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Effect of sodium citrate /polyethylene glycol on plasticization and retrogradation of maize starch

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Abstract: Maize starch was plasticized by mixtures of sodium citrate and polyethylene glycol 200 (PEG200) at varied weight ratios (citric acid/PEG200, 25/0, 20/5, 15/10, 10/15, 5/20 and 0/25). The structure and pasting, aging, moisture absorption and thermal properties of the plasticized starches were studied by means of Fourier transformed infrared, X-ray diffraction, rapid viscosity analysis, tension test and thermogravimetric analysis. Comparing with single plasticizer, co-plasticizers with appropriate proportions are more effective in hindering the retrogradation of starch paste and film. The results also showed that the mechanical property and humidity sensitivity of the starch film worsen after the introduction of PEG200 compared with sodium citrate plasticized starch, but the thermal stability and anti-aging property increase. This is consistent with the association ability of plasticizers with starch observed from FTIR. In addition to the simple additive effect

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of components on some properties, special formulations also show some synergistic effects, such as the co-plasticizer of 20% citric acid and 5% PEG200 has a better comprehensive property for plasticizing the maize starch bulk than sodium citrate or PEG200 alone. The mixture of sodium citrate and PEG200 can be used as a candidate plasticizer for preparing thermoplastic starch for food and packaging industries.

Keywords: Starch, sodium citrate, PEG200, Co-plasticizer, Retrogradation

1. **Introduction**

Starch is an inexpensive, abundant, biodegradable and renewable bio-material, which is widely used in food and non-food industry and can be one of the candidates to replace petroleum-based products. Starch film is brittle because of the massive inter- and intra-molecular interactions between starch chains [1]. Addition of plasticizers could modify the brittleness and improve the flexibility and extensibility of starch film [2]. An ideal plasticizer should reduce the intermolecular force and recrystallization of starch, increase the mobility of starch chains, decrease the moisture absorption and be compatible with starch [2]. Currently, the most commonly used plasticizers for starch are small molecules with polar groups, such as –OH [3], –COOH [4] and $-NH_2$ [5]. However, no single plasticizer still can achieve all the properties required by ideal plasticized starch.

At present, one of the important directions of starch plasticizer research is to use two or more plasticizers to cooperate, so that a variety of plasticizers can complement each other. For example, a glycerol plasticized starch tends to retrograde during a long time and a sorbitol plasticized starch shows a brittle fracture, but the sorbitol/glycerol co-plasticized starch has good mechanical properties, thermal stability and resistance against retrogradation of starch [6-8]. In addition, there are some reports about organic amines and polyol co-plasticized starch. For example, starch plasticized by urea/glycerol has higher tensile strength and better anti-aging than starch plasticized by glycerol [9]. Thermoplastic starch with ethylenebisformamide/sorbitol has better tensile strength, elongation at break and thermal stability than thermoplastic starch with sorbitol [10]. This is because $–NH_2$ groups of ethylenebisformamide can form a strong hydrogen bond with the –OH groups in starch as well as in sorbitol, which can inhibit the recrystallization of starch [11]. The addition of organic amines can inhibit the recrystallization of starch, but they are more or less toxic and so can not be used in food packaging. Sorbitol is safe for human, but its high cost limits its wide application. Some studies have shown that the mixture of citric acid and glycerol could prevent retrogradation of starch and improve the processing ability of starch [12, 13]. Therefore, it is worth trying to use polyacid and polyol as starch plasticizer.

Citric acid is non-toxic and inexpensive, and can be used not only as plasticizer and compatilizer in starch matrix [13, 14], but also as a cross-linker for starch [4]. The plasticized starch with citric acid has superior barrier properties and moisture resistance [15]. Polyethylene glycol (PEG) can promote the biodegradation of starch/PLA composites [16] and can be used to plasticize starch or make starch composite compatible [16-18]. The plasticizing effect of PEG depends on its molecular weight [17], and its plasticizing efficiency increases with the decrease of molecular weight [19]. The PEGs with molecular weight above 300 cannot plasticize starch by melt processing [20]. PEG200 has a good plasticizing effect on starch and can prevent the retrogradation of starch to some extent. When its content is over 15%, the elongation of starch composites can easily exceed 40% [21]. Based on the above consideration, the thermoplastic starch films with co-plasticizers (citric acid/PEG200) were prepared in our laboratory. In order to avoid starch degradation, citric acid was converted to sodium citric before use. The structure and pasting, aging, moisture absorption and thermal properties of these starch films with co-plasticizers were studied and compared with starch films plasticized by the corresponding single plasticizer.

2. Experimental

2.1 Materials and Chemicals

Normal maize starch (MS) that was composed of 75% amylopectin and 25% amylose was purchased from Xi’an Guowei Starch Co., Ltd. (China). The viscosity-average molecular weight (M_v) of MS is 1.53×10^7 [22]. The water content of MS is 14%. All other chemicals are analytical grade, including polyethylene glycol 200 (PEG200), sodium hydroxide and citric acid (CA), and were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (China). Distilled water was used in all experiments. CA and PEG200 were added at a certain weight ratio throughout the experiment, but CA was converted to sodium citrate when used.

2.2 Rapid viscosity analysis (RVA)

RVA-Mzi Rapid Visco-Analyzer (Australia) was used to measure maize starch gelatinisation. At first, CA/PEG200 (total weight of 0~0.75 g) was neutralized with dilute sodium hydroxide and dissolved in distilled water (25 mL, including the water in the dilute sodium hydroxide added). The plasticizer solution was added into the testing sample container of the RVA analyzer, along with MS (3g). CA was mixed with PEG200 at weight ratios of 0/0, 25/0, 20/5, 15/10, 10/15, 5/20 and 0/25, respectively. The sample in the container was stirred for 10 s with 960 rpm and then another 50 s with 160 rpm at 50°C. The suspension was then heated from 50°C to 95°C at rate of 13 °C/min and held at 95°C for 2.5 min. At last, it was cooled to 50°C at a rate of 13 °C/min and maintained at 50 °C for 2 min [23]. The viscosity of the starch paste during the gelatinisation process was recorded every 30 s and characteristic values were read by the instrument. The abbreviations of testing samples were SC0P0, SC25P0, SC20P5, SC15P10, SC10P15, SC5P20 and SC0P25, respectively.

