

Dextran/Poly(acrylic acid) Mixtures as Miscible Blends

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ABSTRACT: Bioartificial polymeric materials based on blends of dextran and poly(acrylic acid) were prepared in form of films and characterized in order to evaluate the miscibility of the natural component with the synthetic one. Films with different composition ratios were prepared by solution casting and analyzed by dynamic mechanical-thermal analysis, differential scanning calorimetry, and scanning electron microscopy. The obtained results indicate that dextran is miscible with poly(acrylic acid). The miscibility was mainly ascertained on the bases of the occurrence of a single composition-dependent glass transition temperature in each blend and also on the bases of the transparency and homogeneity of the films. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2089–2094, 1997

Key words: miscibility; polymer blends; dextran; poly(acrylic acid); bioartificial polymeric materials

INTRODUCTION

Blends of natural and synthetic polymers prepared with the aim of producing new materials for applications in the biomedical field were called “bioartificial polymeric materials.”^{1–3} The idea was to obtain materials in which the physicochemical and biological properties of the two components are well combined. In general, the properties of a blend depend on the interactions occurring between the components, and therefore on their miscibility degree. When no interaction occurs, each polymer has no solubility in the other and the blend behaves as a two-phase system (immiscible blend). When interactions occur, the solubility of each component in the other is high and a single-phase system results. A polymeric system can be defined “compatible” when there is good adhesion between the constituents and average of mechanical properties. The term “miscibility” is

used to describe polymer–polymer blends with a molecular level of mixing adequate to yield macroscopic properties expected for a single-phase material.⁴

Bioartificial polymeric materials studied until now were prepared using mainly collagen, gelatin, hyaluronic acid, and starch as biological components, and poly(vinyl alcohol) and poly(acrylic acid) (PAA) as synthetic components.^{5–12} Blends with different composition ratios were used to prepare materials in the form of films (using the solution casting method), hydrogels (by freeze–thawing), and sponges (by freeze-drying and subsequent thermal treatment). Both chemical and physical crosslinking treatments were performed in order to reduce the solubility in water of these materials. All the obtained materials showed good mechanical properties in a wide range of temperature; however, the results of thermal and mechanical measurements indicated that both crosslinked and untreated materials exhibited a typical biphasic behavior. The variations of the modulus and the loss factor curves observed for the various blends corresponded to the transitions

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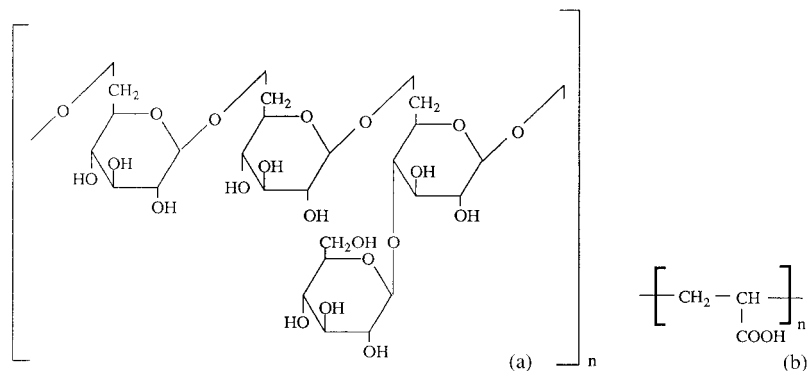


Figure 1 Structure of (a) dextran and (b) poly(acrylic acid).

of the pure components and clearly indicated that the two polymer components tend to create independent structures.

This article concerns the study of bioartificial polymeric materials prepared using PAA as synthetic component and dextran as biological component. The aim was to investigate the miscibility degree between these two polymers using dynamic-mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

PAA is one of the most important polyacids used for biomedical applications; as an example, materials based on PAA and allumine are employed for orthopedics implants.¹³ Dextran is a high molecular weight polymer of D-glucose, pro-

duced by different bacterial strains. Dextran and its derivatives are used as plasma expanders,¹⁴ blood substitutes,¹⁵ bone healing promoters,¹⁶ and also for dermal and subcutaneous augmentation¹⁷ and for drug delivery.^{18,19} Figure 1 shows the chemical structure of the two polymers.

EXPERIMENTAL

Poly(acrylic acid) 35% w/w aqueous solution (average molecular weight = 250,000) was provided by Aldrich Chemie (Steinheim, D); dextran produced by *Leuconostoc mesenteroides* (average molecular weight = 77,000) was provided by Sigma Chemical Co. (St. Louis, MO).

