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Communications

Ionic Liquids Modified Montmorillonite/ Thermoplastic Starch Nanocomposites as Ionic Conducting Biopolymer

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Introduction

The efficient utilization of biodegradable polymers came from renewable sources is becoming increasingly important due to diminishing resources of fossil fuels as well as white pollution caused by un-degradable plastics based on petroleum. Starch is an abundant, renewable, low price, biodegradable and biocompatible nature polymer, which can be processed to thermoplastic starch (TPS) by melt extrusion or casting.¹ However, the properties of TPS, especially the poor mechanical properties and water resistance limit the application of TPS in many areas. Recently a great deal of studies have been reported to improve the performance of TPS.²⁻⁴ Moreover, TPS combined with multiwall carbon nanotube or sodium chloride can be used as solid polymer electrolytes (SPEs) in previous reports.^{5,6}

Montmorillonite (MMT) is a kind of aluminum silicates

classified as phyllosilicates, which is one of the most important reinforcing filler. It can increase the mechanical properties, thermal stability and water resistance of polymer composites dramatically.^{7,8} Subsequently some studies find only the plasticizer (water and glycerol) can intercalate into the narrow *d*-spacing of MMT effectively. However, it is difficult for the macromolecular of starch.⁹ In order to achieve intercalated or exfoliated TPS/MMT nanocomposites, organo-modified MMT (OMMT) with wider *d*-spacing is used.^{9,10} But the effect is not obvious because of the poor compatibility between hydrophilic TPS and hydrophobic OMMT. So the authors point out using hydrophilic modified MMT can be a promising way to further improve the performance of TPS/MMT composites.⁹

Recently ionic liquids (ILs), or room temperature molten salts have gained in interest because of their unique properties including non-volatility, non-flammability, low viscosity, and chemical and electrochemical stability.¹¹⁻¹⁴ It has also been shown that hydrophilic ILs (such as 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and 1-allyl-3-methylimidazolium chloride ([amim]Cl), respectively) can dissolve carbohydrate polymers effectively.^{11,12} Because high Cl⁻ concentration and activity of these ILs can break the extensive hydrogen bonding network and interact with hydroxyl groups of carbohydrate polymers.¹² Moreover, ILs also display high ionic conductivity as a result of their high mobility and high concentration of carrier ions. ILs have been expected to act as non-volatile and non-flammable electrolyte solutions.¹³ So [amim]Cl is used as a novel activated solvent and plasticizer for MMT and starch respectively. Moreover, high performance ionic conducting TPS/MMT nanocomposites can be achieved by casting in this paper. The complex interactions and conductive properties of these nanocomposites are also studied.

Results and Discussion

Ionic conducting TPS/MMT nanocomposites could be successfully prepared by casting. About 3 g [amim]Cl and different MMT (0, 0.1, 0.3, 0.5, 0.7 and 0.9 g respectively) contents were in turn added to 200 mL water. The mixture

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was stirred at 80 °C for 3 h under ultrasonic, then cooled to room temperature, filtered and dried. After being ground and filtered, the [amim]Cl-activated montmorillonite (AMMT) was obtained. Moreover, 10 g dry starch was added in the above mixture. The blend was heat at 80 °C with a constant stirring for 30 min. The mixtures were cast into polytetrafluoroethylene plates and solvent evaporated to dryness in an air-circulating oven at 55 °C until dry (about 8 h). [Amim]Cl plasticized starch (ATPS) and ATPS/AMMT nanocomposites could be achieved. All samples were stored airtight under room temperature immediately.

Figure 1 shows the wide angle X-ray diffraction (WAXD) of MMT, AMMT and ATPS/AMMT nanocomposites. The *d*-spacing could be calculated from Bragg's formula. As shown in Figure 1, MMT exhibited a sharp peak (001) at $2\theta = 8.05^\circ$ corresponding to the spacing of 1.07 nm between individual MMT layers. After MMT was modified with [amim]Cl, this peak shifted to 6.41° , which meant that the *d*-spacing of AMMT expanded to 1.34 nm. It indicated that [amim]Cl could intercalate and enlarge the layers of MMT effectively. Moreover, the enlarged *d*-spacing of AMMT was propitious to the intercalation of starch. As shown in Figure 1, the *d*-spacing of AMMT enlarged to about 1.58 nm in ATPS/AMMT nanocomposites. At the same time, this peak became wider and lower than that of MMT and AMMT. It indicated that the partially exfoliated ATPS/AMMT nanocomposites could also exist.

