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# The influence of PEG molecular weight on the structural changes of corn starch in a starch/PEG blend

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**Abstract** Poly(ethylene glycol) (PEG) is a nonvolatile plasticizer used for starch gelatinization. Blends of starch and PEG at a fixed ratio of 50:50 (based on wt%) were prepared by varying the molecular weight of PEG. Interaction of the PEG and starch was investigated as a function of the PEG molecular weight via FT-IR and DSC experiment. The starch chain conformation changed when the molecular weight of PEG was less than 8,000. Additionally, a decrease of both the melting enthalpy and melting temperature was observed due to the miscibility change of the starch/PEG blend originating from the hydroxyl–hydroxyl interactions with the PEG molecular weight. Therefore, PEG with a molecular weight less than 8,000 can be effectively used for starch gelatinization.

**Keywords** FT-IR · PEG · Plasticizer · Starch

## Introduction

The use of starch as a biodegradable plastic is of growing interest as an alternative for synthetic polymers in applications where biodegradability is required. Potential applications are mainly in the non-food area, including capsules, seed coatings,

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agricultural foils, packaging materials, garbage bags and flower pots. However, native starch requires plasticization to induce thermoplastic behavior and produce thermoplastic starch [1]. Thus, a number of studies on the effects of plasticizers on starch have been performed [2–6] with the aim of producing thermoplastic materials. Water [2], glycerol [3, 4], sorbitol [5] and amides [6] are good examples of plasticizers for thermoplastic starch (TPS).

However, a drawback of these materials is the loss of mechanical properties with time (retrodegradation) [7, 8]. The structural changes are due to the loss of plasticizer with a low molar mass. Therefore, it is important to develop a thermoplastic starch with stable mechanical properties [9]. Poly(ethylene glycol) (PEG) includes oligomer or polymers with –$CH_2CH_2O$- repeating groups and two –OH end groups, and have been reported as a nonvolatile plasticizer for starch gelatinization [10–12]. In a previous study of starch/polycaprolactone/PEG blends [13], we reported the PEG molecular weight effect on the tensile toughness of the blend and an optimum value of the PEG molecular weight. The study implied that there was a limitation of the PEG molecular weight used as a plasticizer. To date, a limited study has been reported on the criteria of PEG molecular weight as a plasticizer of starch. Recently, Pereira et al. [14] reported a PEO/starch blend using PEO as a base matrix with different blend ratios in which the blend was miscible with greater than 5% starch. In this report, blends of starch/PEG with different molecular weight PEGs were studied to investigate the influence of PEG size on starch plasticization.

## Experimental part

### Materials and blend preparation

Corn starch in granular form and PEG were purchased from Sigma and Aldrich, respectively. Seven PEGs with molecular weights of 300, 400, 1,000, 3,400, 8,000, 20,000 and 100,000 were used for blend preparation. Blend films were prepared with a solution casting method using dimethyl sulfoxide (DMSO) as a cosolvent. Ratios of starch and PEG were fixed to 50:50 wt%. DMSO solutions were prepared at a total polymer concentration of 5 wt%, cast on to flat glass plates, followed by solvent evaporation at 80 °C for 1 day. The resulting films were dried in a vacuum at 80 °C for 1 day to ensure complete removal of the solvent.

### FT-IR measurements

All FT-IR spectra were obtained on a Bomem 102 spectrometer at a resolution of 4 $cm^{-1}$ in the wavelength of 4,000–500 $cm^{-1}$, and 20 scans were averaged. Measurements were performed using a deuterated triglycine sulfate detector (DTGS) at room temperature. For FT-IR measurements, films of the starch/PEG blends were cast on to KRS-5 windows at 80 °C. After evaporation of the solvent, the films were dried under vacuum at 80 °C to remove the residual solvent.