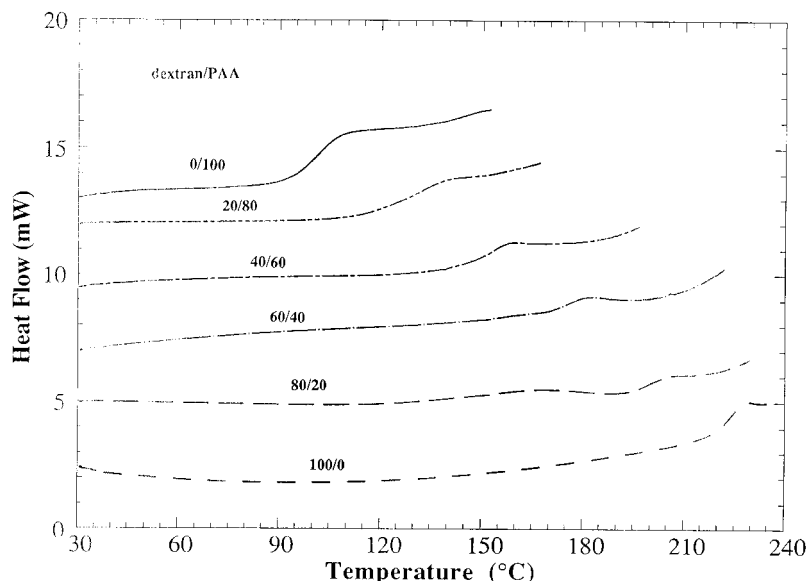


Figure 2 DSC thermograms of dextran/PAA blends at various compositions. Second scan; scan rate = 20°C/min.

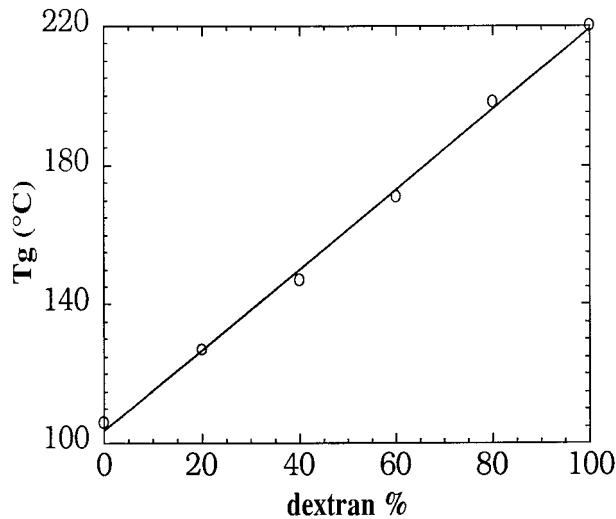


Figure 3 Trend of dextran/PAA mixtures glass transition temperature as a function of dextran content.

Film Preparation

Dextran/PAA mixtures with 0 : 100, 20 : 80, 40 : 60, 60 : 40, 80 : 20, and 100 : 0 (w/w) ratios were prepared using 1% aqueous solutions of the two polymers. The mixtures were poured into Petri dishes at room conditions and films were obtained by casting.

Dynamic-Mechanical Thermal Analysis

The dynamic-mechanical thermal analysis of the materials was carried out by a dynamic-mechani-

cal thermal analyzer (Polymer Laboratories) DMTA MK-1, operating in the "tensile" mode. The scans were performed on samples maintained at room conditions, at 1 Hz frequency, in the 25–250°C temperature range, at a heating rate of 4°C/min.

Differential Scanning Calorimetry

The thermal behavior of the dextran/PAA films was studied by a Perkin–Elmer DSC 7, using aluminum pans. Two consecutive scans were carried out on each sample, at scan rates of 10 and 20°C/min, respectively.

Scanning Electron Microscopy

Morphological analysis was carried out using a Jeol T300 scanning electron microscope. Both film surfaces and cross sections were analyzed after sputter-coating with gold.

RESULTS AND DISCUSSION

Dextran was found to be miscible with PAA. The miscibility was first ascertained on the bases of the transparency of the films and then on the occurrence of a single composition-dependent glass transition temperature (T_g) in each blend.

By definition, a stable homogeneous mixture is transparent, whereas an unstable nonhomoge-