In native form, starch granules are insoluble in cold water. Beyond gelatinization temperature (about 60 °C), starch granules can undergo a disruption into smaller aggregates or particles in the presence of excess of water, and result in gelatinized starch.¹ The TPS is obtained after disruption and

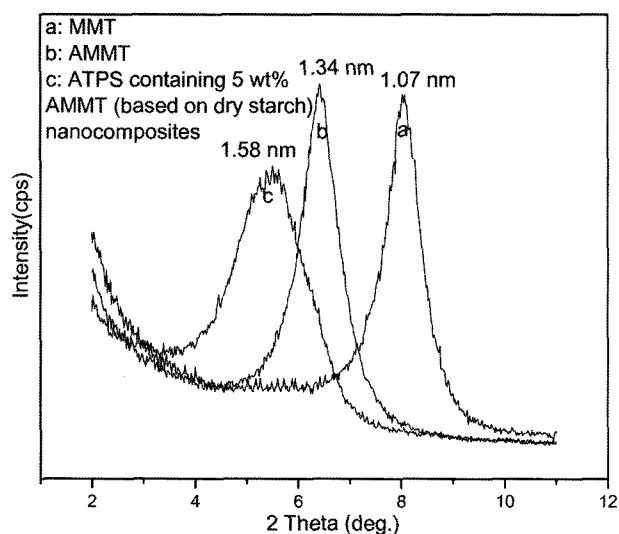


Figure 1. Wide angle X-ray diffraction (WAXD) patterns of MMT, AMMT and ATPS containing 5 wt% AMMT (based on dry starch) nanocomposites.

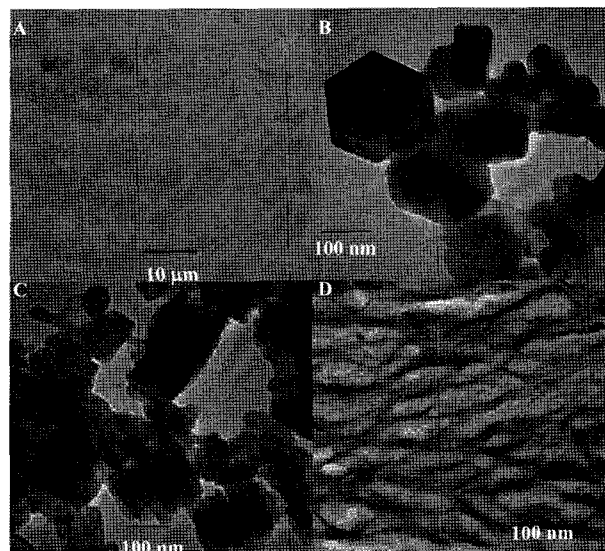


Figure 2. The SEM and TEM photographs of ATPS, MMT, AMMT and ATPS/AMMT nanocomposites. A: SEM of ATPS; B: TEM of MMT; C: TEM of AMMT; D: TEM of ATPS containing 5 wt% (based on dry starch) AMMT nanocomposites.

plasticization of native starch, by temperature and in presence of water and another plasticizer. Native cornstarch existed in the form of solid granules (about 10 μm) detected in our previous study.¹⁵

