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CHARACTERIZATION OF POLY(VINYL ALCOHOL)-KONJAC GLUCOMANNAN BLEND FILMS

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Key Words: Poly(vinyl alcohol), Konjac Glucomannan, Blend Films, Physical Properties, Thermal Stability

ABSTRACT

This article deals with the characterization of blend films obtained by mixing poly(vinyl alcohol) (PVA) and konjac glucomannan (KGM) in aqueous solution. The DTA curves of PVA/KGM blend films showed overlapping of the main thermal transitions characteristic of the individual polymers. The exothermic peak at 312°C, which resulted from the thermal degradation of the KGM, shifted slightly to a higher temperature at low PVA content ($\leq$20 wt%). The weight-retention properties of the blend films indicated that thermal stability of the blend films were better than pure KGM film at PVA content below 20 wt%. The crystallinities, tensile strength, and elongation at break of the films increased with the PVA content, and reached the maximum values at 20 wt% PVA, then decreased. Changes in the carbonyl stretching band of KGM and hydroxyl stretching regions

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of KGM and PVA were detected by FTIR analysis. Those are attributable to the existence of a certain degree of inteaction between KGM and PVA, and resulted from intermolecular hydrogen bonds. Phase separation phenomena were observed by examining the surface of the blend films by SEM.

INTRODUCTION

Today, there is rising concern about environmental tissue, particularly those related to effective management of post consumer waste. This ecological awareness has led to the development of new biodegradable materials which can be a valid alternative in specific situations when recycling or incineration is difficult, or not economically feasible [1]. Consequently, natural polymers and biodegradable polymers have become attractive as suitable materials for environmental conservation.

Poly(vinyl alcohol)(PVA) is a nontoxic water-soluble synthetic polymer, which is widely used in biochemical and biomedical application. Water-soluble PVA is rendered insoluble by the introduction of crosslinks into the specimen. PVA has been exploited as substrate for enzyme immobilization in the form of photocrosslinkable PVA

[2]. PVA gels can be prepared from aqueous solutions by repetitive freezing and thawing [3], which can be used in the medical field because of good biosuitability [4]. PVA also has excellent film-forming ability and good biodegradability. It has been studied as a membrane and a component of blend films in various ways, such as poly(vinyl alcohol)-cellulose [5], poly(vinyl alcohol)-chitosan [6, 7], poly(vinyl alcohol)-silk fibroin [8], poly(vinyl alcohol)-sodium alginate [9].

Konjac glucomannan (KGM) is a nature polysaccharide, whose main chain is composed of β-1,4 pyranoside bond linked mannose and glucose [10]. It has a long history of being used as health food [11]. Konjac is a kind of agriculture product with high yield, which grows profusely in China and a low cost. Its biocompatibility, biodegradability, and hydrophilicity are all very good. Recently, studies of konjac glucomanan and its applications in the food industry, chemical industry and biochemistry [12] were extensive and have made much progress. Particularly, it has excellent film-forming ability [11]. Some researches of blending KGM with another natural or synthetic polymer, such as cellulose-konjac glucomannan [13], hydroxypropyl cellulose-konjac gluco-mannan [14] have been reported. In our previous work [15], blend films of KGM and chitosan were prepared and characterized by FTIR, WAXD, SEM, and other analytical methods, indicating that konjac glucomannan has potential application value, so that the research on KGM is of significance.

It is considered that the PVA/KGM blends prepared, using both of these two potentially important functional polymers, could contribute to produce new functional polymers, which can be used in various industrial domains. The main purpose of this work was to achieve a deeper insight into the fundamental physical properties of the PVA/KGM blend films. The morphological structure, miscibility, thermal stability, mechanical properties of the blend films were studied by infrared (IR) spectra, wide angle X-ray diffraction (WAXD), differential thermal analysis (DTA), scanning electron microscope (SEM) and electron tensile test.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) (DP=1800(100)(purchased from XinLing Chemical Factory, Guangdong) was used without further purification. PVA powder was dissolved in distilled water by heating at 95°C to a concentration of 4 wt%. Konjac glucomannan (KGM) was extracted from the tuber of *amorphallus rivieri* (supplied by Fangxian Konjac Institute, Hubei) according to our previous work [15]. Konjac glucomannan was dissolved in deionized water to a concentration of 3 wt%.

