The Effect of Starch Structure on Starch-based Nanocomposite

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ABSTRCT

Starches, including high amylose cornstarch, normal cornstarch, and waxy cornstarch, were gelatinized and mixed with nanoclay aqueous dispersion and different amount plasticizer. The mixtures were then cast onto Teflon plate and allowed to dry naturally. The dried film were conditioned in an environmental chamber at 25℃, and 50% relative humidity for more than 24 hours before tested for water permission, mechanical strength and XRD. The intercalation of starches into nanoclay depended on the chain length of starch main chain and of side chain in absence of plasticizer. The shorter the chain length of starch was, the higher the degree of intercalation. Plasticizers had much smaller molecular weight than that of starch, plasticizer instead of starch intercalated into the nanoclay as shown by XRD when starch films were prepared in the presence of plasticizer.

Key words: starch, nanocomposite, plasticizer, intercalation, nanoclay

1   INTRODUCTION

The vast majority of plastic products are made from petroleum-based synthetic polymers that do not degrade in a landfill or in a compost-like environment. Therefore, the disposal of these products poses a serious environmental threat. An environmentally-conscious alternative is to design and synthesize polymers that are biodegradable.

Starch is by far the largest natural polymer used in the biodegradable plastics. However, the application of starch-based biodegradable plastics is severely limited by its low mechanical strength and low water resistance. A lot of ways have been proposed and investigated to solve this problem. Chemical modification was the first and most studied approach for starch-based biodegradable plastics [1]. However, low degree of modification did not result in much improvement, while high degrees of modification incurred high cost and low biodegradability of resultant plastics. Blending was the second most common approach used by industries and researchers. Both biodegradable and non-biodegradable polymers have been blended with starch with different level of successes[2]. However, the results were still far from satisfactory. A third approach is polymer-nanoclay hybrids. At present, polymer clay hybrids are one of the most important classes of synthetically engineered materials. They can be transformed into new materials possessing the advantages of both organic materials such as light weight, flexibility and good moldability and inorganic materials such as high strength, heat stability and chemical resistance.

Biodegradable polymers such as PVA[3], collagen[4], chitosan[5] and starch[6] have been engineered with nanoclay in many laboratories. As natural polymers cannot be polymerized from their monomer the same way as synthetic polymers in the laboratory, solution intercalation was used widely. Very few reports are available on the effect of structure of native starch on the properties of polymer clay hybrids. This research investigated the effects of type of starch on the extent of intercalation.

2 MATERIALS AND METHODS

High amylose starch (70% amylose), normal cornstarch and waxy cornstarch, denoted as HAS, NS, and WX, respectively, were purchased from local markets and were used without further purification. Closite Na$^+$-montmorillonite was obtained from Southern Clay, TX, USA. Other reagents were of chemical grade or above. Maltose dextrins were prepared in our laboratory.

Preparation of Nanoclay Dispersions: Closite Na$^+$ was dispersed in distilled water and sonicated for 1 h and then allowed to stand for 24 h at room temperature. The nanoclay was filtered before application.

Preparation of Starch Nanoclay Composites: Starch was gelatinized in pressured cooker at 120℃ for 20 min. The nanoclay dispersion and plasticizer were then added to the starch solution with agitation at 60℃ for 30 min. Then the starch-nanoclay dispersion was cast to Teflon plate and allowed to dry under ambient condition for 4 days. The samples were kept in an environmental chamber set at 25℃ and 50% relative humidity before X-ray and mechanical study. The amount of nanoclay was denoted as the percentage of nanoclay based on dry starch. The amount of plasticizer added was denoted as the proportion of plasticizer to dry starch.

X-ray: Starch nanocomposite films were X-rayed with a Rigaku D/Max-B diffractometer using Ni-filtered CoKa radiation. The scanning speed was 1^0/min over a range of 2 theta = 2 -12^0. The angle of diffraction versus diffraction intensity was recorded.

3 RESULTS AND DISCUSSION

Figure 1 shows XRD curves of high amylose starch hybrids with different amounts of Na$^+$ MMT. The peak 2-theta of pure Closite Na$^+$ was 7.34 degrees while that of high amylose starch with 3%, 5%, 7.5%, and 10% Closite Na$^+$ was 5.38, 5.44, 5.48 and 5.48 degrees, respectively. Obviously, high amylose starch could intercalate into nanoclay. The curves differed mainly in intensity. Chang et

al (2003) ascribed such increases in intensity to the aggregation of nanoclay. Such aggregation, if existed, should be quite different from aggregation of nanoclay under aqueous conditions, as the differences in 2-theta of all curves was quite small with only a slight trend of moving up with concentration of nanoclay.
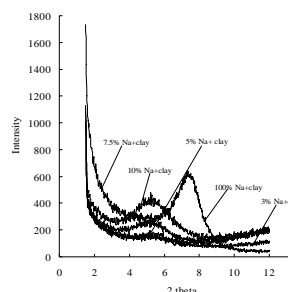