Figure 2(A) shows the scanning electron microscopy (SEM) of ATPS. As shown in Figure 2(A), ATPS presented a continuous phase and no residual starch granules could be found on the fractured surfaces. It ascribed to the active Cl of [amim]Cl could break up the inter- and intra-hydrogen bonds existed in starch and plasticize starch effectively. To further confirm the nanostructure of MMT, AMMT and ATPS/AMMT, transmission electron microscopy (TEM) was carried out. Figures 2(B-D) show the TEM of MMT, AMMT and ATPS/AMMT nanocomposites respectively. MMT mainly exhibited hexagon multilayer structure in Figure 2(B). The particle length was about 150 nm similar as previous report.¹⁶ After MMT was modified by [amim]Cl under ultrasonic, only small irregular particles congregated together could be detected in Figure 2(C). At the same time, [amim]Cl could enlarge the *d*-spacing of MMT had been detected by WAXD. Therefore, AMMT was propitious to the intercalation of ATPS. Figure 2(D) shows the TEM image of ATPS containing 5 wt% AMMT nanocomposites. It exhibited high dispersion and ordered intercalated structure. It ascribed to the wider *d*-spacing and the smaller platelet of AMMT.

The analysis of Fourier transform infrared (FTIR) spectroscopy spectra of TPS-based composites enabled the interactions to be identified.¹⁵ Figure 3 shows the FTIR spectrum of ATPS and ATPS containing different AMMT content nanocomposites. In the fingerprint region of FTIR spectrum of ATPS, three characteristic peaks appeared

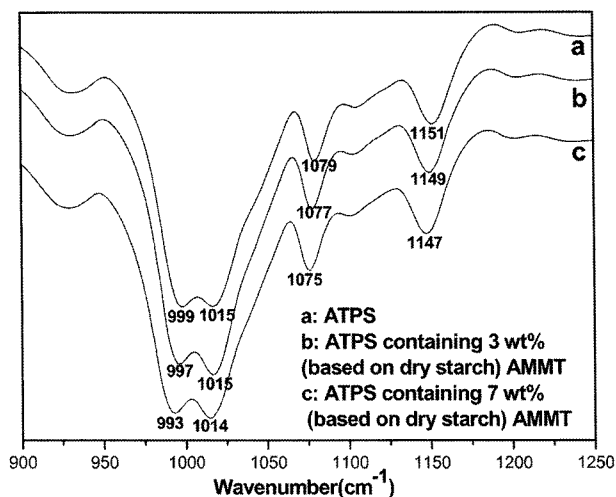


Figure 3. FTIR spectra of ATPS and ATPS/AMMT nanocomposites.

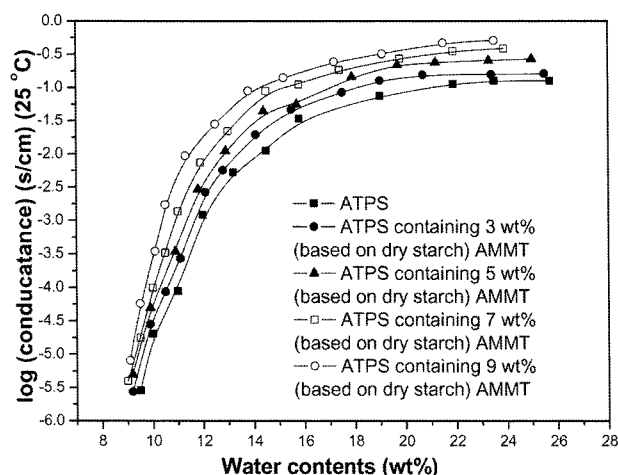


Figure 4. The electrical conductivity of ATPS with different AMMT contents.

between 1200 and 900 cm^{-1} , attributed to C-O bond stretching of starch.¹⁷ The characteristic peak near 1150 cm^{-1} was ascribed to C-O bond stretching of the C-O-H group in starch, while two peaks at 1080 and 1020 cm^{-1} were attributed to C-O bond stretching of the C-O-C group in the anhydroglucose ring.¹⁵ Compared with ATPS, the corresponding characteristic peaks of ATPS/AMMT nanocomposites shifted to lower wavenumber. Especially, in ATPS containing 7 wt% AMMT exhibited the lowest wavenumber. It indicated the intense interactions (the H-bonding and the ion-dipole) existed in these complex nanocomposites.