2.3 Preparation of starch films

MS (16 g), CA/PEG200 mixture in different proportions (4 g) and distilled water (380 g) were added into a three-neck flask. CA was neutralized with sodium hydroxide before it was added. The mixing ratios of plasticizer and abbreviations of samples were the same as that in section 2.2. Then the suspension in the flask was stirred at 150 rpm and heated at 95°C for 1h. Finally, 70 mL starch paste was poured onto a horizontal glass dish with the size of 150 mm × 210 mm and dried at room temperature for 7 days. For comparison, starch suspension without plasticizer was cooked as the blank sample under the same gelatinization and casting conditions.

2.4 The structure of starch film

FTS3000 FTIR Spectrum Scanner (Hercules, USA) was used to measure the functional groups of starch films by ATR sampling. The molecular interaction between starch and plasticizer can be further analyzed. X-ray diffraction (XRD) patterns of starch films stored for 3 and 45 days were recorded with Philips X' Pert Pro MPD system (Netherlands) in the reflection mode over a scattering angle (2θ) from 5° to 40° at 0.026°/s. The calculation procedure for crystallinity consisted of measuring the integrated intensities of the crystalline peaks and the diffuse background that was assumed to be the reflection of the disordered portion.

2.5 Aging property test of plasticized starch film

The films were stored at 15°C in a desiccator where the relative humidity was maintained at 68% with saturated $CuCl_2$ solution for varied days (3, 7, 15, 30 and 45 days). The mechanical performance was evaluated to investigate aging properties of the starch film. The mechanical properties of thermoplastic starch films were performed by YG061-1500 electronic strength tester (Laizhou, China). The gauge-length was 100 mm and the strain-rate was 100 mm/min.

2.6 Moisture absorption and sensitivity of starch film

Moisture absorption of starch films was evaluated in accordance with the method of Mathew [24]. First of all, the starch films were dried at 105°C for 2 days and weighted. Then the starch films were stored for 15 days at varied RH (11%, 33%, 44%, 68% and 80%) and weighted. The moisture content (M_c) of starch films was calculated by equation (1) as follows:

$$Mc(\%) = (M_1 - M_0) / M_0 \times 100\% \tag{1}$$

where M_0 and M_1 represent the weight of the starch films before and after moisture absorption, respectively.

The moisture sensitivity (M_s) of starch films was defined as the ratio between the difference of M_c and the corresponding difference of RH:

$$M_s = (M_{c80} - M_{c11}) / (80\% - 11\%) \tag{2}$$

where M_{c80} and M_{c11} represent the moisture content at RH11% and RH80%, respectively.

2.7 Thermogravimetric analysis of starch film

Thermogravimetric analysis of starch films with and without plasticizer was performed with a TG 209F3 type thermal analyser (NETZSCH, Germany). The weight of starch films was about 5 mg. The programme temperature ranged from

50°C to 600 °C and the heating rate was 10 °C/min.

3. Results and discussion

3.1 Interaction between starch and plasticizer

FT-IR spectra of MS films with different kinds of plasticizers are given in Figure 1(a). The peaks at 3316 cm^{-1}, 1150 cm^{-1} and 995 cm^{-1} are the associated −OH stretching vibration peak, C−O of C−O−H stretching vibration peak and C−O of C−O−C asymmetric stretching vibration peak, respectively, which are the most characteristic absorption peaks of starch [12]. The associated −OH stretching vibration peak at about 3316 cm^{-1} of all the plasticized starch films is stronger than that of MS and shifts to lower wavenumber. It reflects that plasticizers can destroy the interaction between starch molecules to some extent, and combine with starch by hydrogen bonding. Furthermore, the shift of wavenumber decreases as PEG200 increases and sodium citrate decreases. It suggests the interaction of starch with sodium citrate is stronger than that with PEG200.

Kim et al. [25] found that the asymmetric stretching vibration peak of C−O in C−O−C at 1018 cm^{-1} splits into three peaks at 1050 cm^{-1}, 1018 cm^{-1} and 995 cm^{-1}. According to their findings, the peak at 1050 cm^{-1} is related to the ordered phase of starch, while the peaks at 1018 cm^{-1} and 995 cm^{-1} represent the amorphous phase of starch. In addition, the peak area ratio of at 995 cm^{-1} to 1018 cm^{-1} can be used to characterize the ability to inhibit starch retrogradation. The smaller the ratio, the stronger the ability to inhibit starch retrogradation. So the deconvolution was performed at a region of 1200 cm^{-1} to 900 cm^{-1} in FT-IR spectra as shown in Figure 1(b) for SC15P10 sample. The area ratios of 995 cm^{-1} to 1018 cm^{-1} of starch with different kinds of plasticizers are shown in Figure 1(c). It can be seen from Figure 1(c), SC20P5 has the lowest ratio, which indicates that the starch sample with 20wt% CA and 5wt% PEG200 has the best ability to inhibit the starch retrogradation in all the thermoplastic starch films. It may be because a small amount of PEG200 can improve the compatibility of starch and sodium citrate [17]. However, the area ratio of 995 cm^{-1}/1018cm^{-1} increases with the increase of PEG200 content. This further confirms the inhibition of a small amount of PEG200 on recrystallization or retrogradation for the thermoplastic starch with sodium citrate.

3.2 Crystal structure of the starch films during aging

XRD is used to evaluate the crystal structure of thermoplastic starch films with different kinds of plasticizers. The XRD patterns of starch films stored for 3 days are illustrated in Figure 2. The diffraction peaks at 5.6°, 17°, 19.6°, 22.1° and 23.8° in the XRD patterns of thermoplastic starch films are the characteristic peaks of B-type crystal. The crystallinities of starch films are given in Table 1. It can be seen that the crystallinities of thermoplastic starch films are lower than that of starch film without plasticizer owing to the hindrance effect of plasticizers to starch recrystallization during film-forming [26]. Besides, the crystallinities of thermoplastic starch films with co-plasticizers are a little lower than that of thermoplastic starch films with sodium citrate or PEG200 alone. The results showed that the co-plasticizers are more effective in decreasing crystalline portion of starch than single plasticizer.

It can also be found in Table 1 that the crystallinity of all starch films increases with the extension of storage time, which is called long-term retrogradation, mainly due to the recrystallization of amylopectin [24]. Expectedly, the crystallinitiy of thermoplastic starch films with different kinds of plasticizers stored for 45 days is lower than that without plasticizer. It suggests that all of sodium citrate, PEG200 and co-plasticizers can inhibit recrystallization of starch during storage [17]. In terms of inhibiting recrystallization of starch film, co-plasticizers, especially with citric acid of 20wt% and PEG200 of 5wt%, are more effective than with PEG200 and sodium citrate alone. It may be due to the compatibility among starch, sodium citrate and PEG200, as shown in Figure 1(c).