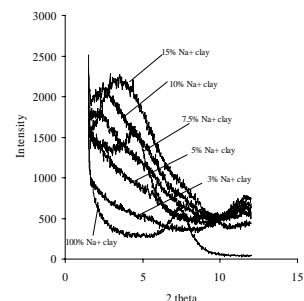Fig 1. XRD curves of HAS nanocomposite in absence of plasticizer

Fig 2. XRD curves of NS nanocomposite in absence of plasticizer

Fig 2 shows the XRD curves of normal starch hybrids with different amounts of MMT. The peak 2-thetas of normal starch with 3%, 5%, 7.5%, and 10% Closite Na$^+$ were 4.50, 4.54, 4.58, and 4.60 degrees, respectively. The angles shifting to lower angles suggested that the basal spacing of nanoclays in normal starch hybrids were wider than those in high amylose starch hybrids. The same trend was found in peak angle of normal starch hybrids with different nanoclay concentrations.
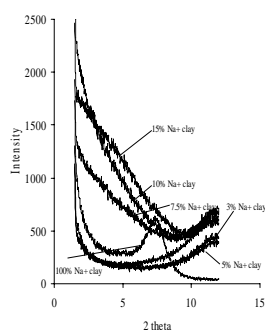

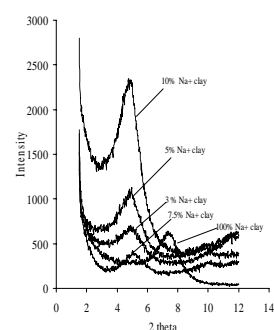Fig 3. XRD curves of WS nanocomposite in absence of plasticizer

Fig 4. XRD curves of glucose Closite Na$^+$ hybrids

Fig 3 shows the XRD curves for waxy starch hybrids with different amounts of MMT. The peaks corresponding

to the basal spacing disappeared. This reveals that the clays in those hybrids were dispersed homogeneously into the starch matrices.

The major differences among the three different types of starch leading to the intercalation difference should be the amounts of waxy starch and the number of side chains. As the functional groups of all starches were the same, the specific interaction between starch and nanoclay, if it existed, should be the same as well.

Fig 4 shows the XRD of glucose nanoclay hybrids. The peak angles for different combinations were about 5.3. The concentration of nanoclay to glucose did not result in too much difference. It is obvious that the peak angle of glucose was very close to that of high amylose starch. It is very likely that the high amylose starch intercalated into nanoclay the same way glucose did.
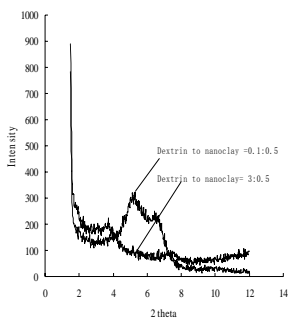

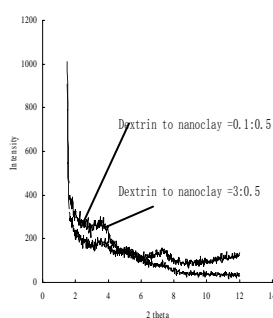Fig 5. XRD curves of dextrin 1 Closite Na$^+$ hybrids

Fig 6. XRD curves of dextrin 2 Closite Na$^+$ hybrids

Fig 5 shows the XRD of dextrin 1 - nanoclay hybrids. The peak angle for sample with a dextrin to nanoclay ratio of 1:5 was 5.26 degrees. The peak angle for sample with that of 6:1 was 3.28 degrees. When nanoclay was added at considerably higher concentrations, the peak angles in XRD were considerably higher than those at lower concentrations. The shift of diffraction theta with nanoclay concentration for dextrin 1 was much higher than that for high amylose starch, normal starch and waxy starch.

Fig 6 shows the XRD of dextrin 2 - nanoclay hybrids. Dextrin 2 had much small molecular weight than dextrin 1. The degree of polymerization of dextrin 2 was between 2 and 3, while that for dextrin 1 was between 8 and 10. The

same trend was found for dextrin 2. At high nanoclay concentration, the peak angle shifted to a higher region.

The difference between the intercalation degrees may be explained by the difference in the concentration of end groups in the different starches and the chain length of the different starches. The high amylose starch had the lowest end group concentration for a given weight concentration, while waxy starch had the highest end group concentration for a given weight concentration. The relatively short outer chain lengths may have contributed to the greater extent of intercalation of starch into nanoclay as well.
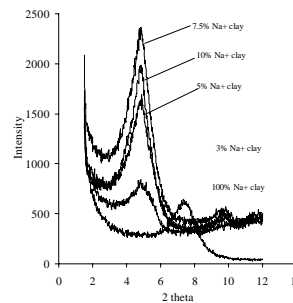

Fig 7. XRD curves of NS nanocomposite in the presence of one-third of glycerol as plasticizer
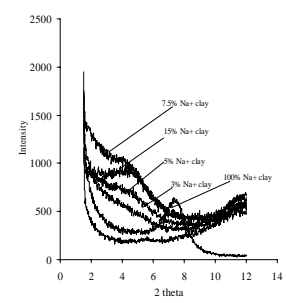
Fig 8. XRD curves of NS nanocomposite in the presence of two-thirds of glycerol as plasticizer