DSC measurements

To obtain the melting point and heat of fusion, thermal analyses of the starch/PEG blends were performed with a differential scanning calorimetry apparatus (DuPont TA 2000) calibrated with indium ($T_m$ = 156.6 °C). For investigation of the melting behavior of PEG in the starch/PEG blend, each sample was scanned from −100 to 200 °C at 10 °C/min for the first run under the nitrogen atmosphere. The melting point of the PEG was obtained from the heating curve by taking the minimum point of the endothermic peak, and the heat of fusion was calculated with the endothermic peak area of PEG.

## Results and discussions

FT-IR is a powerful method for investigating the conformational changes in biopolymer systems [15]. Previous works with starch gelatinization and retrodegradation suggest that they are highly sensitive to polymer conformation and can provide insight into changes at the molecular level [16, 17]. van Soest et al. [18] reported that the C–C and C–O stretching region (1,300–800 cm$^{-1}$) was sensitive to the retrogradation process, and the retrogradation kinetics were described in terms of structural changes on a molecular level by using the ratio measurements between selected peaks. The group monitored the retrogradation kinetics of starch-water systems in which water evaporation occurred with time, resulting in changes of the starch chain conformation that were especially related to C–C and C–O bonds. FT-IR measurements of the blends were conducted and the spectra of starch/PEG blends with various PEG molecular weights are shown in Fig. 1. The assignment of individual bands was difficult since the bands in this region of the IR spectrum were highly coupled, therefore the peaks were deconvoluted. All of the spectra showed eight major bands in the region of 1,200–900 cm$^{-1}$ at similar frequencies and a representative image of the deconvoluted bands are shown in Fig. 2. In starch/PEG blends, PEG is not a volatile compound and remains in the blend with the time. In this study, FT-IR spectra represented the difference of PEG molecular weight, rather than storage time. Thus, the conformation of the starch chain was explained by the differences of starch/PEG miscibility from the degree of hydration rather than retrodegradation.

The most pronounced changes in Fig. 1 occur at 1,002, 1,056, 1,102, 1,121 and 1,151 cm$^{-1}$ across eight major bands. These observations represent the polymer conformation transformation of the gelatinized disordered state to a more ordered system with a reduced spread of conformations. However, the peaks of 1,102 and 1,121 overlapped with the C–O stretching of PEG. Therefore, those peaks were not considered for the starch conformation change. For the ratio measurements, the absorbance ratios of band intensities at 1,002/1,026 and 1,056/1,043 were measured at different PEG molecular weights and displayed in Fig. 3. A maximum peak intensity at 1,026 cm$^{-1}$ represents amorphous starch, which corresponds to a 1,021 cm$^{-1}$ peak in a different study [18]. This previous study indicates that the peak at 1,021 cm$^{-1}$ splits into three peaks, 1,053, 1,022, and 1,000 cm$^{-1}$, with storage time due to retrodegradation of the TPS. The 1,045 cm$^{-1}$ peak represents the ordered phase of starch (crystalline).
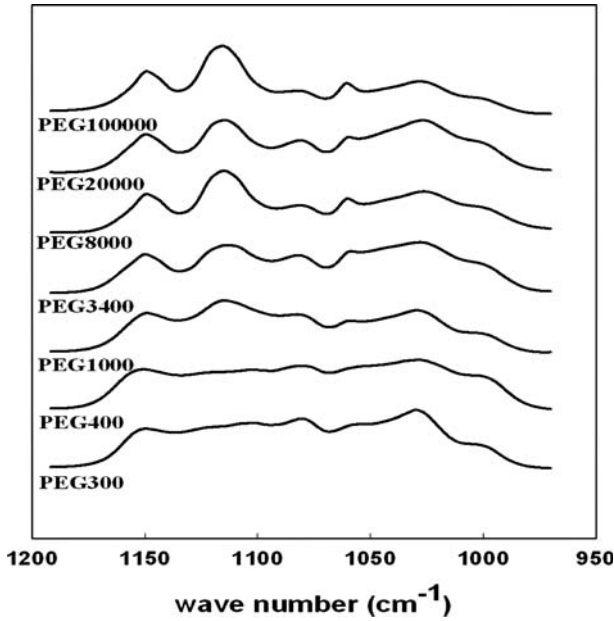
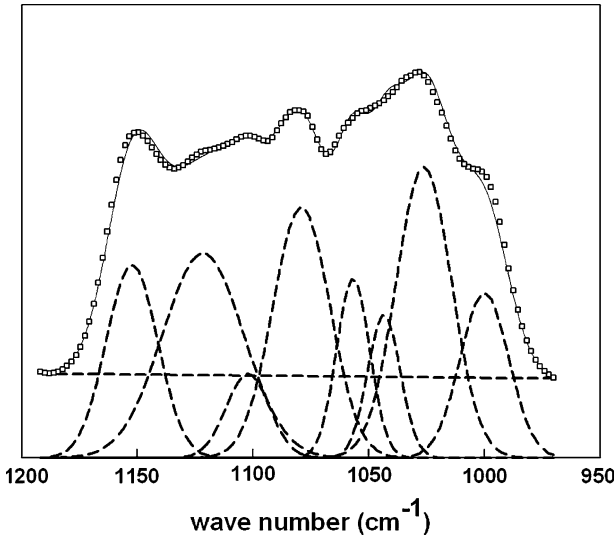**Fig. 1** FT-IR spectra of starch/PEG blends with various PEG molecular weights in a range of 1,200–950 cm$^{-1}$



