

Research Article

Thermal Properties and X-Ray Diffraction (XRD) Results for Carboxymethyl Cellulose /Polyvinyl Alcohol /Clay Nanocomposite Packaging Films

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Abstract

The use of natural polymers is increasing in food packaging applications in order to reduce the consumption of nondegradable synthetic polymer materials. However, due to some poor characteristics of natural polymers, recently, nanotechnology has been employed in various applications like food packaging. Therefore, to use the nanomaterials as a constituent in the packaging material structure, in a research project, the CMC/PVA/nanoclay films were prepared by casting method and their properties were evaluated. This article presents the XRD study results that it was done to evaluate the presence and distribution of the nanoparticles in the polymer. In addition, thermal characteristics of the prepared films are discussed in this paper. The result of XRD shows that the clays well dispersed in the CMC/PVA matrix. DSC results shows that the degradation temperature of CMC/PVA/nanoclay (0.5, 1, 3 %) samples is appeared at a lower temperatures than that of CMC/PVA film.

Keywords: Carboxymethyl Cellulose (CMC); Differential Scanning Calorimetry (DSC); Nanoclay; Packaging; Thermal properties; X-ray Diffraction (XRD)

Introduction

Packaging system is a necessary step in the food processing due to preserve the organoleptic, nutritional and hygienic characteristics of foods during storage and consumption. Nowadays, most materials used for food packaging are petrochemical-based and non-biodegradable, leading to environmental pollution and serious ecological problems [1]. In order to solve problems caused by plastic wastes, many efforts have been done to obtain environmental friendly packaging materials. Many researchers have focused on substitute bio-based plastics by biodegradable materials with similar

properties. Therefore, new bio-based materials have been exploited to develop biodegradable films to extend shelf life and improve quality of food while reducing packaging waste [2]. For the past 10 years, research on natural films and coatings is driven by food engineers due to the high demand for longer shelf life and better quality of fresh foods as well as environmentally friendly packaging [3,4]. In addition, such films and coatings can be used as a carrier for incorporating natural or chemical antimicrobial agents, antioxidants, enzymes or functional ingredients such as probiotics, minerals and vitamins [5].

Since biodegradable polymers require improvement in terms of brittleness, low thermal stability and poor barrier properties [6], several composites have been developed by adding reinforcing compounds to polymers to enhance their thermal, mechanical and barrier properties. Most of these reinforced materials present poor interactions at the interface of both components. Macroscopic reinforcing components usually contain defects, which become less important as the particles of the reinforcing component are smaller [7]. Thus, the application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the cost-price-efficiency [6]. A number of researchers have therefore explored the concept of fully bio-derived nanocomposites as a route to development of bioplastics or bioresins with better properties [8-10]. Biopolymer-based nanocomposites have also been the subject of recent reviews [8, 11-13].

Polymer composites are mixtures of polymers with inorganic or organic fillers with certain geometries (fibers, flakes, spheres, particulates). The use of fillers which have at least one dimension in the nanometric range (nanoparticles) creates polymer nanocomposites [14,15]. Nanoparticles have comparatively bigger surface area than their micro scale equivalents, which favors the matrix-filler interfaces. Nanoparticles and nanoreinforcements can also have other tasks when added to a polymer, for instance antimicrobial activity, immobilization of enzymes, biosensing, etc. [15]. Different types of fillers can be distinguished, depending on how many dimensions are in the nanometric range. A uniform dispersion of nanoparticles leads to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior, and the consequent thermal and mechanical properties of the material. Fillers with a high ratio of the largest to the smallest dimension (i.e., aspect ratio) are particularly interesting because of their specific high surface area, providing better reinforcing effects [16-18]. For example, in study of physicochemical properties of starch-CMC-nanoclay biodegradable films by Almasi et al (2010), they reported that the Montmorillonite (MMT) addition at content of 7% (w/w), caused to increase in ultimate tensile strength (UTS) by more than threefold in comparison to starch-CMC biocomposites [19].

Poly vinyl alcohol (PVA), as a water-soluble polymer, has been widely used as a matrix for the preparation of nanocomposites. The main reason is due to its easy processability, high optical clarity and biocompatibility [20]. Glycerol is one of the most popular plasticizers used in the preparation of films and coatings due to its stability and compatibility with the hydrophilic nature of the biopolymer chains. The main advantage of this plasticizer is a high boiling point, lack of odour, water solubility and miscibility with those components [21-23].

Application of MMT is a great interest these days due to its natural source, high modulus of clay platelets, and low content necessary to attain the most wanted mechanical properties.