Preparation of Films

Chosen volumes of PVA were added into the required amount of KGM solution. The resulting solutions were stirred energetically and degassed, then were spread over a glass plate. Blend films with different weight ratios were obtained after dried at 28°C for 2 days. By changing the weight percent content of PVA, 11, 14, 20, 33, and 50, a series of blend films were coded as KP-1, KP-2, KP-3, KP-4, and KP-5, respectively. The films obtained from pure KGM and PVA were coded as KGM and PVA. The thickness of the films was measured to be 80±5μm.

Characterization of Films

The differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the film samples were performed by a DT-30B thermal analyzer

(Shimadzu Co., Japan) under nitrogen atmosphere with a flow capacity of 30ml/min from 5°C to 500°C at a heating rate of 15°C/min.

Wide angle X-ray diffraction of the films were performed with a Rigaku Dmax-II X-ray diffractrometer (Japan) and used CuKα target at 40KV and 50MA. The diffraction angle was ranged from 5° to 50°. The crystallinities of the films were calculated by: [16]

$$X_c = F_c / (F_c + F_a) \times 100\%$$

where F_c and F_a are the areas of crystalline and noncrystalline regions, respectively.

Infrared (IR) spectra of the pure and blend films were measured with a Nicolet 170SX FTIR (USA) spectrometer and used as KBr pellets.

The surfaces morphology of the film samples was examined with a Hitachi X-650 (Japan) scanning electron micrograph (SEM) after coated with gold in 0.1τ vacuum degree and photos were taken.

The tensile strength and breaking elongation of the films were measured on an electron tensile tester AG-A (Shimadzu Co., Japan) with a tensile rate of 10 mm/min, at a gauge length of 60 mm. The temperature and relative humidity were 28°C and 53.6%, respectively.

RESULTS AND DISCUSSION

DTA Curves

The thermal behavior of pure and blend films was investigated by means of DTA measurement (Figure 1). The curves of all the films showed an endothermic peak at 60-90°C, which was due to the loss of moisture. The 100% PVA displayed a major endothermic peak at about 230°C, which is attributed to the melting of PVA [17, 18]. The exothermic peaks around 312°C in the DTA thermogram of pure KGM film resulted from the thermal degradation of konjac glucomannan.

The sequence of DTA events typical of konjac glucomannan also characterized the thermal behavior of blend films containing ≤20 wt% PVA [Figures 1(b), (c) and (d)]. However, the thermal degradation peak of KGM has shifted to a higher temperature: 317°C, 318°C, and 318°C in the films of KP-1, KP-2, and KP-3, respectively. For the KP-4 film, the degradation peak became flat, which may be due to the overlapping of exothermic peak in PVA and the endothermic peak in KGM.

