

# Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch

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## Abstract

Pea starch nanocrystals (PSN) dispersion containing nanocrystals in a range of 30–80 nm was prepared from native pea starch (NPS) granules by acid hydrolysis. Two series of films were prepared by blending poly(vinyl alcohol) (PVA) with NPS and PSN, respectively. The effects of NPS and PSN on the structure and properties of the resulting films were comparatively investigated by FTIR, XRD, SEM, and testing of light transmittance, tensile, and moisture uptake. The light transmittance ( $Tr$ ), tensile strength ( $\sigma_b$ ), and elongation at break ( $\epsilon_b$ ) of the PVA/NPS films were lower than that of PVA film and decreased with an increase in NPS content. However, the PVA/PSN nanocomposite films containing 5 and 10 wt% of PSN content exhibited improved physical properties over the PVA film. The PVA/PSN films showed higher  $Tr$ ,  $\sigma_b$ , and  $\epsilon_b$ , and lower moisture uptake ( $Mu$ ) than the corresponding PVA/NPS films with the same component ration. For example, the values of  $Tr$ ,  $\sigma_b$ ,  $\epsilon_b$ , and  $Mu$  of the PVA/PSN film containing 10 wt% of PSN content were 91%, 40 MPa, 734% and 71%, respectively; while those of the corresponding PVA/NPS film were 69%, 35 MPa, 579% and 73%, respectively. The results revealed that PSN, comparing with NPS, had much smaller sizes and dispersed more homogeneously in PVA matrix, resulting in stronger interactions with PVA. New applications of native pea starch and its nanocrystals as low-cost fillers were explored in this work, and PSN exhibited greater potential than NPS to improve the properties of PVA-based composites. Crown copyright © 2007 Published by Elsevier Ltd. All rights reserved.

**Keywords:** Pea starch; Poly(vinyl alcohol); Nanocrystals; Blend; Nanocomposite; Film

## 1. Introduction

Poly(vinyl alcohol) (PVA) is the largest synthetic water-soluble polymer produced in the world (Ramaraj, 2007a). It is also a versatile polymer with many industrial applications because of its biodegradability, biocompatibility, chemical resistance, and excellent physical properties (Paradossi, Cavalieri, Chiessi, Spagnoli, & Cowman, 2003; Zhai, Yoshii, & Kume, 2003). It has been reported that PVA with an average molecular weight as high as  $10^6$  could be completely degraded by soil bacteria, especially by *Pseudomonads* (Lenz, 1993). However, the degradation process of pure PVA is quite slow, particularly

under anaerobic conditions (Pšejja, Charvátová, Hruzík, Hrnčířík, & Kupec, 2006); and the degradation rate strongly depends on the residual acetate groups (Corti, Cinelli, D'Antone, Kenawy & Solaro, 2002). Another shortcoming of PVA is its high-cost, which has to compete with low-cost thermoplastic materials like polyethylene, polypropylene, and poly(vinyl chloride) in practical applications (Ramaraj, 2007b). Hence, a potential solution to enhance the biodegradation rate and lower the cost of PVA lies in preparing composites with more biodegradable, cheaper, and easily processable fillers or polymers. For example, many kinds of PVA-based biodegradable composites have been prepared by blending PVA with natural polymers such as starch (Follain, Joly, Dole, & Bliard, 2005b; Lawton, 1996; Siddaramaiah, Raj, & Somashekar, 2004), cellulose (Ramaraj, 2006), cellulose