3.3 Gelatinization analysis via RVA

Gelatinisation is an important property of starch, which corresponds to other properties of starch. The viscosity changes and the corresponding characteristic values during the gelatinisation of starch with different kinds of plasticizers are illustrated in Figure 3 and Table 2, respectively. Parameters during the gelatinisation of starch were shown in Figure 3(a). T_{pasting}, η_{peak}, η_{trough} and η_{final} represent the pasting temperature, peak viscosity, trough viscosity and final viscosity during the gelatinisation. After being heated, the starch granules in excess water expand rapidly. At the same time, the starch molecules leach out of the granule resulting in an increase in viscosity. With the increase of expansion strength and leaching rate, the viscosity of the suspension will increase rapidly at a certain temperature that is the pasting temperature. The viscosity continues to increase to the maximum (peak viscosity) until all the molecules disperse into water. Molecule orientation and break of interactions between starch molecules under heating and shear force lead to the trough viscosity. When the suspension is cooled, intermolecular interactions brings it to the higher and final viscosity in the end. Differences in (η_{peak}-η_{trough}) and (η_{final}-η_{trough}) represent the breakdown value and the setback value, separately. The decrease from η_{peak} to η_{trough} is due to heating while the shearing rate is constant, so it reflects the thermal stability. The increase from η_{trough} to η_{final} is attributed to the re-formation of intermolecular interaction, normally between starch molecules. So (η_{final}-η_{trough}) is used to show the tendency of starch rearrangement and recrystallization [27].

It can be seen from Table 2 that the T_{pasting} of SC0P0 blank is 78.0°C, while the T_{pasting} values of starch with different kinds of plasticizers are higher than the blank. It is attributed to two reasons as follows. Both sodium citrate and PEG200 are hydrophilic plasticizers which would bind with water in the slurry and reduce the amount of free water which swells and dissolves the starch granule [28]. Besides, starch would preferentially associate with the plasticizers with stronger eletrophilicity or nucleophilicity comparing with water [29]. So the diffusion rate of starch molecules into water would be suppressed. In addition, the T_{pasting} values of starch with plasticizers decrease with the decrease of sodium citrate content or with the increase of PEG200 content. It indicates that the declining T_{pasting} of starch with different kinds of plasticizers is coincident with the declining nucleophilicity of oxygen atom in those plasticizers and the declining H-bond ability. In other words, the interaction between sodium citrate and water is stronger than that between PEG200 and water, and the interaction between sodium citrate and starch is stronger than that between PEG200 and starch [30].

η_{peak} and η_{final} values of MS with plasticizer during gelatinisation are lower than that of MS without plasticizer, which means that the plasticizer could reduce the entanglement of the starch chains during the gelatinisation. SC25P0 has the lowest value of (η_{peak}-η_{trough}) in all the samples, meaning that MS with sodium citrate has the best thermal stability during starch gelatinisation. On the contrary, PEG200 decreases the thermal stability of MS with co-plasticizers during starch gelatinisation.

(η_{final}-η_{trough}) values of SC25P0 and SC0P25 are separately 440 cp and 707 cp, which are lower than the value of MS. It suggests both sodium citrate and PEG200 can inhibit retrogradation of the starch paste, and the ability of sodium citrate in inhibiting retrogradation of the starch paste is stronger than that of PEG200. (η_{final}-η_{trough}) values of SC20P5, SC15P10 and SC10P15 are all lower than that of SC25P0, where SC20P5 has the smallest (η_{final}-η_{trough}) values. It reflects that co-plasticizers with an appropriate proportion are more effective than sodium citrate or PEG200 alone in inhibiting the retrogradation of MS during the gelatinisation. This is consistent with the results in discussion of the crystal structure of the starch films.

3.4 Mechanical property of starch films during aging

Measuring the changes of mechanical properties of materials with time is an effective way to evaluate their aging properties. Mechanical properties of thermoplastic starch films with different kinds of plasticizers and varied storage time are shown in Figure 4. As can be seen from Figure 4(a), the elongation at break of thermoplastic starch films decreases as the storage time increases, especially the first 14 days. But the tensile strength of thermoplastic films decreases and then increases in the Figure 4(b). The reason for the above phenomenon is that the crystallinity of thermoplastic starch films increases as the storage time increases, because the structure of thermoplastic starch films has a certain effect on their mechanical property [31]. The ordered structure of thermoplastic starch films is the main reason for the strength increases and elongation decreases.

At the beginning of aging, the elongations at break of the co-plasticized thermoplastic starch seem to exhibit average values of sodium citrate and PEG200, except SC20P5. Then, elongations at break of SC20P5, SC15P10 and SC10P15 films become higher than that of SC25P0 film when stored for more than 14 days, showing lower rate of initial decrease of the elongation at break. The results suggest that co-plasticizers can not only plasticize starch effectively, but also inhibit the aging of starch significantly. This may be because PEG200 in the appropriate dose range can improve the compatibility between starch and sodium citrate [17]. What cannot be ignored is that SC20P5 shows obvious synergistic effect of plasticity, and the elongation at break is the highest in all aging stages, which is at least 30% higher than SC25P0. View from the tensile strength of the films, the mixing of sodium citrate and PEG200 have little effect on the films. The tensile strength of co-plasticized starch films is lower than that of the two plasticized starch films with single plasticizer at the early stage of aging, and gradually increased with the aging time, between the higher SC25P0 and the lower SC0P25. All in all, an appropriate proportion of co-plasticizer (20wt% CA and 5wt% PEG200 in this study) is more effective than its single-component plasticizer in plasticizing starch and has a better stabilizing effect on the mechanical properties of MS during storage.

The aging phenomenon of a starch film comes from its recrystallization in nature, which results in the decrease of elongation at break and the increase of breaking strength for the film. As can be seen from Table 1, the initial crystallinity of the native starch film was the highest, but the rate of increase in crystallinity after 45 days aging ($(C_{45}$-$C_3)/C_3$) was the lowest among all the films. This suggests the plasticizers or co-plasticizers can reduce starch initial crystallization, but promoted the recrystallization of starch. It can also be seen from the table that sodium citrate promotes recrystallization of starch significantly more than PEG200. However, a combination of a main plasticizer and an auxiliary one, such as SC20P5, can significantly reduce the adverse effect of the plasticizer on starch recrystallization.