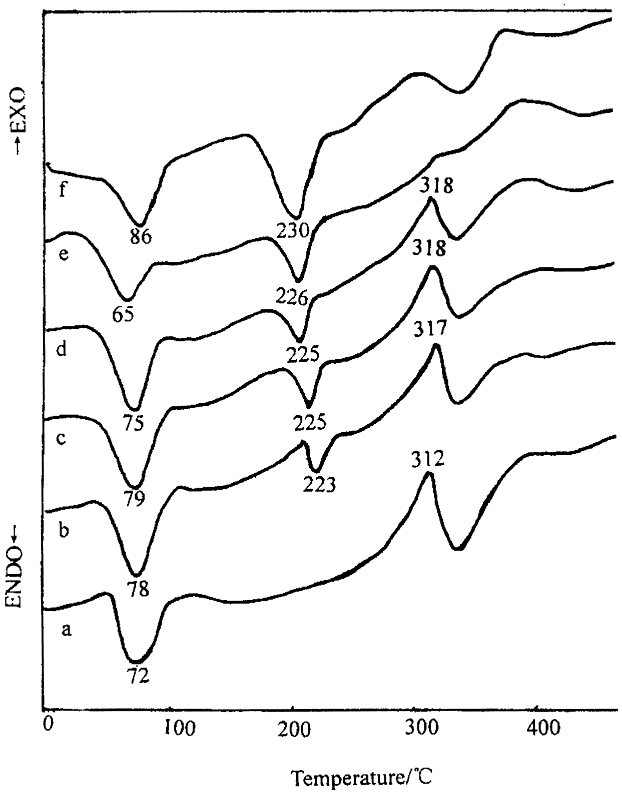

Figure 1. DTA thermograms of pure and blend films. (a)KGM; (b)KP-1; (c)KP-2; (d)KP-3; (e)KP-4; (f)PVA.

Overlapping of the characteristic thermal transitions of konjac glucomannan and PVA seems to be the main feature emerging from the above DTA results. But the upward shift of the degradation peak may suggest that a certain degree of interaction was established between KGM and PVA. As it will be shown later (see SEM results), the polymers formed separate domains in the blends. However, this feature does not exclude a certain degree of molecular mixing occurred, especially at the boundary of the two-phase structure.

TG Curves

The results of TG measurements are shown in Figure 2. The pure PVA showed three steps of weight loss, located at about 100°C, 200°C, and 300°C The former is attributable to a loss of moisture, while those at higher temperature coincided with the DTA endotherms of PVA film (Figure 1(f)). The drop of TG

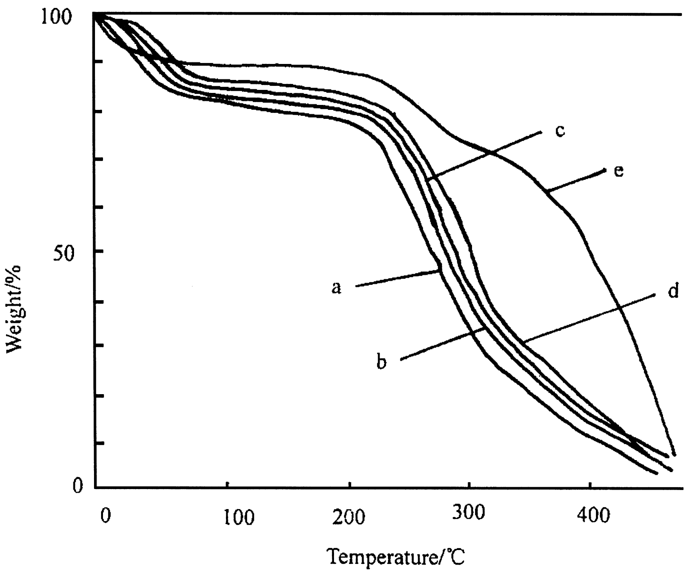

Figure 2. TGA thermograms of pure and blend films. (a)KGM; (b)KP-1; (c)KP-2; (d)KP-3; (e)PVA.

curve at 200°C can be related to processes involving both melting of PVA chains and the onset of degradation. On the other hand, another drop at above 300°C is indicative of the occurrence of more extensive thermal degradation processes.

The three active weight loss steps of KGM, KP-1, KP-2, KP-3, and KP-4 were found at 60°C-100°C, 210°C-310°C, 310°C-500°C. The first step was due to the loss of moisture; the second step was attributed to the disintegration of intermolecular side chains [19]. The third weight loss was believed to be caused by some type of chemical reaction, such as main chain disintegration or rearrangement of some carbon atoms [20]. From the TG curves of the films, we can find that the weight-retention properties of the blend films were intermediate between those two constituents. A slightly higher thermal stability of konjac glucomannan was attained by blending with PVA.