These layered materials exist in the form of the cumulatives bonded with physical forces, accordingly that they can be exfoliated even to single nanolayers [24]. The natural MMT is hydrophilic and is miscible with hydrophilic polymers [25,26]. However, to evaluate and characterize the distribution of nanoclay reinforcement in the nanocomposite formulation, there are a number of experimental techniques, such as X-ray diffraction (XRD) and differential scanning calorimetric (DSC). For instance, Almasi et al [19] used XRD and DSC in study of physicochemical and thermal properties of starch-CMC-nanoclay biodegradable films. XRD test showed that the 0 01 diffraction (d_{001}) peak of nanoclay was shifted to lower angles in the bionanocomposites and it may be implied that the clay nanolayers formed an intercalated structure. However, completely exfoliated structure formed only in the pure starch-MMT nanocomposites (without CA and CMC) [19].

However, the focuses of this paper is to study of the presence and distribution of the nanoclay particles in the CMC/PVA/clay nanocomposite films as well as investigate the effect of montmorillonite clay content on the thermal properties of these films. DSC is used for thermal properties and XRD for nanoparticles distribution and nanocomposites morphology.

Materials and methods

Materials

To prepare the nanocomposite films, carboxymethyl cellulose (CMC), with an average molecular weight of 41,000 (practical grade) and PVA (poly vinyl alcohol) were purchased from Tetrachem agency (Tehran, Iran). Modified Montmorillonite (Cloisite Na⁺), as nanoclay particles were prepared from Southern Clay (Gonzales, TX, USA). Glycerol was purchased from Merck company agency (Tehran, Iran).

Nanocomposites Preparation

CMC/PVA/nanoclay composite films were prepared using casting technique. All materials were weighted by digital scale 0.0001 (with an accuracy of 0.1 mg, Japan). Distilled water was used as solvent for all components. At first, 10%v of CMC and PVA were dissolved in the 60ml of distilled water by heating at 90°C, for 40 min separately. Nanoclay particles (MMT) in concentrations of 0.5, 1 and 3 wt% (based on the weight of CMC) dispersed in 100ml of distilled water, followed by ultrasonication in a water bath for 20 minutes. MMT solution was mixed in the PVA and CMC solutions for 30 min, under strong magnetic stirring at room temperature. 2 ml glycerol (40 ml per 100g of CMC) was added. Films were then cast into Petri dishes and air-dried for 18h, at room temperature and relative humidity. The thickness of the films was measured as 0.8mm.

Differential Scanning Calorimetric (DSC)

DSC is one of the applied methods to study thermal properties of polymers. Thus, DSC was used to study the thermal properties of CMC/PVA/nanoclay films. The test was performed with a DSC (Mettler Toledo, Swiss) equipment, fitted with a cooler system using liquid nitrogen according to ASTM D3417 [27]. Instrument was first equilibrated in point of temperature and enthalpy with Indium ($T_{m, onset} = 156.6^\circ\text{C}$, $H = 28.45\text{J/g}$). Then 2-3mg samples were weighed in aluminum pans (Crucible) and hermetically sealed; an empty pan was used as reference. DSC analysis of neat CMC/PVA and CMC/PVA/clay nanocomposites was obtained by heating program from -50 to 250°C at a scanning rate of $2^\circ\text{C}/\text{min}$. The Glass transition temperature (T_g) and decomposition or degradation temperature (T_d) were defined as the midpoint of the transition inflection observed in thermograms.

X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) is a method properly indicating the layered structure of the films containing clay with all level of concentrations. XRD applies to obtain the information on the basal spacing and the clay particles inside the matrix, in general. For XRD analysis, film samples were folded several times to increase the sample thickness. The XRD patterns of samples were recorded using an Xray diffractometer (Model Xpert-philips, Pw 3040/60, MI, USA). The 2θ range was from 0 to 80° with a velocity of $5^\circ/\text{min}$

Results and Discussion

DSC analysis

The thermal degradation behavior of CMC/PVA/MMT nanocomposites as well as pure CMC/PVA samples has been analyzed. According to the results, thermal stability of nanocomposite has not been significantly improved compared to the pure CMC/PVA.