**Fig. 2** Deconvolution of starch/PEG400 blends in a region of 1,200–950 cm$^{-1}$

The work herein is based on the solution blend and the 1,021 cm$^{-1}$ peak split is due to the solvent evaporation that is similar to the retrodegradation procedure of TPS induced by the volatilization of small plasticizers. The 1,002/1,026 ratio was used to explain the
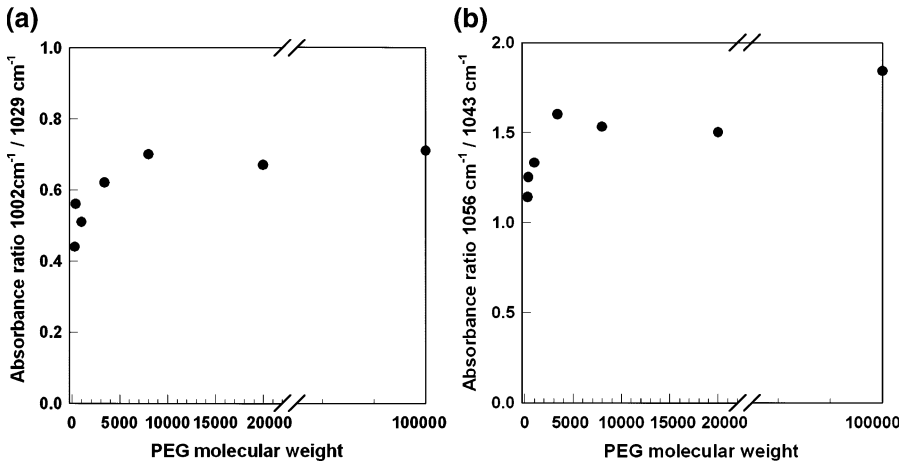
**Fig. 3** The absorbance ratio of (**a**) 1,002/1,029 cm$^{-1}$ and (**b**) 1,056/1,043 cm$^{-1}$ with the PEG molecular weight in starch/PEG (5/5) blends

effect of PEG Mw on the blend and indicates the extent of the 1,002/1,026 peak split. The low ratio value illustrates that PEG effectively acts to prevent retrodegradation due to the solvent evaporation. The 1,056/1,043 ratio was chosen to support the data of 1,002/1,026, and the absorbance ratio increased with PEG molecular weight and was sustained when the molecular weight was greater than 8,000. The absorbance ratio represents the conformation difference of the starch chain. Therefore, the conformations of the starch chain in the starch/PEG blends changed with PEG molecular weight and were unchanged when the molecular weight of PEG was greater than 8,000. Therefore, the high molecular weight PEG did not affect the starch conformation due to the immiscibility with starch.