X-ray Diffraction

Figure 3 shows the X-ray diffraction patterns of the pure and blend films. The pure PVA is semicrystalline, the diffraction peak corresponding to 2θ=20°C in agreement with the literature data [21]. However, the pure KGM shows non-crystalline state and only has a very broad peak around 2θ=18° [22]. PVA has a flexible backbone, while KGM has a bulky and rigid backbone structure. The flexible PVA is favorable for the close molecular packing and crystallization. Therefore, the crystallinity increases with increasing PVA content at low PVA content (≤20 wt%), coincided with the calculated values, which can explain the improvement of thermal stability. But when PVA content is 33 wt% in KP-4, the film shows a small amount of crystallinity (from very weak crystalline peak at 2θ). From these results, it was found that the two polymers, PVA and KGM, were mixed together in a certain range and affected each other in the crystallization.

IR Spectra

FTIR is of importance to study the molecular structure. Width and intensity of spectrum as well as position of peaks are all sensitive to environment

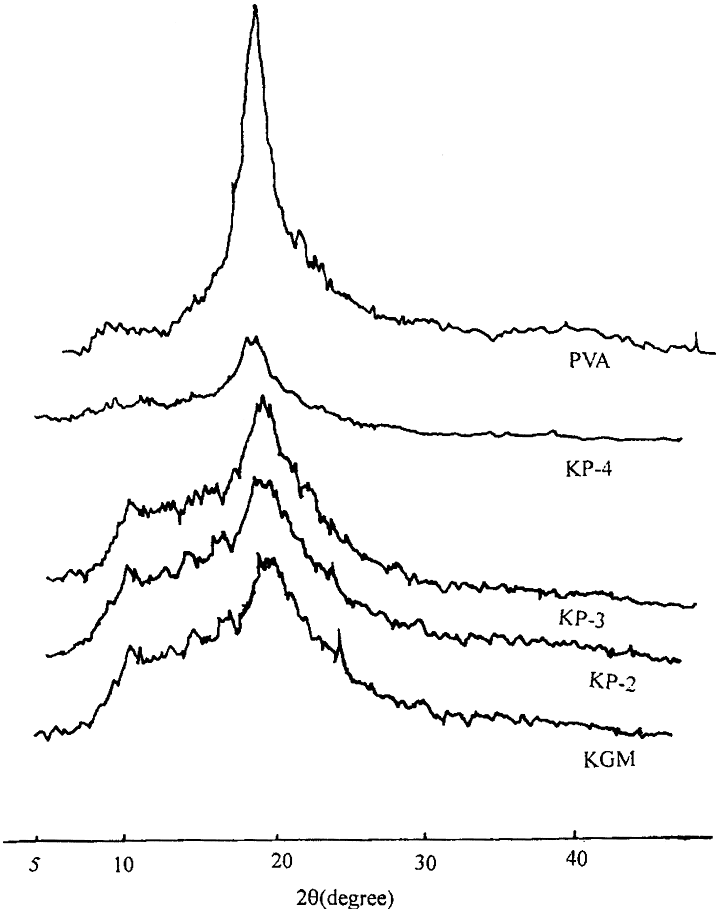

Figure 3. X-ray diffraction patterns of pure and blend films.

changes and conformations of macromolecular on molecular level. The IR spectra of the PVA/KGM blend films with different composition are shown in Figure 4. For pure PVA film, the absorption bands around 3200 cm^{-1} is concerned with OH stretching vibration, and the crystallization-sensitive band is at 1143 cm^{-1} [23]. The stretching peaks of C-H of methyl at 2898 cm^{-1} and 2780 cm^{-1} and of carbonyl at 1729 cm^{-1} are assigned to the aceto group in KGM [24], and the absorption band at 1641cm^{-1} is assigned to the stretching of intramolecular hydrogen bonds in KGM. The characteristic absorption bands of mannose in KGM appear at 878 cm^{-1} and 809 cm^{-1} [25]. In the blend films KP-2 and KP-3, the stretching of carbonyl at 1729 cm^{-1} of KGM has shifted to 1726 cm^{-1}, and the absorption region of hydroxyl for pure PVA has slightly broaden and shifted to higher wavenumbers. While hydroxyl absorption bands in KGM has changed to lower wavenumbers, indicating the existence of intermolecular hydrogen bonds. In the spectra of blend films with low PVA content (≤20 wt%), the characteristic absorption peak at 878 cm^{-1} has shifted, especially in film KP-3, from 878 cm^{-1} to 895 cm^{-1}. It should be noted that the intensity and frequency of crystallization-sensitive band of PVA at 1143 cm^{-1} has changed in blend films, it shifted to higher wavenumbers and the intensity became weak, which indicated the interaction between KGM and PVA has affected the crystallinity of PVA, in agreement with the results of WAXD. Although these changes were not very notable in contrast to KGM-hydroxypropyl cellulose [14], and KGM-chitosan [15] systems, we cannot deny the existence of a certain degree of interaction which resulted from intermolecular hydrogen bonds between KGM and PVA at low PVA content (≤20 wt%).