3.5 Moisture absorption of starch film

Starch is a hygroscopic material due to its plenty of –OH groups. The addition of some hydrophilic plasticizers, such as glycerol, may enhance the moisture absorption of thermoplastic starch. Water is a plasticizer of starch, but will accelerate recrystallization of starch [24]. In this sense, water-sensitive plasticizer is not conducive the application of thermoplastic starch, especially in packaging materials. Therefore, the ideal plasticizer should reduce the moisture absorption of starch.

Moisture content and humidity sensitivity of starch films with different kinds of plasticizers at varied RHs are shown in Table 3, where M_s represents the moisture sensitivity obtained by the equation (2). As can be seen from Table 3, the M_c values of SC25P0 film under all RHs are lower than those of SC0P0 film and its M_s value is the lowest. The –COO^- group of sodium citrate and –OH of MS can form stronger and more-stable interactions, which can block hygroscopic groups in MS and decrease the hygroscopic sensitivity [6]. This also confirms the aforementioned discussion on the interaction between sodium citrate and starch. Oppositely, M_c values of SC0P25 film at all the RHs, together with M_s, are higher than those of blank SC0P0 film. This is due to the strong hydrophilicity [32] and weak ability of PEG200 to associate with starch, as can be seen from Figure 1. For starch films with co-plasticizers, their M_c values at high RHs increase with the increase of PEG200 content. The M_s values of all plasticized starch films, except SC20P5, exceed that of SC0P0. In addition, the M_c values of SC20P5 film at all the RHs are lower than those of SC0P0. This indicates that the co-plasticizer, 20wt% CA and 5wt% PEG200, is a relative effective starch plasticizer in reducing moisture absorption and the moisture humidity sensitivity of starch film.

3.6 Thermogravimetric analysis of starch films

Thermogravimetric curves of starch films are shown in Figure 5(a). There are three degradation stages for starch or thermoplastic starch in the figure. The first stage below 100°C is due to the loss of free water in starch films. The second stage between 100°C and 250°C is attributed to the evaporation of combined water and plasticizer in starch films. The third stage is resulted from the degradation of plasticizer and starch. The differential curves of thermogravimetric analysis of starch films are shown in Figure 5(b). It can be seen that for all thermoplastic starch films containing sodium citrate or co-plasticizer, the temperature corresponding to the maximum mass loss rate is lower than that of blank starch film, and increases with the increase of PEG200 proportion in the total plasticizers. However, the temperature corresponding to the maximum mass loss rate of thermoplastic starch film with PEG200 alone is higher than that of the blank starch film. It suggests that PEG200 can improve the thermal degradation temperature of the thermoplastic starch film.

4. Conclusions

Sodium citrate and polyethylene glycol 200 (PEG200) were used as plasticizer alone or co-plasticizers to prepare thermoplastic starch films. Rapid viscosity analysis showed that sodium citrate plasticized starch had the lowest breakdown value in all the pastes of starch samples with or without plasticizers, and its plasticized starch film was the best to reduce the moisture absorption of the starch and the highest tensile strength. However, its disadvantage was the highest rate of increase in crystallinity after aging. On the other hand, PEG200 had a low binding strength with starch, and the setback value and breakdown value of the starch paste with PEG200 were the highest in all the paste samples. The moisture absorption rate of the starch film plasticized by PEG200 was the highest at all RHs, together with poor moisture sensitivity, the lowest elongation at break and tensile strength. Its advantage is only the lowest rate of increase in crystallinity after aging. These indicate that PEG200 is not suitable for plasticizing starch, although it has an advantage of the lowest rate of increase in crystallinity after aging.

However, once sodium citrate and PEG200 were mixed to plasticize the starch, the structure and properties of plasticized starch film changed greatly, showing a good synergism. For example, SC20P5 sample, i.e. the starch plasticized by citric acid 20wt%/PEG200 5wt%, showed the lowest crystallinity, low humidity sensitivity and the maximum elongation at break before and after aging. At the same time, the paste had the lowest breakdown value and setback value during the gelatinisation. Comparing with PEG200 or sodium citrate alone, the co-plasticizers with an appropriate proportion could promote the stability of starch film and paste, and prohibit the recrystallization and retrogradation more efficiently. The reason may be related to the difference between the molecular morphology and functional groups of the two plasticizers, about which we still know little and so further study is needed.

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Competing financial interest

The authors declare no competing financial interest.

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Captions of Figures and Tables

Figure 1 The interaction between starch and different kinds of plasticizers, (a) FT-IR spectra, (b) Deconvolution of MS1510 in a region of 1200 cm^{-1} to 900cm^{-1}, (c) The ratio of 1018 cm^{-1} to 995 cm^{-1}

Figure 2 The XRD patterns of starch films stored for 3 days

Figure 3 Pasting curves of the starch with different kinds of plasticizers (a) pasting parameters, (b) pasting curves

Figure 4 Mechanical properties of starch films with different kinds of plasticizers stored for varied days, (a) Elongation at break, (b) Tensile strength

Figure 5 TG curve (a) and DTG curve (b) of thermoplastic starch films with different kinds of plasticizers

Table 1 Crystallinities of starch films with different kinds of plasticizers stored for 3 and 45 days

Table 2 Pasting properties of the starch with different kinds of plasticizers

Table 3 Moisture rate and sensitivity of starch films with different kinds of plasticizers at varied RHs

Table 1 Crystallinities of starch films with different kinds of plasticizers stored for 3 and 45 days

Sample	C_3 (%)	C_{45} (%)	$(C_{45}-C_3)/C_3$ (%)
SC0P0	13.6	15.2	11.8
SC25P0	7.0	10.5	50.0
SC20P5	6.5	8.7	33.8
SC15P10	6.7	9.3	38.8
SC10P15	6.8	10.1	48.5
SC5P20	7.1	9.6	35.2
SC0P25	7.3	9.5	30.1

Note: C_3 and C_{45} represent crystallinities of starch films stored for 3 and 45 days, respectively.