As shown in Figure 4, the conductance of ATPS was very much dependent on water and AMMT content. The initial conductance of ATPS (9.5 wt% water content) was about $10^{-5.6}$ S cm^{-1} . It could achieve to $10^{-0.8}$ S cm^{-1} (the improvement was about 5 orders of magnitude) at about 26 wt% water content. Because water had been recognized as an effective

plasticizer to weak the interaction of starch molecules and improve the movement of starch chains.¹⁸ So high water content was advantageous to the transference of ion in ATPS films. On the other hand, the increasing MMT content also improved the conductance of ATPS as shown in Figure 4. It attributed to the improvement MMT (sodium-MMT was used in this paper) content increased Na^+ concentration. At the same time, high dispersion and ordered intercalated structure of ATPS/AMMT nanocomposites might be propitious to the transference of ion.

In summary, hydrophilicity ILs, [amim]Cl containing high chloride ion concentration had strong hydrogen bond-forming abilities with starch. It could be used to plasticize cornstarch by casting. At the same time, [amim]Cl could modify MMT (increase the d -spacing) effectively. Therefore, ionic conducting biopolymer nanocomposites could be achieved. Moreover, MMT and water contents exerted an important influence on the conductance of ATPS film. The maximum conductance of ATPS containing 9 wt% MMT could achieve to about $10^{-0.3}$ S cm^{-1} with 23 wt% water content, which was higher than alkali metal doped TPS.⁵ So ILs-plasticized-starch/MMT nanocomposites would be a promising alternative for the development of new SPEs, which had a wide variety of potential applications such as antistatic plastics, electronic shielding, biosensor, environmentally sensitive membranes and so on.

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Supporting Information: Materials, experimental procedure for the syntheses of [amim]Cl, [amim]Cl-activated MMT, ATPS, ATPS/AMMT nanocomposites, and characterizations data are available *via* the Internet at <http://www.polymer.or.kr>.

References

- (1) L. Averous, *J. Macromol. Sci.-Pol. R*, **C44**, 231 (2004).
- (2) B. Y. Shin, G. S. Jo, K. S. Kang, T. A. Lee, B. S. Kim, and S. I. Sang, *Macromol. Res.*, **15**, 291 (2007).
- (3) N. Wang, J. G. Yu, P. R. Chang, and X. F. Ma, *Carbohydr. Polym.*, **71**, 109 (2008).
- (4) N. Wang, J. G. Yu, X. F. Ma, and Y. Wu, *Carbohydr. Polym.*, **67**, 446 (2007).
- (5) X. F. Ma, J. G. Yu, K. He, and N. Wang, *Macromol. Mater. Eng.*, **292**, 503 (2007).
- (6) X. F. Ma, J. G. Yu, and N. Wang, *Compos. Sci. Technol.*, **68**, 268 (2008).
- (7) J. G. Ryu, J. W. Lee, and H. Kim, *Macromol. Res.*, **10**, 187 (2002).
- (8) H. M. Jeong, M. Y. Choi, and Y. T. Ahn, *Macromol. Res.*, **14**, 312 (2006).
- (9) Q. X. Zhang, Z. Z. Yu, X. L. Xie, K. Naito, and Y. Kagawa, *Polymer*, **48**, 7193 (2007).
- (10) J. C. Kim and J. H. Chang, *Macromol. Res.*, **15**, 449 (2007).

- (11) J. Wu, J. Zhang, H. Zhang, J. S. He, Q. Ren, and M. Guo, *Biomacromolecules*, **5**, 266 (2004).
- (12) R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, *J. Am. Chem. Soc.*, **124**, 4974 (2002).
- (13) B. Singh and S. S. Sekhon, *Chem. Phys. Lett.*, **414**, 34 (2005).
- (14) S. W. Kang, K. Char, J. H. Kim, and Y. S. Kang, *Macromol. Res.*, **15**, 167 (2007).
- (15) N. Wang, J. G. Yu, X. F. Ma, and C. M. Han, *Polym. Composite*, **28**, 89 (2007).
- (16) S. S. Ray and M. Okamoto, *Macromol. Rapid Comm.*, **24**, 815 (2003).
- (17) J. M. Fang, P. A. Fowler, and J. Tomkinson, *Carbohydr. Polym.*, **47**, 245 (2002).
- (18) D. Lourdin, L. Coignard, H. Bizot, and P. Colonna, *Polymer*, **38**, 5401 (1997).