Mechanical Properties

The study of the mechanical properties is very important for determining the performance of a material that is expected to undergo various kinds of stresses during use. The tensile strength and breaking elongation of PVA film was measured to be 4.5 MPa and 310%. The values of tensile strength and elongation at break of KGM/PVA blend films were plotted as a function of the blend ratio (Figures 5 and 6). The addition of PVA to KGM was effective in inducing an improvement of the mechanical properties of blend films. In fact, both tensile strength and elongation at break increased with increasing the PVA content, the optimum weight ratio for reaching the desired effect being at 20 wt% content. And the improvement on breaking elongation is much more significant than that of tensile strength, which may be due to the good ductility of PVA. However, the improvement on mechanical properties were much smaller than those observed

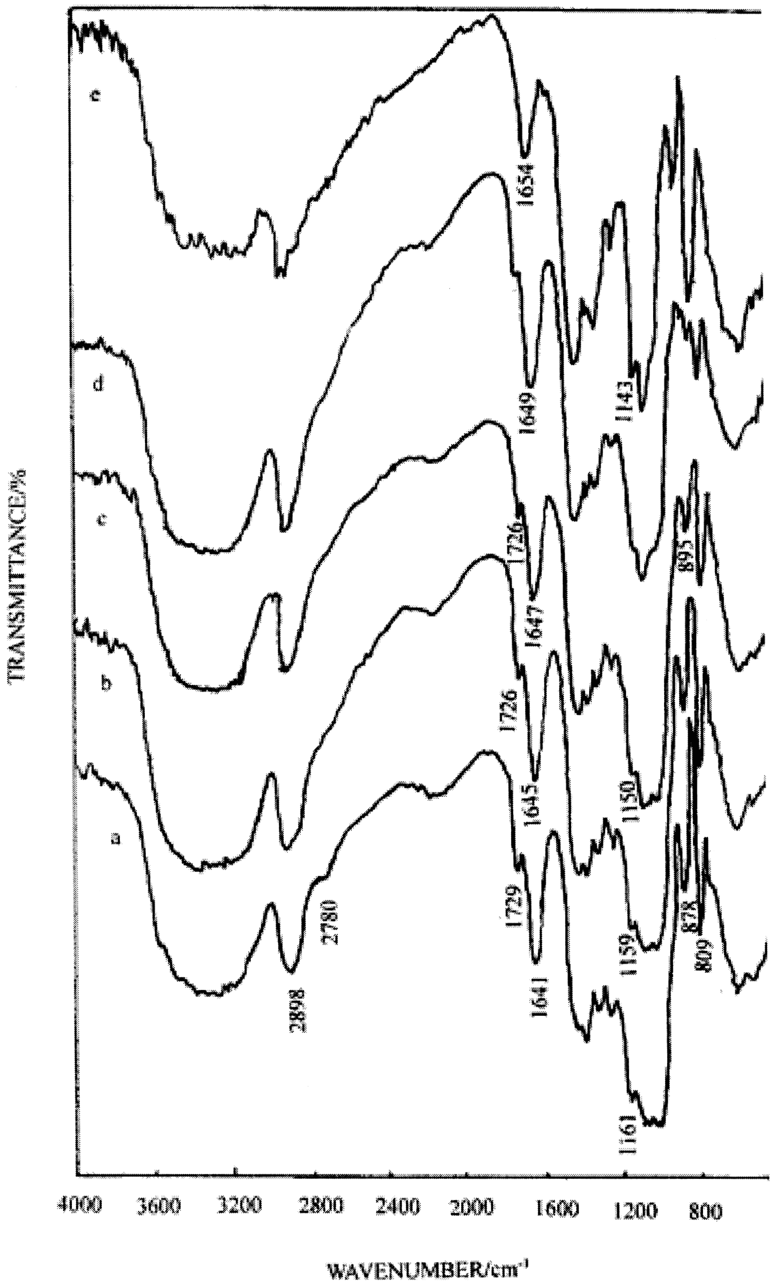

Figure 4. IR spectra of pure and blend films. (a) KGM; (b) KP-2; (c) KP-3; (d) KP-4; (e) PVA.

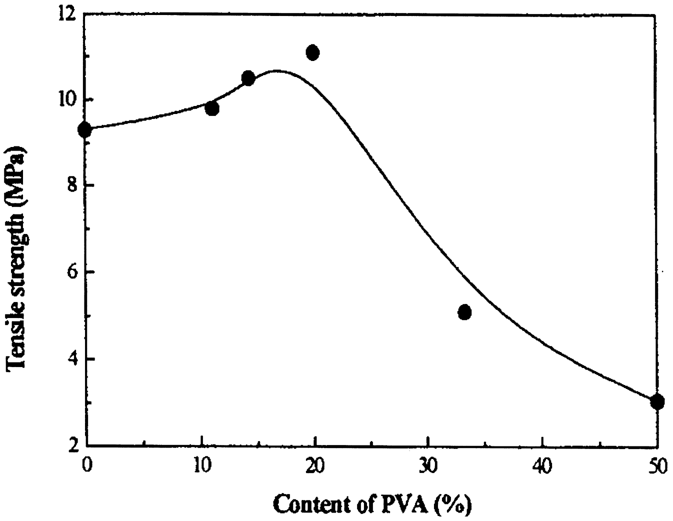

Figure 5. Dependence of tensile strength of blend films on PVA content.

by blending KGM with other polymers, such as chisotan [15], hydroxypropylcellulose [14]. As observed by SEM (Figure 7), the PVA/KGM blend films displayed phase separation morphology. For this kind of material, the mechanical properties should be strongly influenced not only by the performance of the individual components, but also by the adhesion at the interphase between them.

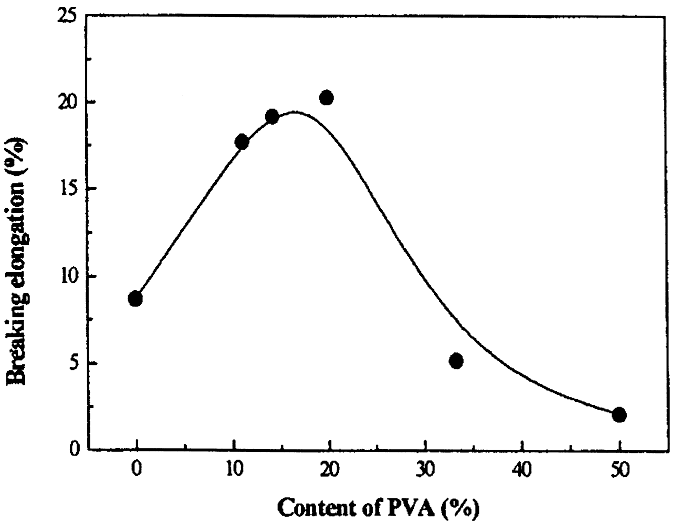

Figure 6. Dependence of breaking elongation of blend films on PVA content.