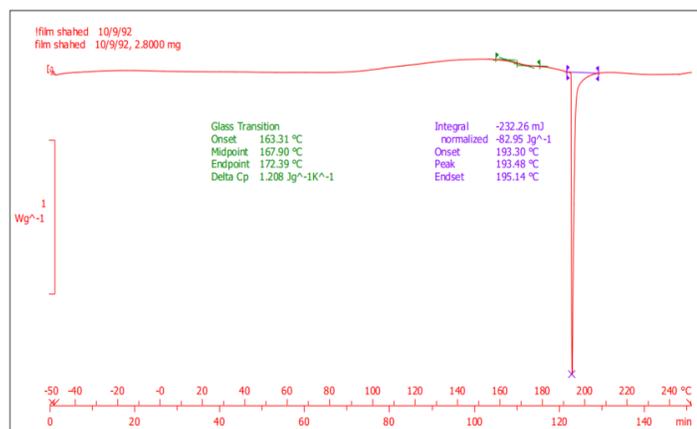


Figure 1. DSC curve for CMC/PVA film.

Nanocomposite melt process was occurred over a period of time/temperature. As shown in figures 1 and 2, the highest range of the glass transition temperature (T_g) of the samples belonged to CMC/PVA (i.e. 167.90°C), compared with the samples with nanoparticles. The biggest peak of CMC/PVA sample (i.e. 193.48°C) in compare with the other samples indicates that the affinities of these specimens are stronger and more complex. As a result, more energy was consumed to melt the material.

For better comparison, Fig. 2 shows DSC results for all samples of CMC/PVA/clay (0.5, 1, and 3 %) and the samples without clay. These data are obtained from the first run and during the heating process. The temperature corresponding to the endothermic peak for each sample is considered to be T_g of CMC/PVA/nanoclay (0.5, 1, and 3%) and the samples without clay. For all samples at T_g , there is a step like change, which is due to enthalpy relaxation. This type of step like change at T_g , has also been recognized for some other polymers [28]. On the other hand, all samples show an endothermic peak, and that can be correlated to the degradation of CMC/PVA in every sample; the corresponding temperature is known as the degradation temperature, T_d . This peak is appeared at lower temperature for all samples than that of CMC/PVA.

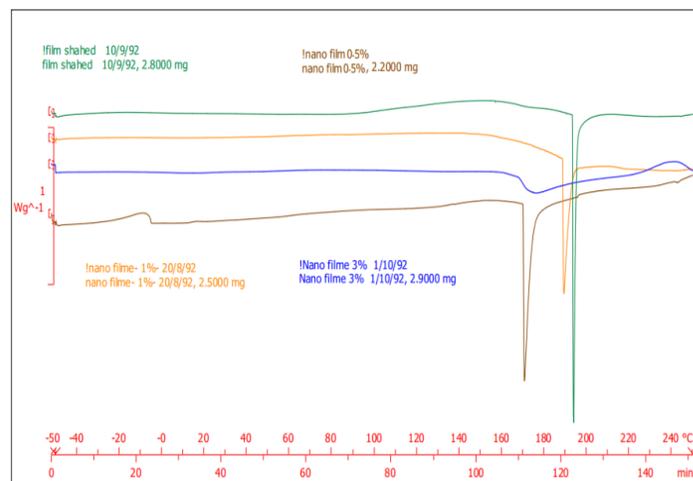


Figure 2. Overlap curves of different samples (curves from up to down, the first: CMC/PVA; the second: CMC/PVA/1%nanoclay; the third: CMC/PVA/3%nanoclay; and the forth: CMC/PVA/0.5%nanoclay)

It has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers [25, 29-31]. That is the incorporation of clay fillers into the polymer matrices results to the improvement of their thermal stability [32]. Yoo et al., [33] observed that the thermal decomposition behaviour and linear dimensional changes of recycled PVC (RPVC) could be improved by the incorporation of organically modified clays. In the case of RPVC/clay nanocomposites the degree of improvement of the above properties was proportional to the

clay content. Vyazovkin et al., [34] reported the thermal stability of polystyrene/clay nanocomposite compared to pure PS. They have shown that PS/clay nanocomposites have 30-40°C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions. Other studies have been showed that the nature of the clay modifier can affect on the thermal stability of modified clay and related nanocomposites [35]. However, results of this study showed that the degradation temperature (T_d) of all samples (CMC/PVA/0.5, 1 and 3%nanoclay) is lower than T_d of CMC/PVA films.

XRD analysis

The X-ray diffraction (XRD) analysis was used to examine the dispersion of nanoparticles in a polymer matrix. When polymer chains set between the clay layers and fit between the two phases, the layer structures are produced. The layer structure makes X-ray diffraction peak broadening or move towards smaller angles [36]. In the X-ray diffraction pattern of the amorphous state, for more influence polymer clay layers, the clay layers are separated and the parallel between them and the sheets are gone. In this case, X diffraction peak completely disappears [37].

