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Microstructure changes of on the extruded high-amylose bionanocomposites as affected by moisture content via synchrotron radiation studies

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ABSTRACT

The crystalline domain changes and lamellar structure observations of sorbitol-plasticized starch nanocomposite had been investigated via synchrotron. Strong interactions were found between amylose–sorbitol, resulting in reduced inter-helix spacing of the starch polymer. Achievable $d_{spacing}$ of nanoclay was confirmed to be correlated to the moisture content (mc) within the nanocomposites. SAXS diffraction patterns changed from circular (high mc samples) to elliptical (low mc samples), indicating the formation of long periodic structure and increased heterogeneities of the electron density within the samples. Two different domains sized at around 90 Å and 350 Å were found for the low mc samples. However, only the ~90 Å domain was observed in high mc samples. Formation of the 380 Å domain is attributed to the retrogradation behaviour in the absence of water molecules. Meanwhile, the nucleation effect of nanoclay is another factor leading to the emergence of the larger crystalline domain.

1. Introduction

The wide application of biodegradable polymers has lured increasing attention from numerous researchers. Starch is a natural polymer which is cheap and readily available. Literatures about utilization of starch-based materials in various aspects had been reported continuously [1]. However, the properties of starchy products are mostly undergoing unexpected time-dependent changes such as phase-separation and recrystallization of starch chains. This process had been intensively studied via different methods (DSC, NMR, DMTA, mechanical properties, etc.) and is collectively defined as retrogradation. Such retrogradation, referred to as structure relaxation in low moisture system, might introduce significant changes in the polymeric network, thus leading to pronounced distinctness in end-products' physical and chemical properties [2]. Van Soest et al. in 1997 investigated the influence of glycerol and water content on the structure and properties of extruded starch sheet; the effects of controlled storage on a similar topic had been carried out by Mali et al. in 2006 [3,4]. Addition of nanoclay had been widely used in thermal plastic starch preparation, which was reported to have equivalent properties to that from oil-based plastic in some main aspects. However, there are few publications that have investigated the combined effect of plasticizer and nanoparticles on the retrogradation behaviour of the extruded-starch bionanocomposites.

Small angle X-ray Scattering (SAXS) is a powerful and efficient method to investigate the dispersion of particles in nano-scale, and investigate the crystalline domains that are formed due to the interactions between the polymer and the additives, with a structure size of 10 Å or larger [5]. SAXS has been widely applied in nano/polymer science to quantify the crystallization behaviour [6].

In such a context, the objective of the current study is to study the microstructure of the bionanocomposites and the crystallization domain characteristic upon dehydration. The approach in the current study is that the samples are subjected to different durations of drying under controlled condition. To our knowledge, this is the first report on starch-based sorbitol-plasticized nanocomposite where we examined the combined effect of sorbitol and nanoclay on the structure relaxation behaviour.

2. Materials and method

2.1. Materials and extrusion

High amylose starch (70% amylose) was purchased from National Starch Company (New Jersey, USA); sorbitol was obtained from Food

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Table 1
Experimental sheet for sample preparation and characterization results (moisture content, $d_{spacing}$ and domain sizes).

Ageing days	Moisture (%)	P_{starch} (nm^{-1})	Size distribution[a]	
			Domain 1(Å)	Domain 2(Å)
S020				
1	16.68	0.36	106.48	–
2	12.75	0.36	101.46	–
4	13.52	0.36	98.76	–
5	7.192	Shoulder	91.08	358.09
Ageing days	**Moisture (%)**	**$d_{spacing}$ (Å)**	**Size distribution**	
			Domain 1(Å)	Domain 2(Å)
S420				
1	17.38	20.9	91.04	–
2	7.12	19.3	88.31	339.7
4	10.38	20.4	86.89	363.82
5	3.575	20.4	83.66	350.15

[a] Size distribution was obtained based on the Irena Macro for Igor package [9].

Department Melbourne Company (Melbourne, Australia); and nanoclay (Cloisite – Na$^+$ Montmorillonite, 99.5%) was supplied by Niche-Plas Ltd. (Sydney, Australia). Samples were prepared with different ratios of nanoclay/sorbitol, Table 1, via extrusion; for detailed extrusion conditions please refer to our earlier work [7]. Each formulation was presented as a label such as S020, where 'S' refers to the sorbitol, the first digit '0' refers to the nanoclay content in weight percentage (e. g., 0 wt% in S020) and the last two digits '20' refer to the weight percentage of sorbitol within the samples. Samples are subjected to air-drying at controlled environment (35 °C and 55% RH) for the required duration and then kept within sealed glass vials (8 mm diameter, 2 cm height).

2.2. Characterization studies

The moisture-meter (CA-100, Mitsubishi Chemical Corporation, Japan) was used to measure the moisture content for all the samples. Measurement was conducted in triplicates.