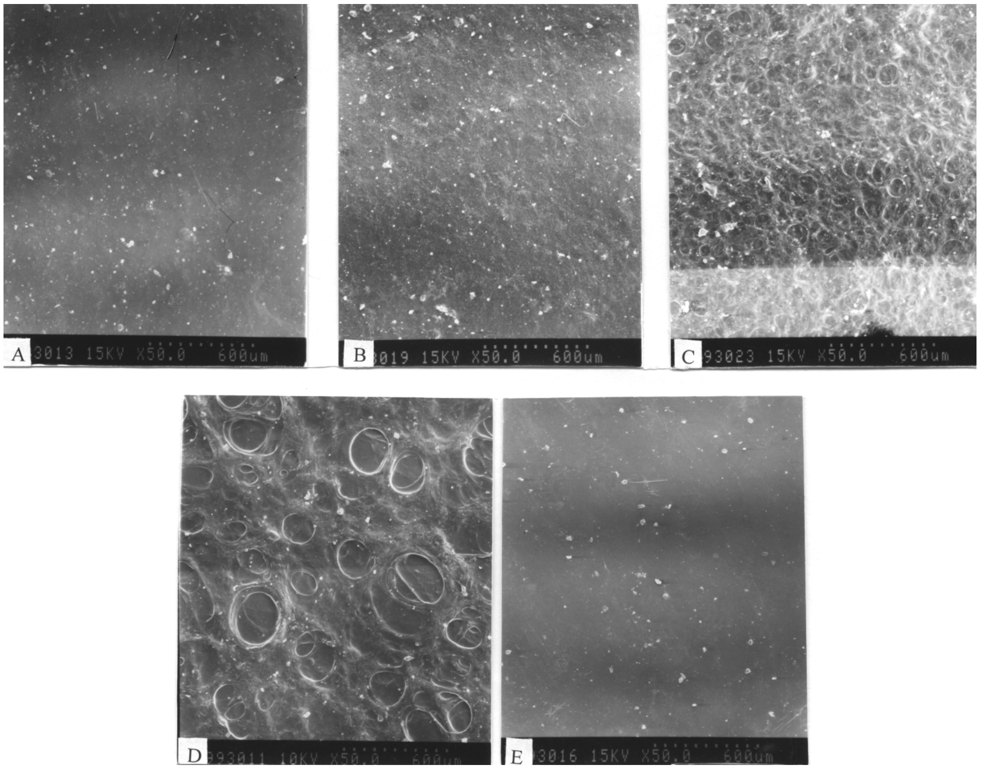

Figure 7. SEM photographs of pure and blend films. (A) KGM; (B) KP-2; (C) KP-3; (D) KP-4; (E) PVA.

From our results, it appears that the interaction was weaker than those brought about by other polymers [14, 15], which showed a higher degree of blending miscibility, and could establish stronger inter-molecular interactions by hydrogen bonding when mixed with KGM.

Morphological Characteristics

Air surfaces of the pure and blend films were examined by SEM (Figure 7). The pure KGM film showed a smooth surface structure. Also, pure PVA film exhibited an uniform surface morphology. The presence of spherical pores immersed in a homogeneous matrix was observed in the blend films KP-2, KP-3, KP-4, as well as in the other blends prepared in this study. The size of spherical pores increased with the increasing of PVA content. From these results, we can conclude that the two polymers gave rise to separated phases in the blend films. But the presence of spherical particles at different dimensional levels may bring about a great increase in contact area between the two polymeric phases, therefore, favoring mixing and interaction at the boundary, with predictable improved performance of the blend materials.

CONCLUSION

The results reported in this study show that KGM/PVA blend films could be easily prepared by using the conventional casting method, and that the resulting films exhibited some interesting properties. It is noteworthy that blend films exhibited increased thermal stability and improved mechanical properties compared to pure KGM film at low PVA content (≤20 wt%). These effects were attributed to the formation of specific intermolecular interaction between konjac glucomannan and PVA. Although phase separation was the main morphological feature emerging from the SEM analysis of the blend films, molecular mixing between KGM and PVA should have occurred to a certain extent, especially at the boundary zones.

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