Figures 3 to 5 show the XRD results for the standard cloisite, the CMC/PVA film, and the composites with 3% of clay, respectively.

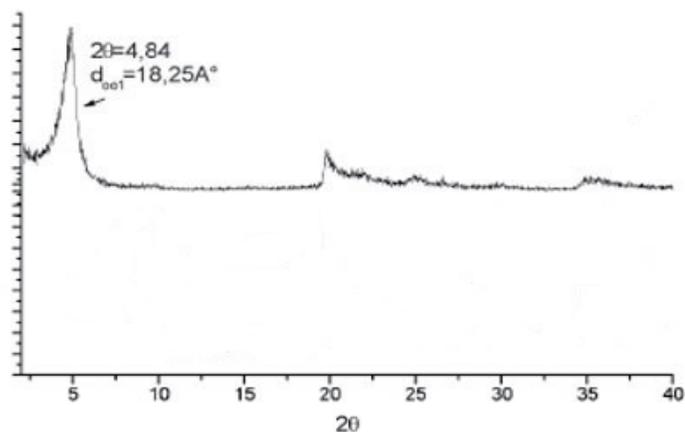


Figure 3. XRD pattern for standard nanoclay.

As shown in Fig. 5, the diffraction peak is not observed for the clay. No peak indicates that the incorporation of CMC/PVA and nanoclay in the film is a kind of layered. This result is in agreement with the Ray et al., [37] result. The results show that CMC/PVA polymer chains can enter the space between the layers of clay nano-layers and mixing thoroughly distributed throughout the matrix. Comparing Figures 4 and 5 shows that the average distance between particles containing clay nanocomposite films has decreased and the number of interactions between the matrix and the filler has increased. Fig. 5 also shows that the peak of Cloisite Na⁺ in the composite dis-

appears when 3% percent of clay was used, indicating possible exfoliation of the clay.

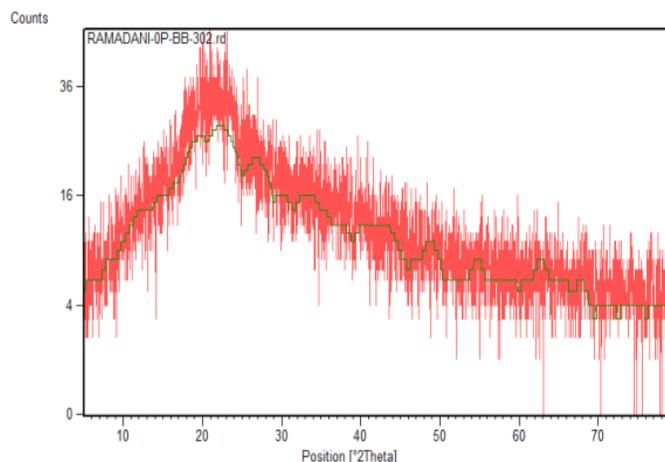


Figure 4. XRD pattern for the CMC/PVA film.

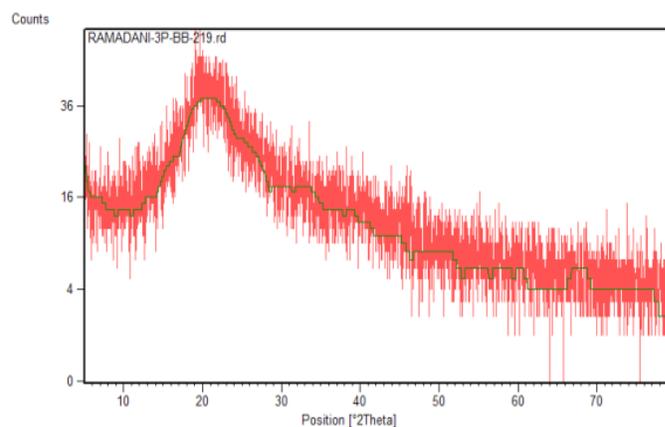


Figure 5. XRD pattern for the CMC/PVA/3%nanoclay film.

Conclusions

Due to problems such as environmental pollution and lack of adequate resources for the continued use of petroleum derivatives, use of biodegradable natural polymers like CMC/PVA/nanoclay films would bring an extensive change to the packaging industry. In spite of this, the thermal behavior study of CMC/PVA/nanoclay films by DSC showed that the clay particles do not have very significant effect in increasing the nanocomposites thermal stability. XRD results showed that films containing 3% clay have proper mixing and exhibited the best intercalation and exfoliation. However, it is necessary to study and research more and more about packaging nanocomposites in the future to provide higher quality products.

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