Corrigendum

Physico-mechanical and structural characteristics of blend film of poly (vinyl alcohol) with biodegradable polymers as affected by disorder-to-order conformational transition

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ABSTRACT

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The binary blend films of poly (vinyl alcohol) (PVA) were prepared with selected biodegradable polymers (Na-alginate, gelatin, chitosan, κ-carrageenan and carboxymethyl cellulose) at the point of their chain entanglement. The water resistance, water vapor permeability and mechanical assays were considered as a benchmark to select the superior blend film. The highest water resistant and water barrier property belonged to the blend that contains κ-carrageenan. Introducing the biodegradable polymers into PVA led to an increase in tensile strength, among which κ-carrageenan being further effective than the others. Accordingly, the influence of conformational change of κ-carrageenan chains from disorder-to-order mode on PVA matrix was monitored by hydrophobicity assay, FT-IR, FE-SEM and XRD. The conformational transition of κ-carrageenan chains to ordered mode increased PVA hydrophobicity. Moreover, κ-carrageenan chains, which were present in ordered form, noticeably decreased the surface free energy of the PVA-based film. The emergence of new characteristic bands regarding κ-carrageenan found in the fingerprint region of PVA at above κ-carrageenan coil-overlap concentration. FE-SEM exhibited that PVA surface became uniform along with the disappearance of micro-cracks after κ-carrageenan inclusion. The pronounced κ-carrageenan peak appeared in X-ray diffraction pattern of PVA after the conformational transition of κ-carrageenan chains.

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1. Introduction

There is a growing trend within the food industry toward the development of the innovative packaging based on the application of biodegradable polymers, rather than the use of the more traditional non-degradable ones (Mikkonen et al., 2007). A main reason for this tendency is reducing the environmental impacts of the non-degradable polymers (Hoagland & Parris, 1996).

Poly (vinyl alcohol) (PVA) is a well-known biodegradable thermoplastic polymer with a wide range of applications in the food

and pharmaceutical industries (Lei, Jie, Jun, & Ruiyun, 1994). PVA has a semi-crystalline structure with high hydrophilic character due to the ability of forming hydrogen bonding with water molecules (Skeist & Miron, 1990, pp. 3—20). PVA, such as other biodegradable polymers, is essentially unsuitable for most packaging applications, and therefore needs to be modified to increase its usefulness and value through using many different physical and chemical methods. Blending method is a desirable physical approach for synthesizing a polymeric film when polymers, in terms of thermodynamic properties, are compatible. The performance of PVA film through blending can be modified in relation to resistance against water (Guohua et al., 2006), increasing mechanical strength and improvement of water barrier property (Limpan, Prodpran, Benjakul, & Prasarpran, 2010).

The biodegradable polymers from the plant and animal sources, including Na-alginate, gelatin, chitosan, κ-carrageenan and carboxymethyl cellulose, are broadly used as the film matrix, which

can also be introduced into the other polymers to make blend films. Na-alginate, chitosan and gelatin are commonly used for modification of the films based on konjac glucomannan (Xiao, Gao, & Zhang, 2000), cellulose (Naidu, Sairam, Raju, & Aminabhavi, 2005) and soy protein isolate (Denavi et al., 2009). Carboxymethyl cellulose and κ-carrageenan are also incorporated into various polymers with the aim of improving the physico-mechanical properties of the resulting blend films (Paula et al., 2015; Zhang, Zhang, Lu, & Liang, 2013).

The functional properties of a polymeric film such as physical, thermo-mechanical and structural properties are influenced by the conformation mode of the polymer chains, whereby if they have a disordered structure, then their chain interactions relate closely to the degree of space-occupancy by the chain coils. On the other hands, if they exist as ordered modes, then they are capable of stable association into compact networks (Chronakis & Kasapis, 1995; Lazaridou, Biliaderis, & Kontogiorgos, 2003). Moreover, the role of structural conformation of a polymer chain is of almost prominent in the kinetics of water solubility, their water vapor permeability and the tensile strength of films formed by such polymers (Kyotani & Kanetsuna, 1972; Lazaridou et al., 2003).

The coil-overlap concentration (c*) represents the point where the individual polymer chains begin to come into contact with each other and can be considered as a border concentration between the dilute and the semi-dilute regimes. During conformational change above c*, overlapping of the chains occurs and separate chains become entangled with one another. Due to overlapping and entanglement of the chains in this region, there are fairly strong interactions between polymer strands under the semi-dilute condition (c > c*). It leads to the formation of macrostructure assemblages and subsequently increasing the rigidity of the polymer. In contrast, below the coil overlap region (c < c*), the biopolymers have a brittle structure with a weak tensile strength (Doi & Edwards, 1988).