In general, compatible blends of crystalline polymers show a substantial depression of the crystalline melt temperature ($T_m$) [19]. For the gelatinization of starch, the decrease in the total degree of crystallinity indicates the miscibility of the blend. This decrease was previously observed with the blends of polylactic acid/starch [20]. In the starch/PEG blend, the heat of fusion and melt temperature of the PEG were investigated in order to describe the miscibility. Figures 4 and 5 illustrate the changes in the heat of fusion and melting point of PEG in the starch/PEG blend, respectively. $\Delta H_{m,pure}$ is the heat of fusion of the pure PEG and $\Delta H_{m,blend}$ is the heat of fusion of the PEG blend. When the $\Delta H_{m,pure}$ and $\Delta H_{m,blend}$ are the same, the PEG forms its own crystalline phase and the starch of the blend does not prohibit the PEG crystal formation. As shown in Fig. 4, low molecular weight PEG smaller than 8,000 showed a $\Delta H_{m,blend}/\Delta H_{m,pure}$ value which was lower than unity. Therefore, PEG with molecular weight smaller than 8,000 was partially miscible with starch, and the crystal formation was prohibited by the starch.

The difference of melting temperatures between the pure PEG ($T_{m,pure}$) and PEG blend ($T_{m,blend}$) in Fig. 5 also displayed a similar behavior as the melting enthalpy. It was also observed from Fig. 5 that the $\Delta T_m$ value with PEG molecular weight was sustained at a molecular weight greater than 8,000. A lower $\Delta T_m$ suggests that the

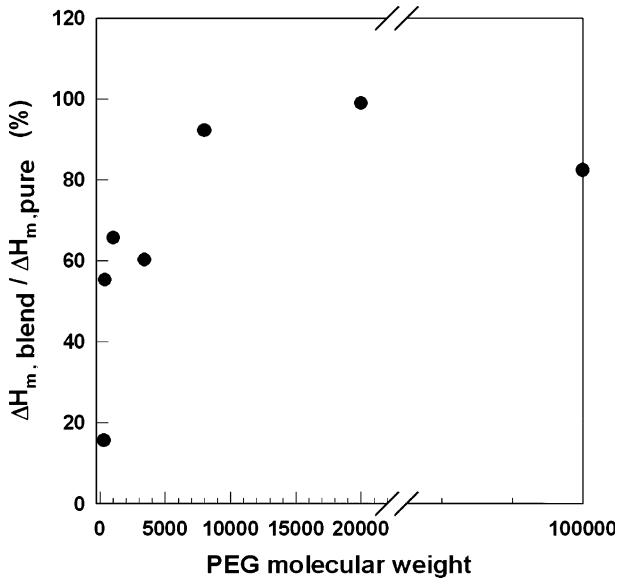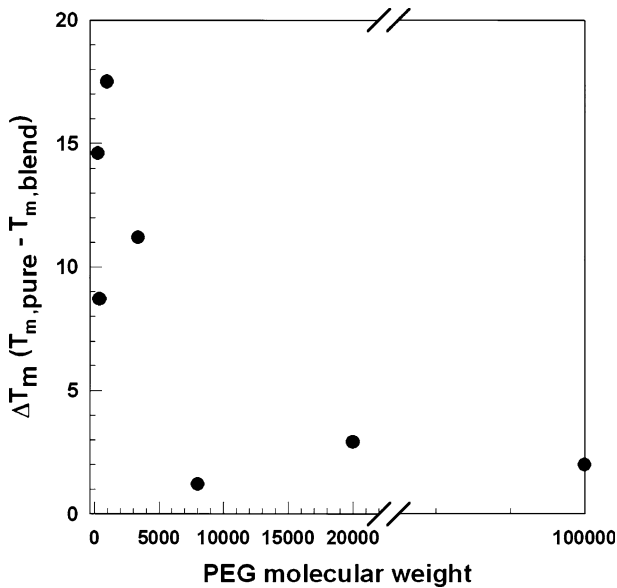**Fig. 4** Heat of fusion of PEG in starch/PEG blends