SAXS was carried out at beamline BL40B2 of Spring-8 synchrotron facility in Hyogo, Japan. The beam was monochromatized to a wavelength of 0.1 nm with an object distance of 1151.767 mm. All the patterns recorded were calibrated by the diffraction rings from the AgBH (Silver Behenate) reference sample. The data reduction was completed with FIT2D software. Size distributions profiles for the obtained samples were calculated according to the Maximum Entropy Method (MEM) developed by Potton et al. [8] from Irena modelling macros [9].

3. Result and discussion

3.1. Synchrotron studies

3.1.1. SAXS profile analysis

The raw patterns from samples and its corresponding SAXS profiles are shown in Fig. 1(a). The shape of the diffraction pattern for S020 changed from a circle (S020$_{1day}$) to an elliptical (S020$_{5days}$) shell which indicated a more distinguishable long order structure formation in S020$_{5days}$ [10,11]. Heterogeneities across the polymeric network could be directly reflected on the diffraction intensity from different samples due to the electronic density heterogeneities [12]; higher intensity observed in S020$_{5days}$ supports the argument that a higher degree of dehydration (low mc samples) favoured the

growth of long order lamellar morphology within the polymeric network. Greater ellipticity of the diffraction patterns for the 5 days drying samples indicated the above-mentioned heterogeneity, as seen in Fig. 1. Furthermore, similar finding had been reported by Grubb et al. in 2010 in the X-ray patterns of nylon-6 fibres during dehydration [13]. Such a change in ellipticity was the direct reflection of the electron density heterogeneities and lamellar structure which indicated that the removal of weakly bonded water (low mc samples) led to the emergence of different crystalline domains; see Section 3.1.2. Presently, the diffraction patterns for samples that incorporated nanoclay showed obvious lamellar structure (elliptical diffraction shape) regardless of their drying duration; this was considered to arise from polymeric crystalline growth using the typical lamellar structure of nanoclay itself. It could be seen from Fig. 1(b) that the longer the drying time, the more obvious the lamellar structure observed.

There is a distinct lack of a well-defined 9 nm ($Q=0.07$ Å^{-1}) spacing for native starches that could be observed in the extruded samples (Fig. 1) and, instead, a broad 'shoulder' appeared around $Q=0.04$–0.06 Å^{-1} in low degree aged samples (S010$_{1day}$/S020$_{2days}$/S020$_{4days}$ and S420$_{1day}$/S420$_{2days}$/S420$_{4days}$) which were similar to the value (16 nm) reported by Lemake et al. [14]. Such a 'shoulder' typically corresponds to the long periodic structure of the processed amylose polymer [14] and for the samples with higher equilibrium moisture, which typically meant that greater plasticiser (both sorbitol and water) quantities allowed larger 3-dimensional periodic growth. However, this peak was not well defined in low mc samples (S020$_{5days}$ and S420$_{5days}$). This finding indicated the formation of 'dispersed' heterogeneities within the network structure. It would be further interesting to observe the heterogeneities in the lamellar structure, which would result from the different crystalline domains formed by the removal of weakly associated water molecules. On the other hand, these observations could be related to the gelatinization upon extrusion which destroyed the granule/nanoclay organization in layers crystals [15]. The retrogradation process reorganized the polymeric network and the loss of water molecules allowed the amylose–sorbitol assemblage to form various domain sizes within the matrix. It is likely that the removal of water 'aggravated' the heterogeneities within the sample, as discussed in the earlier section (Section 3.1), and reduced the well-defined diffraction rings (Fig. 1(a,b)).

Bragg peaks occurred at a series of Q values satisfying the relationship $d \approx 2\pi/Q$ [5]. The corresponding $d_{spacing}$ values for nanoclay-contained samples are presented in Table 1. It could be read from Table 1 that the $d_{spacing}$ value increased from 11.7 Å ($d_{spacing}^{pristine}$) to 20.9 Å (S420$_{1day}$) after extrusion (the characteristic peak of nanoclay ($P_{nanoclay}$) located in $Q=0.30$ Å^{-1}). This indicated that the starch chain successfully penetrated into the gallery of nanoclay platelets as mentioned in the literature [7,16–18]. It is also noticeable that $d_{spacing}^{S420_{2days}}$ decreased to 19.3 Å; this might be correlated with the low moisture content when compared with S420$_{4days}$ sample, where the loss of water molecules resulted in the reduction in $d_{spacing}$ value for S420$_{2days}$. Table 1 shows the moisture content increased within S420$_{4days}$; meanwhile, $d_{spacing}^{S420_{4days}}$ value increased from 19.3 to 20.4 Å as a result of the water-rich environment. However, no further change was observed between S420$_{4days}$ and S420$_{5days}$ samples.

3.1.2. Size distribution of the various crystalline domains

The size distribution analysis was carried out based on the algorithm (maximum entropy algorithm) developed by Potton et al. which had been successfully applied to evaluate the particle size distribution in polymers based on SAXS [8,19,20]. In this method, the unique solution for the problem of size distribution was complementarily tracked by the maximum entropy method.