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(Ramaraj, 2006), chitin and chitosan (Jia et al. 2007), soy protein (Su, Huang, Liu, Fu, & Liu, 2007), wheat protein (Zhang, Burgar, Loubakos, & Beh, 2004), egg protein (Yi, Lu, Guo, & Yu, 2004), lignin (Fernandes, Hechenleitner, Job, Radovanovic, & Pineda, 2006), and sodium alginate (Çaykara & Demirci, 2006), etc. Among the above-mentioned natural polymers, starch is one of the most promising materials for the modification of PVA because of its abundant supply, low-cost, good processability, biodegradability, and ease of physical and chemical modifications (Follain et al., 2005b; Mohanty, Misra, & Hinrichsen, 2000). The following sources of starch have been used to blend with PVA for the preparation of PVA/starch composites: potato (Cinelli, Chiellini, Lawton, & Imam, 2006; Ramaraj, 2007b), corn (Imam, Cinelli, Gordon, & Chiellini, 2005; Zhai et al., 2003), wheat (Follain, Joly, Dole, & Bliard, 2005a; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004), and sago (Khan, Bhattacharia, Kader, & Bahari, 2006). Noticeably, no work on PVA-based composites using pea starch was reported. However, in the PVA/starch composites, starch is just partially compatible with PVA. It was reported that the tensile strength, elongation at break, and transparency of the PVA/starch composites decreased with an increased starch content (Ramaraj, 2006; Siddaramaiah et al., 2004). In general, the addition of starch into PVA does not improve the physical properties because of the poor compatibility between PVA and starch (Siddaramaiah et al., 2004). Thus, the physical properties of PVA/starch composites need further improvement to meet the demands of extensive applications. Some of the effective means commonly used to modify the PVA/starch composites for the improvement of properties include: (1) using chemically modified PVA or starch instead of native PVA and starch (Nabar, Draybuck, & Narayan, 2006); (2) using chemical or physical modifications to the PVA/starch composites during or after the blending process, such as cross-linking reactions, grafting (Beliakova, Aly, & Abdel-Mohdy, 2004; Khan et al., 2006), and surface modification (Jayasekara et al., 2004). The cross-linking reagents and methods reported in PVA/starch composite were glutaraldehyde (Ramaraj, 2007a), boric acid (Yin, Li, Liu, & Li, 2005), epichlorohydrin (Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006), radiation (Zhai et al., 2003), and photocross-linking (Follain et al., 2005a). Grafting and cross-linking reactions improve the compatibility between PVA and starch molecules, resulting in the improvement of the mechanical properties, transparency and water-resistivity or swelling properties, while retaining the biodegradability (Nabar et al., 2006; Ramaraj, 2007a; Yin et al., 2005).

In recent years, nanowhiskers and nanocrystals have been prepared from natural polymers and applied to reinforce biodegradable or non-biodegradable polymeric matrix (Lu, Weng, & Zhang, 2004; Paillet & Dufresne, 2001; Samir, Alloin, Gorecki, Sanchez, & Dufresne, 2004). Interestingly, Dufresne and his coworkers reported on the preparation of starch nanocrystals from native waxy maize starch (Angel-

lier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004; Dufresne, Cavallé, & Helbert, 1996) and potato starch (Dufresne & Cavallé, 1998) granules, and their utilizations to reinforce natural rubber (Angellier, Molina-Boisseau, & Dufresne, 2005), poly( $\beta$ -hydroxyoctanoate) (Dubief, Samain, & Dufresne, 1999), and starch (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006). The physical properties of the resulting nanocomposites were improved by the incorporation of starch nanocrystals. Canada is the largest producer ( $\sim 25\%$  of total world production) and the largest exporter ( $\sim 40\%$  of the total world exports) of field pea in the world (Ratnayake, Hoover, & Warkentin, 2002). Pea starch and pea protein are the two main products from wet process in the pea industry. The market value for pea starch is relatively low and is affected by the market demand and supply from other sources (Cao, Chen, Chang, & Huneault, 2007). This suggests more attention should be paid to explore new and novel applications of pea starch. Thus, we attempted to introduce pea starch to PVA using two different methods. One method utilized the direct blending of native pea starch with PVA to prepare low-cost biodegradable composites. The other method was involved the preparation of starch nanocrystals from native pea starch by an acid hydrolysis process, followed by the blending of the obtained pea starch nanocrystals with PVA to provide property-enhanced composites. The different effects of native pea starch and pea starch nanocrystals on the structure and properties of the two series of PVA-based composites were comparatively investigated.

## 2. Experimental

### 2.1. Materials

Native pea starch (NPS), prepared from Golden Canadian field peas and composed of 35% amylose and 65% amylopectin, was supplied by Nutri-Pea Limited Canada (Portage la Prairie, Canada). Poly(vinyl alcohol) (PVA) with  $M_w$  of  $1.15 \times 10^5$  and minimum degree of hydrolysis of 87% was purchased from BDH Limited (Poole, England). NPS and PVA were vacuum-dried at 50 °C for 24 h before use. Glycerol (99.5% purity) and other chemicals were purchased from Sigma-Aldrich Canada Ltd. (Oakville, Canada) and used without further treatment.

### 2.2. Preparation of pea starch nanocrystals dispersion

Pea starch nanocrystals (PSN) dispersion was prepared by a previously described method (Angellier et al., 2004) with minor modifications. Briefly, native pea starch (NPS) granules were mixed with 3.16 M  $H_2SO_4$  solution at a starch concentration of 15 wt% in a 500 mL Erlenmeyer flask. The suspensions were then continuously stirred at 100 rpm under 40 °C. After 5 days of hydrolysis, the suspensions were washed by successive centrifugations in distilled water until neutrality was achieved. They were dialyzed for 3 days and then diluted with distilled water

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