Table 2 Pasting properties of the starch with different kinds of plasticizers

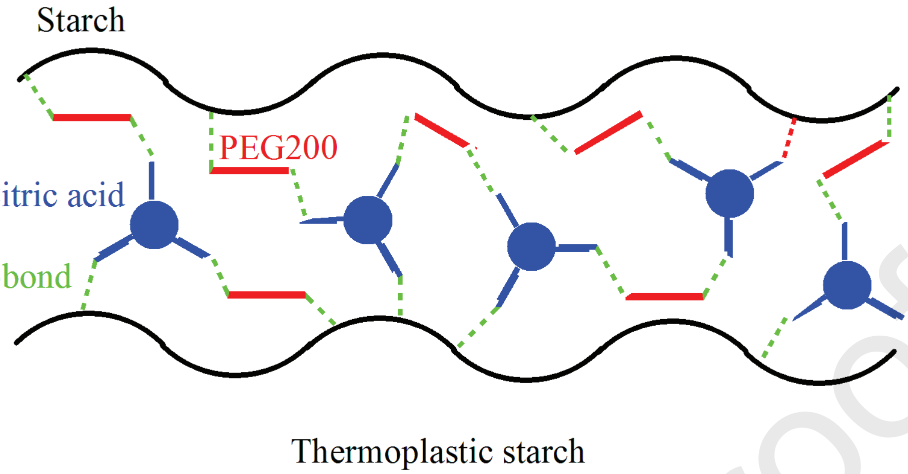
Sample	T_{pasting} (°C)	η_{peak} (cp)	η_{trough} (cp)	η_{final} (cp)	η_{peak}-η_{trough} (cp)	η_{final}-η_{trough} (cp)
SC0P0	78.0	2662	1988	2975	674	987
SC25P0	84.1	2298	2120	2560	178	440
SC20P5	83.9	2356	2150	2479	206	329
SC15P10	82.5	2314	2082	2413	232	331
SC10P15	82.2	2381	2088	2453	293	365
SC5P20	80.5	2349	1967	2502	382	535
SC0P25	79.8	2592	2090	2797	502	707

Note: T_{pasting}, η_{peak}, η_{trough}, η_{final}, (η_{peak}-η_{trough}) and (η_{peak}-η_{trough}) represent the pasting temperature, peak viscosity, trough viscosity, final viscosity, breakdown value and setback value during the gelatinisation, respectively.

Table 3 Moisture content (M_c) and sensitivity (M_s) of starch films with different kinds of plasticizers at varied RHs

Sample	RH (%)					M_s
	11	33	44	68	80	
	M_c (%)					
SC0P0	9.56	13.57	14.14	22.61	29.36	0.29
SC25P0	8.48	11.40	13.04	20.34	25.89	0.25
SC20P5	8.27	11.09	13.15	20.40	27.78	0.28
SC15P10	6.82	9.80	12.27	20.52	28.92	0.32
SC10P15	6.07	9.27	12.26	20.69	30.23	0.35
SC5P20	6.71	11.46	12.40	22.36	32.09	0.37
SC0P25	11.79	16.04	18.10	29.44	35.59	0.34