**Fig. 5** Change of the melting point of PEG in starch/PEG (5/5) blends

crystal structure of pure PEG was similar to that of the PEG blend, and that the PEG was immiscible with the starch. Therefore, PEG with a molecular weight greater than 8,000 was immiscible with the starch and could not effectively act as a starch plasticizer.

Starch has three hydroxyl units per anhydroglucose unit. Therefore, starch is very hydrophilic and the hydrogen bonding between hydroxyl groups is very strong. To be miscible with starch, this hydrogen bonding must be disturbed and the conformational structures have to be changed by the addition of PEG. To investigate the change of the hydroxyl group interactions, the FT-IR spectra in the region of 3,700–3,000 cm$^{-1}$ that is caused by the stretching band of the hydroxyl group was obtained. The FT-IR spectra of the hydroxyl region are shown in Fig. 6. The peak
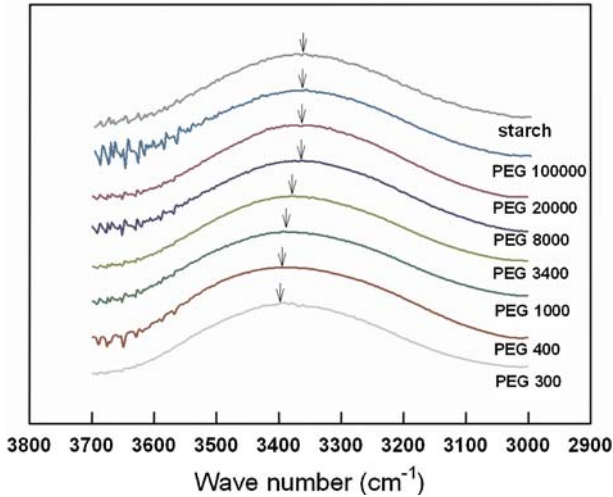


**Fig. 6** FT-IR spectra of starch/PEG blends with variation of PEG molecular weight in the region of 3,700–3,000 cm$^{-1}$
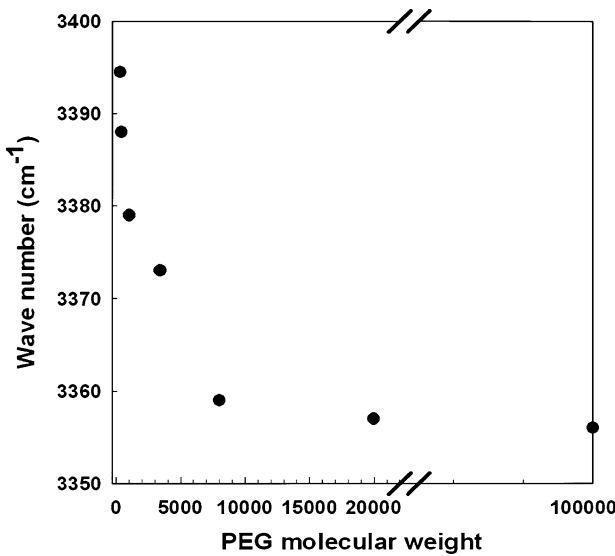


**Fig. 7** Peak wave number of starch/PEG blends with different PEG molecular weights

wave number shifted to a lower wave number as the PEG molecular weight increased in the starch/PEG blends. When the PEG molecular weight was greater than 8,000, the FT-IR spectrum of the hydroxyl region in the starch/PEG blend was nearly the same as the pure starch. The peak wave number as a function of PEG molecular weight is displayed in Fig. 7. The peak wave number decreased as the PEG molecular weight increased and the wave number did not change at molecular weights greater than 8,000. This phenomenon was also due to the miscibility change between the starch and PEG as the PEG molecular weight increased.