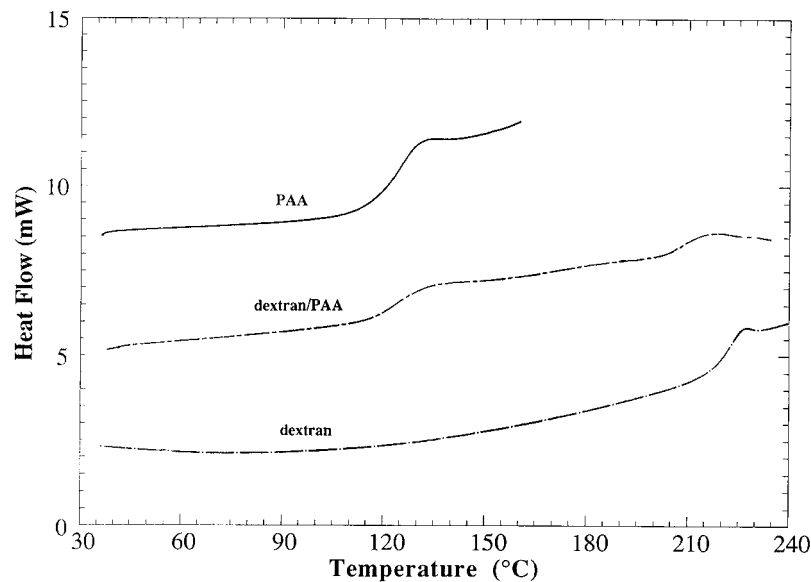


Figure 4 DSC thermogram of 0 : 100, 50 : 50, and 100 : 0 dextran/PAA films.

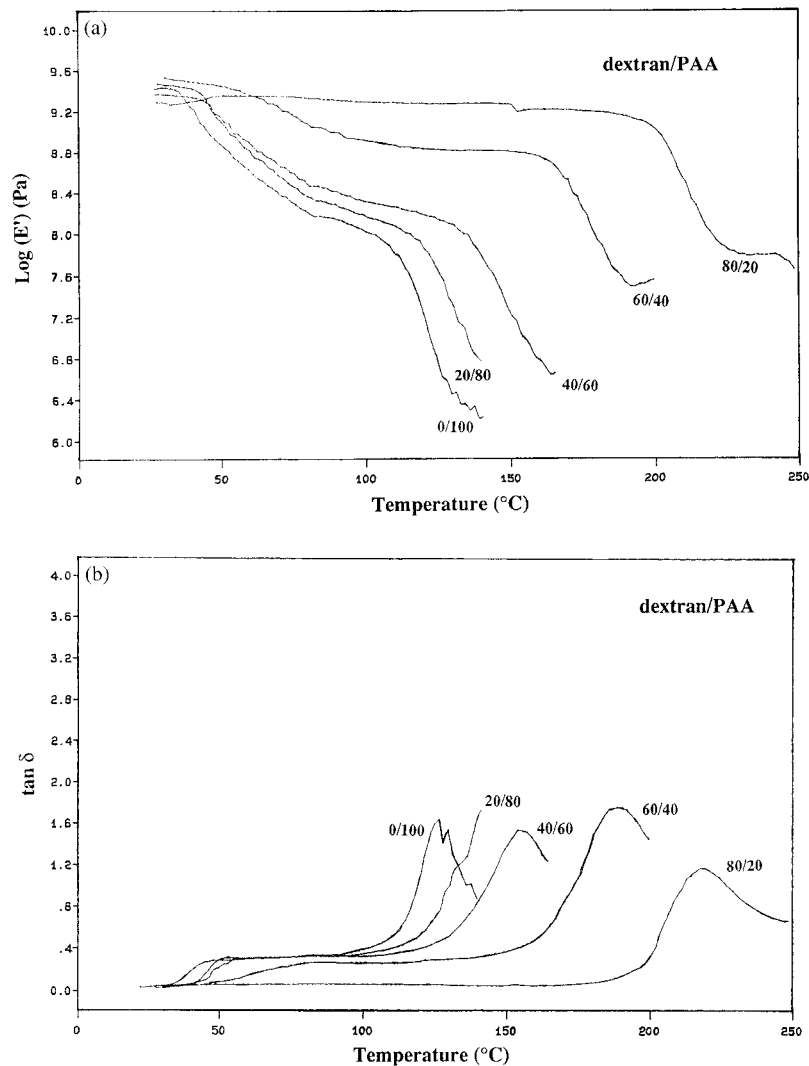


Figure 5 (a) Trend of the Young modulus (E') of dextran/PAA blends with various compositions (heating rate $4^{\circ}\text{C}/\text{min}$; frequency 1 Hz). (b) Trend of the loss factor ($\tan \delta$) of dextran/PAA blends with various compositions (heating rate $4^{\circ}\text{C}/\text{min}$; frequency 1 Hz).

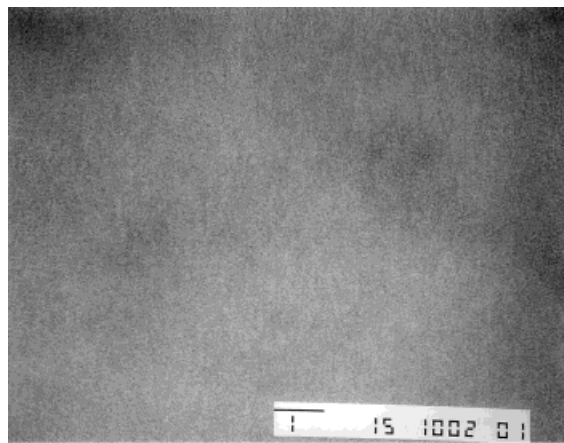
neous mixture is turbid. Variations of temperature, pressure, and so on can induce the transition of a homogeneous blend from the transparent to the turbid state.