Graphical abstract

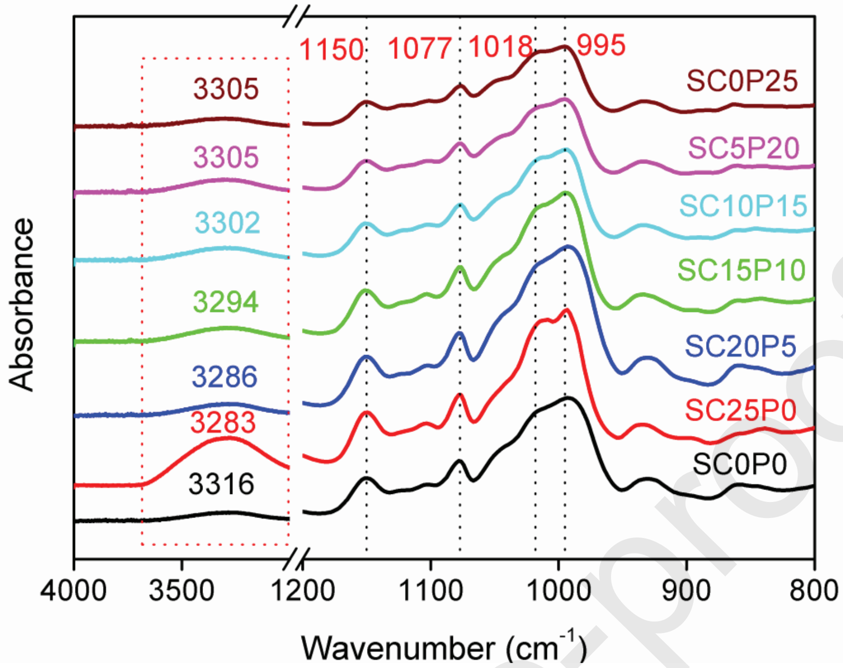


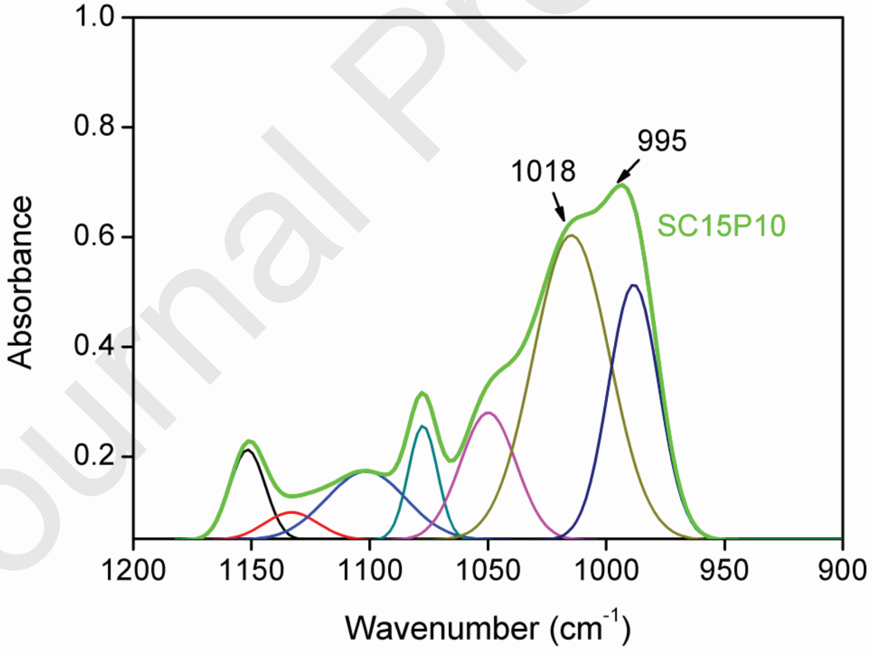
Highlights

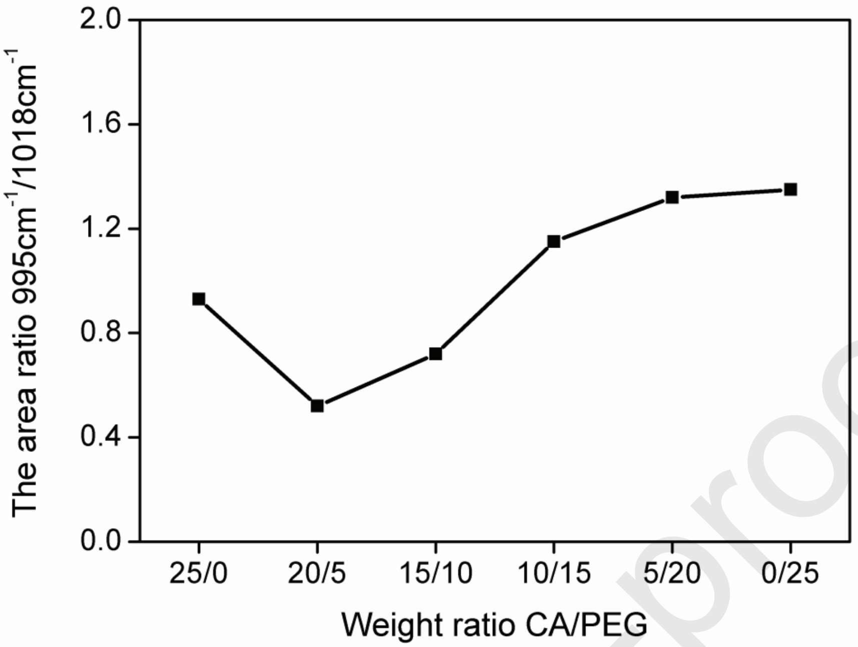
1. Sodium citrate and PEG200 were used as co-plasticizers for starch.

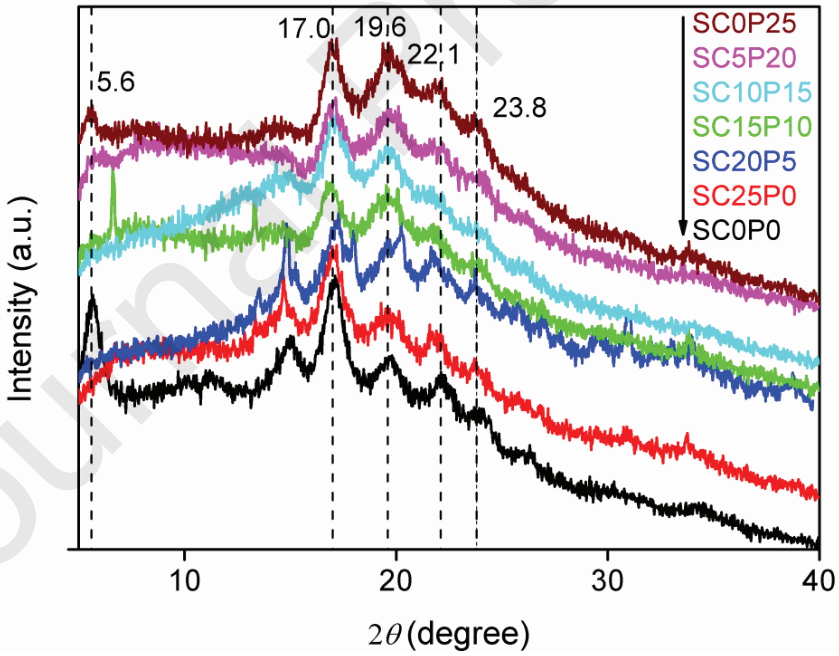
2. Co-plasticizers are more effective in hindering the retrogradation of starch.

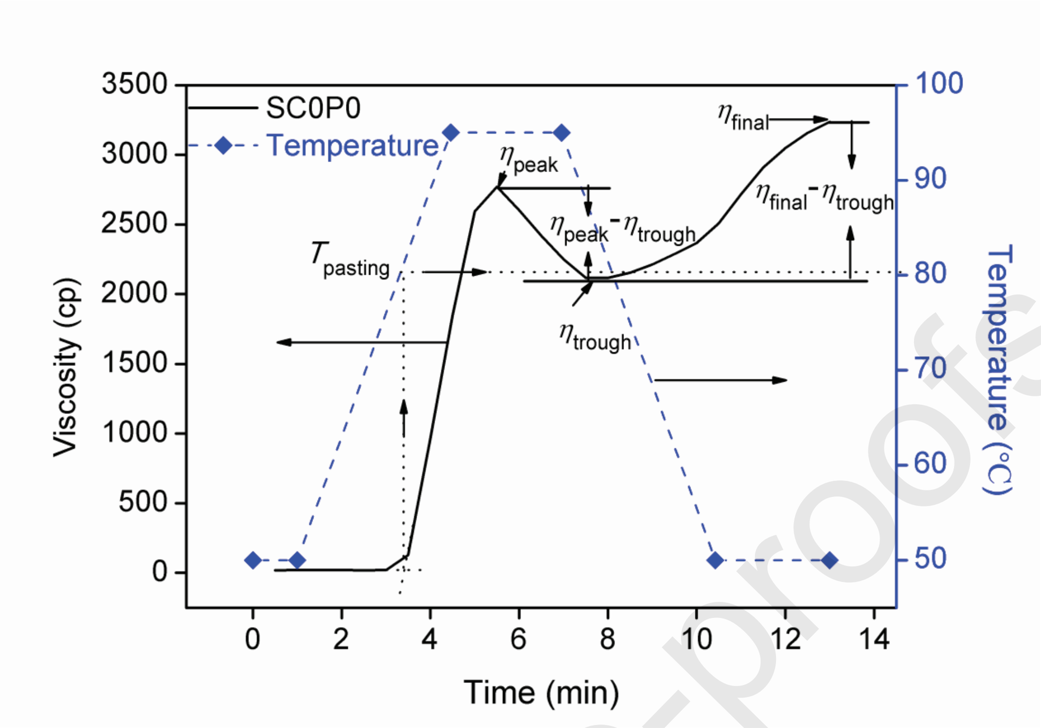
3. There are synergistic effects with some special recipes.

