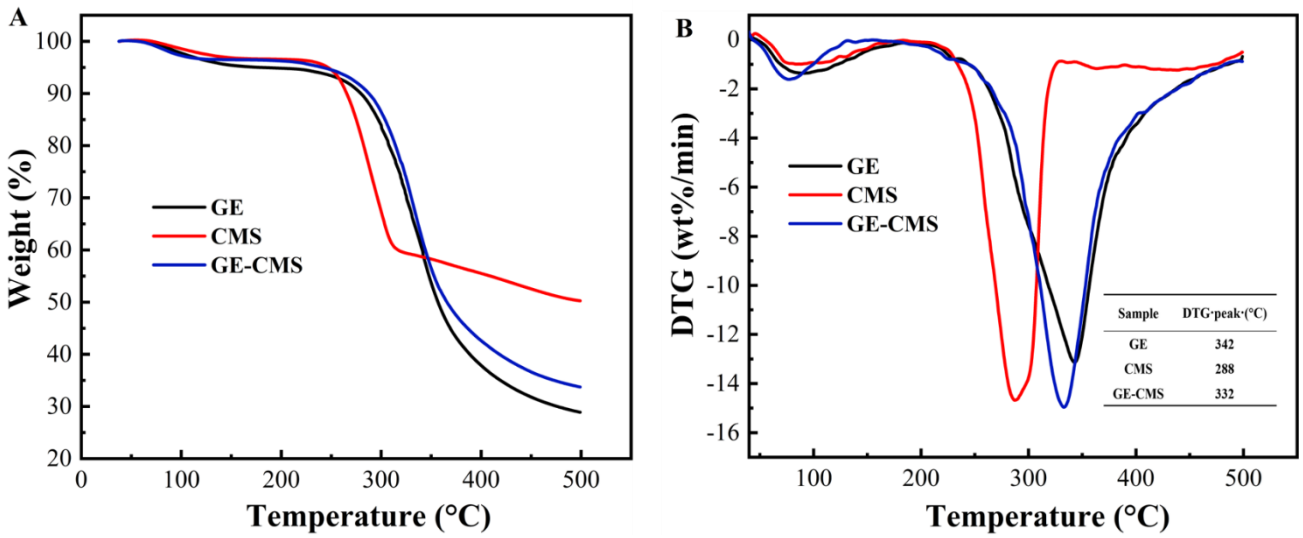

Fig. 5. TGA thermograms of GE, CMS and GE-CMS coacervates.

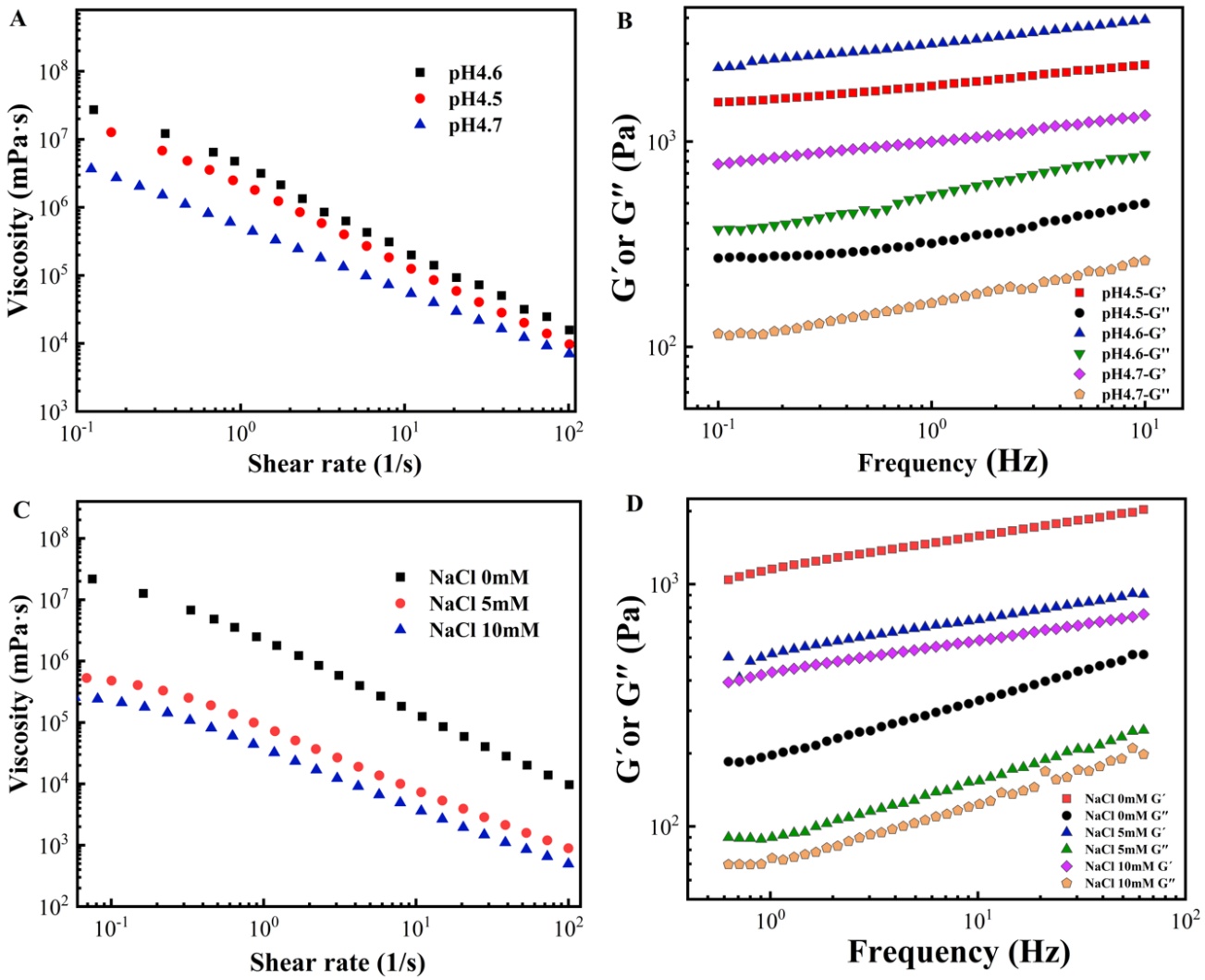

Fig. 6. Viscosity curves and frequency sweep results of GE-CMS coacervates at different pH (A/B) and different C_{NaCl} (C/D).