## Conclusions

Starch/PEG blends with different molecular weights were prepared. The nonvolatile property of PEG due to a higher molecular weight compared to a small plasticizer in a starch/blend is advantageous for the resistance of the retrogradation of TPS. However, as seen from this work, for PEG to be used in plasticization, the molecular weight must be small. PEG with a molecular weight less than 8,000 was a suitable candidate as a starch plasticizer.

## References

1. Tomka I (1991) Thermoplastic starch. Adv Exp Med Biol 302:627–637
2. Hulleman SHD, Janssen FHP, Feil H (1998) The role of water during plasticization of native starches. Polymer 39:2043
3. Martin O, Averous L, Della Valle G (2003) In-line determination of plasticized wheat starch viscoelastic behavior: impact of processing. Carbohydr Polym 53:169
4. Fishman ML, Coffin DR, Konstance RP, Onwulata CI (2000) Extrusion of pectin/starch blends plasticized with glycerol. Carbohydr Polym 41:317
5. Wang L, Shogren RL, Carriere C (2000) Preparation and properties of thermoplastic starch-polyester laminate sheets by coextrusion. Polym Eng Sci 40:499
6. Ma X, Yu J (2004) The plasticizers containing amide groups for the thermoplastic starch. Carbohydr Polym 57:197
7. Ottenhof MA, Hill SE, Farhat IA (2005) Comparative study of the retrodegradation of intermediate water content waxy maize, wheat, and potato starches. J Agric Food Chem 53:631
8. van Soest JJG, de Wit D, Vliegenthart JFG (1996) Mechanical properties of thermoplastic waxy maize starch. J Appl Polym Sci 61:1927
9. Wang XL, Yang KK, Wang YZ (2003) Properties of starch blends with biodegradable polymers. J Macromol Sci C43:385
10. Stepto RFT, Dobler B (1989) Method for producing destructurized starch. European Patent Application 0 326 517, 1989
11. Tomka I (1991) Single or multiple layer foil partially composed of starch. International Patent Application WO 1991/016375, 1991
12. Wittwer F, Tomka I, Bodenmann HU, Raible T, Gillow LS (1988) Method for forming pharmaceutical capsules from starch compositions. US Patent 4 738 724, 1988
13. Kim CH, Choi EJ, Park JK (2000) Effect of PEG molecular weight on the tensile toughness of starch/PCL/PEG blends. J Appl Polym Sci 77:2049
14. Pereira AGB, Gouveia RF, de Carvalho GM, Rubira AF, Muniz EC (2009) Polymer blends based on PEO and starch: miscibility and spherulite growth rate evaluated through DSC and optical microscopy. Mat Sci Eng C 29:499

15. Goodfellow BJ, Wilson RH (1990) A fourier transform IR study of the gelation of amylase and amylopectin. Biopolymers 30:1183

16. Wilson RH, Kalichevsky MT, Ring SG, Belton PS (1987) A Fourier-transform infrared study of the gelation and retrodegradation of waxy-maize starch. Carbohydr Res 166:162

17. Wilson RH, Belton PS (1988) An Fourier-transform infrared study of wheat starch gels. Carbohydr Res 180:339

18. van Soest JJG, de Wit D, Tournois H, Vliegenthart JFG (1994) The influence of glycerol on structural changes in waxy maize starch as studied by Fourier-transform infrared spectroscopy. Polymer 35:4722

19. Runt JP (2000) Crystalline polymer blends. In: Paul DR, Bucknall CB (ed) Polymer blends, vol 1. Wiley, New York, pp 167–186.

20. Park JW, Im SS, Kim SH, Kim YH (2000) Biodegradable polymer blends of poly(L-lactic acid) and gelatinized starch. Polym Eng Sci 40:2539