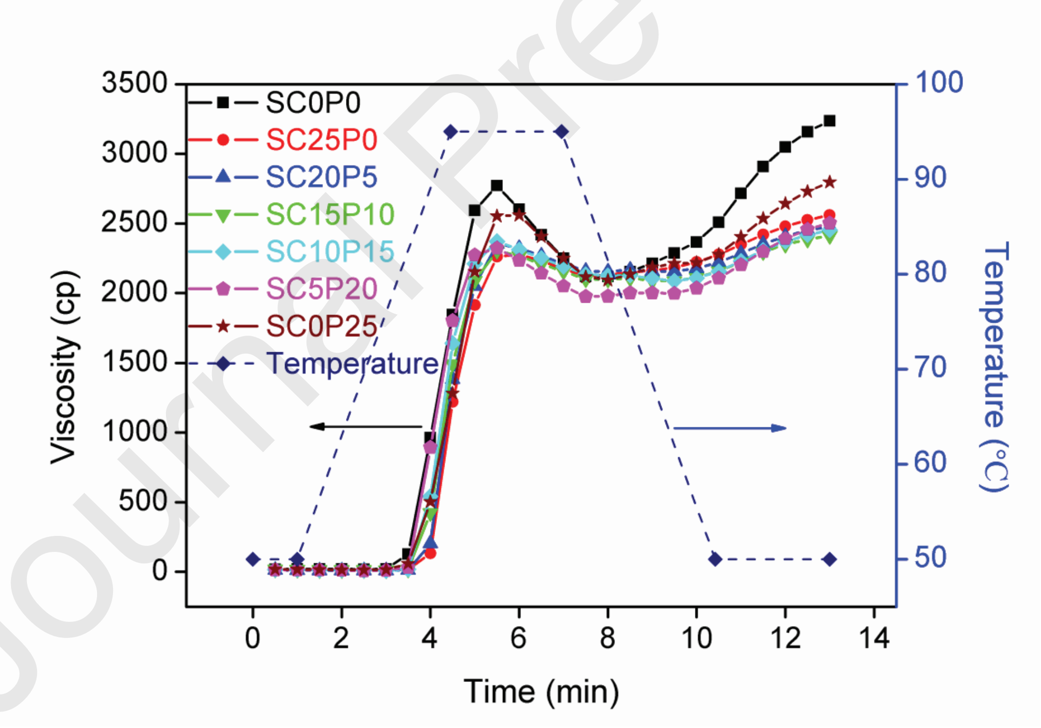

Absorbance
Wavenumber (cm^{-1})
4000
3500
1200
1100
1000
900
800
1150
1077
1018
995
3305
3305
3302
3294
3286
3283
3316
SC0P25
SC5P20
SC10P15
SC15P10
SC20P5
SC25P0
SC0P0

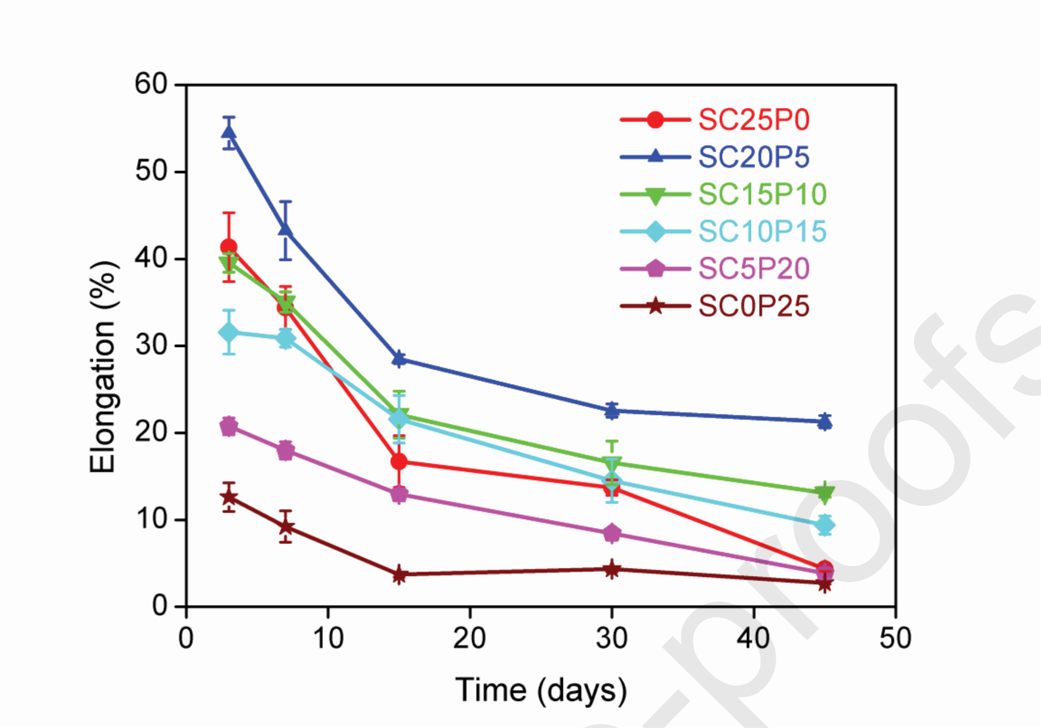

Absorbance
Wavenumber (cm^{-1})
1.0
0.8
0.6
0.4
0.2
1200
1150
1100
1050
1000
950
900
1018
995
SC15P10