Fig 7 shows the XRD of normal starch in the presence of glycerol (plasticizer). The peak angles were about 5.06 degrees for all glycerol - nanoclay combinations. This angle was greater than that of normal starch - Closite Na$^+$ hybrids but smaller than that of high amylose starch - Closite Na$^+$ hybrids. It was very likely that the glycerol replaced the starch or combined with the starch somehow in the nanoclay galleries because of its small size. Fig 8 shows the XRD curves of normal starch with two thirds glycerol. The average peak angle was 4.82 degrees. The peak angle shifting toward a lower region was indicative of a higher degree of intercalation. A likely explanation for that may be that the glycerol starch complex instead of glycerol or starch intercalated into nanoclay or glycerol. Fig 9 shows the XRD curves of glycerol-nanoclay hybrids. The peak angel was 5.5 degrees, which was higher than the peak angle of normal starch and normal starch-glycerol combinations. An explanation of the mechanism by which

the plasticizer interacts with starch or nanoclay is yet to be investigated.
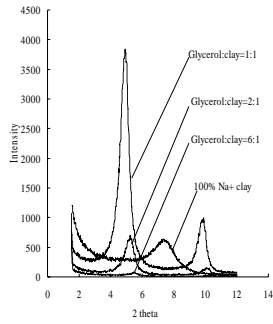
sorbitol as plasticizer

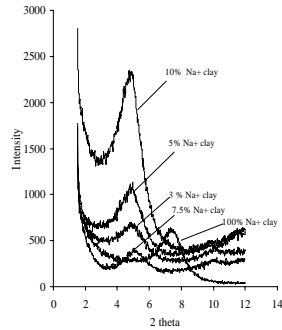Fig 9. XRD curves of glycerol Closite Na⁺ hybrids

Fig 10. XRD curves of NS nanocomposites in the presence of one-third of sorbitol as plasticizer

Fig 10 shows the XRD of normal starch in the presence of one-third of sorbitol. The average peak angle was 4.96 degrees. The peak was much less obvious than that of starch-glycerol-clay hybrids. The angle was a little smaller than that of glycerol counterpart. Fig 11 shows that as the content of sorbitol was increased, the average angle dropped a little. Fig 12 shows the XRD curve of sorbitol nanoclay hybrid. The peak angle was 5.5 degrees, which was about the same as that of glycerol, even though sorbitol and glycerol have about the same intercalation distances. But when added to normal cornstarch, the mixtures behaved a little differently. This may result from the difference in plasticizing effects of the two plasticizers.
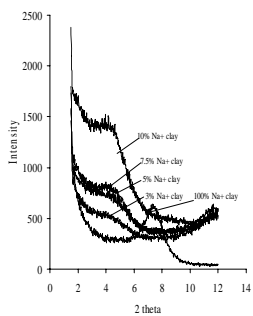

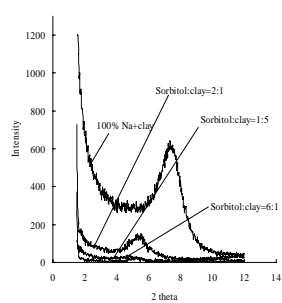Fig 11. XRD curves of NS nanocomposite in the presence of two-thirds of

Fig 12. XRD curves of sorbitol Closite Na⁺ system

4 CONCLUSIONS

Waxy starch with numerous short side chains exfoliated nanoclay while high amylose could only intercalate nanoclay in the absence of plasticizer. Glycerol and sorbitol behaved difference when mixed together with nanolclay and normal cornstarch, although they intercalated about the same degree into the nanoclay when interacted with nanolclay alone.

REFERENCES

[1] Zhou, Jiahua, Hanna, Milford, (2005), Effects of the properties of blowing agents on the processing and performance of extruded starch acetate, 97(5), 1880 - 1890

[2] Sathyanarayanan, K, (2005). Starch- Polycaprolactone Nanocomposites From Reactive Extrusion: Synthesis, Characterization, Properties And Scale-up Considerations, Dissertation, 11-Apr-2005, University of Cornell. USA

[3] Nayar, Suprabha; Sinha, Arvind. (2004). Systematic evolution of a porous hydroxyapatite-poly(vinylalcohol)-gelatin composite. Colloids and Surfaces, B: Biointerfaces, 35(1), 29-32.

[4] Fischer, S; De Vlieger, J; Kock, T; Batenburg, L; Fischer, H. (2001). Green nano-composite materials - new possibilities for bioplastics.Materials Research Society Symposium Proceedings, 661(Filled and Nanocomposite Polymer Materials), ISSN: 0272-9172.

[5] Hu, Qiaoling; Li, Baoqiang; Wang, Mang; Shen, Jiacong. (2004). Preparation and characterization of biodegradable chitosan/hydroxyapatite nanocomposite rods via in situ hybridization: a potential material as internal fixation of bone fracture. Biomaterials, 25(5), 779-785.

[6] Meng Chen, Biqiong Chen and Julian R G Evans, (2005). Novel thermoplastic starch–clay nanocomposite foams, Nanotechnology 16, 2334-2337