Although there are many articles in the literature concerning the fabrication, development and also more fundamentally revealing the functional properties of the biodegradable films, there are rather limited published studies that provide the effect of conformational transition of polymer chains from disorder-to-order mode on physico-mechanical and structural properties of a polymeric film.

Therefore, the first aim of the current work is to designate the superior binary blend from PVA with several biodegradable polymers at the point of their coil-overlap concentration by using conventional physical and mechanical assays. The second is to test the behavior of the superior PVA blend film under the effect of conformational changes of biopolymer chains from dilute to semi-dilute regimes by some of the most structural experiments. Our initial hypothesis is based on the fact that the disorder-to-order transition of the biodegradable polymer chains can change the physico-mechanical and structural properties of the PVA-based film in a profound manner.

2. Materials and methods

2.1. Materials

The commercial Na-alginate (50–60 kDa), gelatin (43 kDa with bloom 93) and κ-carrageenan (25–30 kDa) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The carboxymethyl cellulose (90 kDa with the degree of substitution ~0.51) and low molecular weight chitosan (45 kDa and >75% deacetylated) obtained from Merck Co (Merck, Germany). PVA with average molecular weight of 72,000 g/mol (~1600 polymerization) and moisture content of 11.2% was kindly provided from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Coil-overlap point, intrinsic viscosity and coil-overlap parameter

The point of coil-overlap concentration was considered for incorporation of the selected biodegradable polymers into the PVA matrix. Coil-overlap concentration (c*), intrinsic viscosity (η) and coil-overlap parameter c[η] were measured by an Ostwald viscometer with nominal constant 0.011 $mm.s^{-2}$ (Witeg Co., Germany) that's equipped with a thermostatic water bath under precise temperature control. Various amounts of the biodegradable polymers (0.05–0.45 g/dL), excluding chitosan, were dissolved in deionized water to cover the span of concentrations from dilute to the semi-dilute regions. Chitosan although insoluble in water at pH = 7, is nonetheless soluble in acetic acid solution. So, the chitosan was dissolved in 1% (v/v) of acetic aqueous solution and stirred at 60 °C for 30 min to obtain a homogeneous solution. Starting with, exactly 2 ml of each solution, the system was manually diluted after generating at least three efflux time readings at each concentration. Then, the relative viscosity (η_{rel}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) were calculated by using Eqs. (1)–(3), respectively as follows:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \cdot \frac{\rho}{\rho_0} \tag{1}$$

$$\eta_{red} = \frac{(\eta_{rel} - 1)}{C} \tag{2}$$

$$\eta_{inh} = \frac{Ln\ (\eta_{rel})}{C} \tag{3}$$

where, t/t_o and ρ/ρ_o are the ratio of efflux time of solution to solvent and the ratio of the density of the solution to the solvent, respectively. (η_{rel}-1) is specific viscosity (η_{sp}) and concentration of the biopolymers is represented as C.

The intrinsic viscosity is obtained from the extrapolation of Ln (η_{rel})/C and η_{sp}/C to infinite dilution according to the Huggins's equation (4) and Kraemer's equation (5) as follows (Huggins, 1942; Kraemer, 1938):

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 C \tag{4}$$

$$\frac{Ln(\eta_{rel})}{C} = [\eta] + K_2[\eta]^2 C \tag{5}$$

Here, K_1 and K_2 are the Huggins's and the Kraemer's constants, respectively (Morris, Cutler, Ross-Murphy, Rees, & Price, 1981).

2.3. Preparation of blend films

PVA as a film matrix was prepared by the casting method. The PVA powder was dissolved in deionized water (4 g/dL) at 75 °C for 2 h. Separately, the specific concentration of each biodegradable polymer, in the accordance with their c*, dissolved in deionized water (in the case of chitosan, 1% (v/v) of acetic acid) and heated at 75 °C under constant stirring. Each biodegradable polymer solution were incorporated into the PVA solution to obtain binary blend solutions and keep stirring for 2 h at 75 °C.

After the assessment, 20 ml of each solution was poured into the glass plate and transferred into the oven set at 48 °C with a RH of 40%. The films were peeled off from the glass plates after 18 h and conditioned for 36 h at 45% RH in the ambient temperature for further experiments.