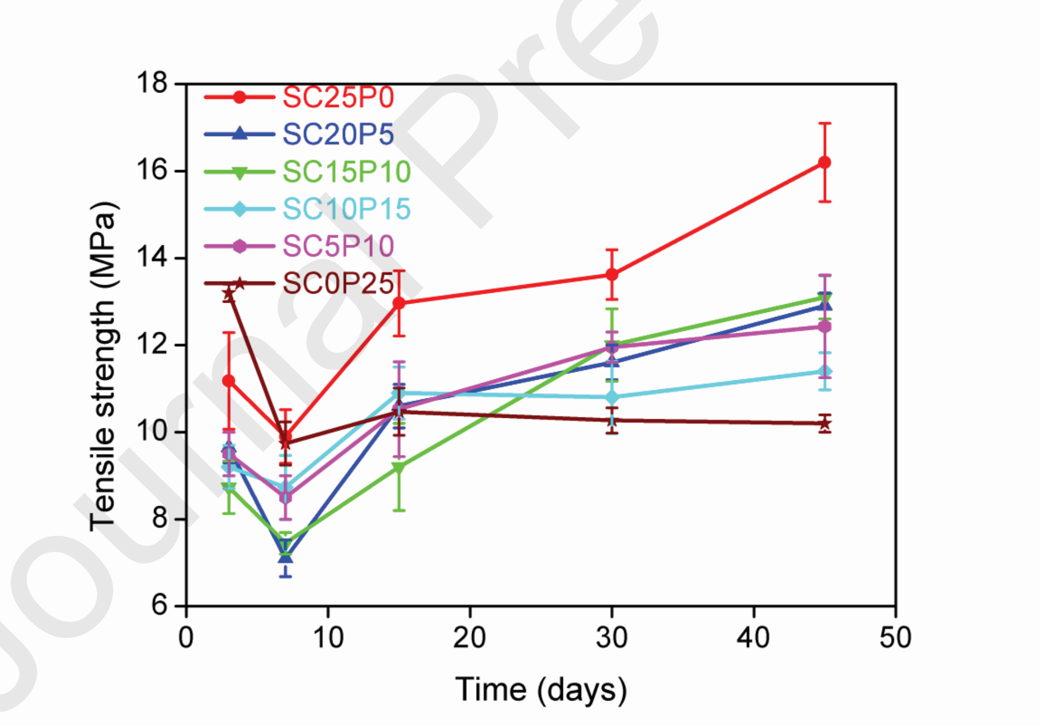

The area ratio 995cm-1/1018cm-1
2.0
1.6
1.2
0.8
0.4
0.0
25/0
20/5
15/10
10/15
5/20
0/25
Weight ratio CA/PEG

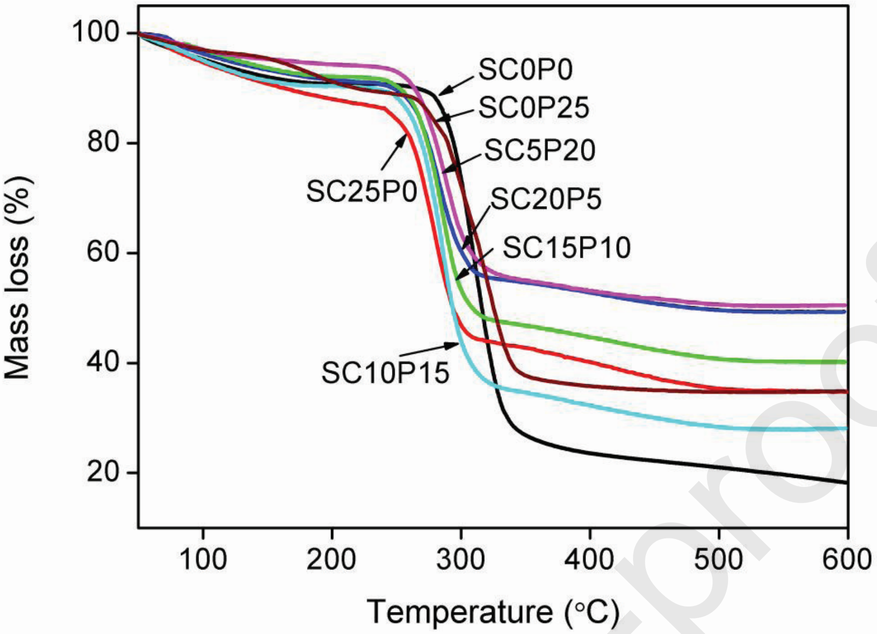

5.6
17.0
19.6
22.1
23.8
SC0P25
SC5P20
SC10P15
SC15P10
SC20P5
SC25P0
SC0P0
Intensity (a.u.)
10
20
30
40
2θ (degree)

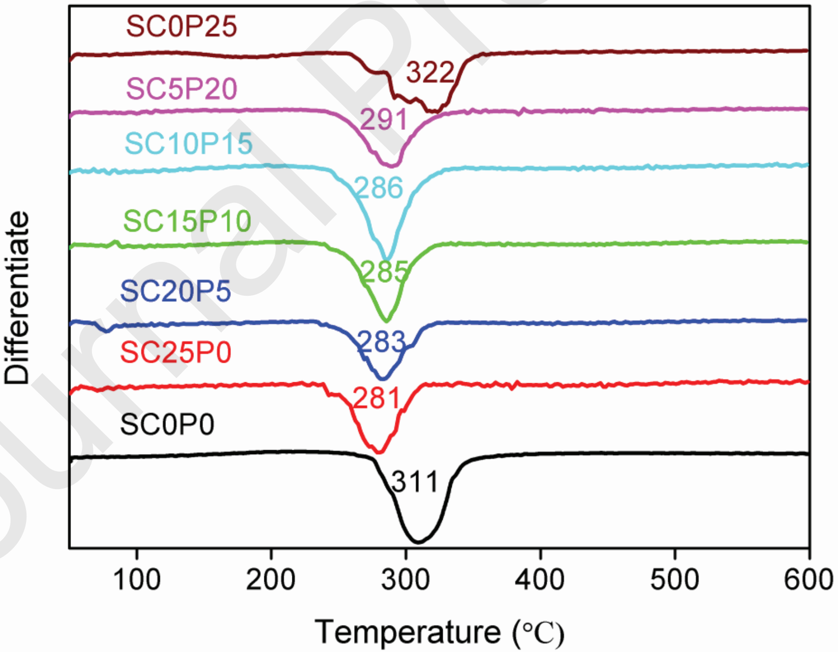

3500
3000
2500
2000
1500
1000
500
0
Viscosity (cp)
SC0P0
Temperature
η_{final}
η_{peak}
η_{final}-η_{trough}
η_{peak}-η_{trough}
$T_{pasting}$
η_{trough}
100
90
80
70
60
50
Temperature (°C)
0
2
4
6
8
10
12
14
Time (min)


3500
3000
2500
2000
1500
1000
500
0
Viscosity (cp)
SC0P0
SC25P0
SC20P5
SC15P10
SC10P15
SC5P20
SC0P25
Temperature
100
90
80
70
60
50
Temperature (°C)
0
2
4
6
8
10
12
14
Time (min)


SC25P0
SC20P5
SC15P10
SC10P15
SC5P20
SC0P25
Elongation (%)
0
10
20
30
40
50
60
Time (days)
0
10
20
30
40
50


SC25P0
SC20P5
SC15P10
SC10P15
SC5P10
SC0P25
Tensile strength (MPa)
6
8
10
12
14
16
18
Time (days)
0
10
20
30
40
50


100
80
60
40
20
Mass loss (%)
SC0P0
SC0P25
SC5P20
SC25P0
SC20P5
SC15P10
SC10P15
100
200
300
400
500
600
Temperature (°C)


SC0P25
322
SC5P20
291
SC10P15
286
SC15P10
285
SC20P5
283
SC25P0
281
SC0P0
311
Differentiate
100
200
300
400
500
600
Temperature (°C)