All dextran/PAA blends were examined for the existence of lower critical solution temperature (LCTS). Each film was sandwiched between two microscope glasses and heated in an optical microscope at a heating rate of $\sim 4^{\circ}\text{C}/\text{min}$. All the blends remained transparent when heated up to 200°C . On further heating the films turned yellow because of degradation of the components.

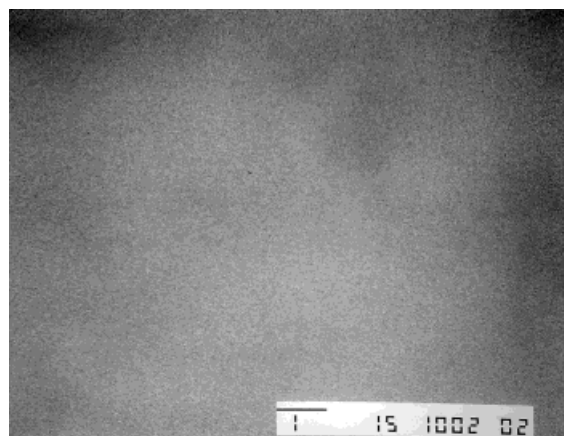
With regard to the determination of the glass transition temperature, this represents a very

useful tool in order to evaluate the miscibility of a polymer blend. A miscible polymer blend shows a single T_g different from, and in general intermediately between, those of the two pure components; on the contrary, an immiscible blend exhibits two different T_g corresponding to those of the single constituents.

Figure 2 illustrates typical second scan thermograms of dextran/PAA films. The curve corresponding to pure PAA shows a single slope change corresponding to the glass transition at $\sim 106^{\circ}\text{C}$. This value corresponds to that reported in the literature.²⁰ Similarly, the curve corresponding to pure dextran shows a single thermal phenome-



(a)



(b)

Figure 6 SEM images (cross sections) of dextran/PAA blends with (a) 40 : 60 and (b) 60 : 40 composition ratios.

non, corresponding to the glass transition, which occurs at a temperature (220°C) higher with respect to the one of pure PAA. In the case of the blends, it can be observed that all the curves exhibit a single transition occurring at a temperature, intermediate between those of the pure components, that moves toward higher values by increasing the dextran content of the mixtures. The temperature at which this transition occurs depends linearly on the blend composition as shown in Figure 3. In order to demonstrate that the presence of a single transition in the blends is the result of interactions occurring because of the mixing of the two polymers, thermal analysis was performed on a dextran/PAA (50 : 50) sample prepared putting together films of pure PAA and pure

dextran. The thermogram corresponding to this sample is reported in Figure 4, together with those corresponding to pure dextran and PAA. In this case the curve shows two separate transitions corresponding to the glass transitions of the pure constituents.

In Figure 5(a and b) the modulus curves (E') and the loss factor ($\tan \delta$) curves of dextran/PAA films with different compositions are reported. The curves of pure dextran are not reported because these films were too brittle and therefore not suitable for this analysis. In the case of pure PAA a main variation of both E' and $\tan \delta$ can be observed at $\sim 120^{\circ}\text{C}$, corresponding to the glass transition of the polymer. All the blends show a single glass transition, as is evident by a peak in the $\tan \delta$ curves and a sharp decrease of the modulus value, which moves toward higher temperatures by increasing the dextran content. Moreover, by increasing the content of the natural component, the modulus value and the yield temperature increase. In addition, for temperatures ranging between $30\text{--}100^{\circ}\text{C}$, a modulus decrease can be observed for pure PAA and blends with a high PAA content show a gradual modulus decrease.

Eventually, the morphological analysis evidenced, for all the investigated samples, a very homogeneous structure independently on the composition, confirming the results obtained by the other techniques. As an example, cross section images (magnification $10,000\times$) of 40 : 60 and 60 : 40 dextran/PAA films are shown in Figure 6.

CONCLUSIONS

Bioartificial polymeric materials based on dextran/PAA blends were prepared in form of films and their properties were investigated by thermal, mechanical, and morphological analysis in order to evaluate the miscibility degree of the two polymers.

Natural/synthetic blends studied until now behave in general as two-phase systems in which the components tend to create independent structures. They show good mechanical properties and thermal stability, but limited molecular-level miscibility and homogeneity.

In the case of dextran/PAA films, the transparency, the occurrence of a single glass transition, and the homogeneous structure shown by these materials clearly demonstrates that these mix-

tures can be considered as miscible blends. This is particularly interesting as far as the different nature of the two components is concerned: a significant example of joining between synthetic and natural systems.

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