

Preparation, Characterization, and Surface Energetics of Hydroxypropyl Cellulose/Polyethylenimine Blends

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ABSTRACT: Blend films composed of hydroxypropyl cellulose (HPC) and polyethylenimine (PEI) were prepared by solution casting method. The structure and mechanical properties of the blend films were analyzed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and tensile strength tests. The ATR-FTIR results indicated that there is a 5 cm^{-1} band shift to higher wave number due to the formation of hydrogen bonding between HPC and PEI components. The mechanical properties of the blends, such as breaking stress, elongation at break, and Young modulus were greatly affected with increase of PEI component. The contact angles of water, ethylene glycol, formamide, and

diiodomethane drops were measured on the blend films. The contact-angle results were evaluated in terms of surface free energy components using van Oss-Good methodology. It was shown that the surface free energy components of HPC and its blends did not differ so much with the composition. However, the apolar Lifshitz-van der Waals component (γ_S^{LW}) values are higher than those of the Lewis acid–base interactions component (γ_S^{AB}) values. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2751–2754, 2009

Key words: hydroxypropyl cellulose; polyethylenimine; blends; surface free energy

INTRODUCTION

Hydroxypropyl cellulose (HPC) is a cellulose derivative that finds applications in coatings, excipients, encapsulations, binding materials, foaming agents, protection colloids, and flocculants for a wide variety of materials such as food, drugs, paper, ceramics, and plastic materials.¹ Nowadays, many formulations in the pharmaceutical industry are based on HPC. For example, some tablets are now commercially available for apthia treatment, based on HPC and homo- or copolymers of acrylic acid as major excipients.² This kind of tablets demonstrates good oral mucosal adhesion properties and controlled drug release features. However, HPC is inadequate to meet the diversity of our demands for materials. Blending is also one of the most effective methods for providing new, desirable materials for biomedical applications.

HPC and polyethylenimine (PEI) do not exist together as blends in nature, but the specific properties of each may be used to produce synthetic blends that confer unique structural and mechanical properties. The use of relatively low cost, low pollution biomaterials with specific properties has great potential, for example in developing a new generation of prosthetic implants.^{3–5}

The determination of the surface energetic of the polymeric systems gives an idea of the thermodynamic work of adhesion between the natural and synthetic polymer chains. Also, it helps the selection of the appropriate pairs. As known from acid–base adhesion theory, when the surface acidity of one component is high and the surface basicity of the other component is also high, then strong adhesion between the components, and better compatibility occurs.^{6,7} However, in actual practice, thermodynamic work of adhesion calculations is not sufficient to decide on a suitable pair of polymer components. The experimental investigations of the adhesion and compatibility are also required due to the different chain diffusion and viscoelastic behavior of the polymer component.⁶

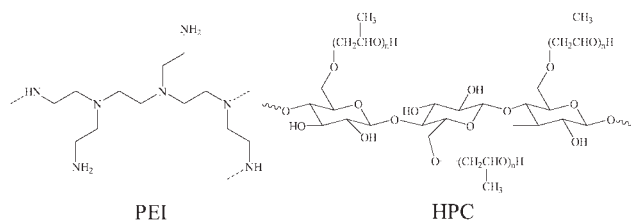
The objective of this study is to determine the structure and mechanical properties of HPC/PEI blended films prepared by solution casting method, using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, mechanical testing (Instron), and also measuring surface free energy components by van Oss-Good methodology,⁸ because these surface states should affect biomolecule attachment behavior.

EXPERIMENTAL

Materials

HPC (M_W : $1.0 \times 10^5\text{ g mol}^{-1}$) and PEI (M_W : $75 \times 10^4\text{ g mol}^{-1}$, 50% aqueous solution) were purchased

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Scheme 1 The structures of polyethylenimine and hydroxypropyl cellulose.

from Aldrich Chemical Co. (Milwaukee, USA). The main chain of HPC consists of glucopyranosyl units linked in the (1-4) β position (Scheme 1). The hydroxyl substituents exist either as a unit or as short side chains containing up to six hydroxypropyl monomers.⁹

HPC/PEI blend films were prepared by the following procedure. Aqueous solutions of the individual polymers (5 wt %) were mixed to obtain the desired proportions and stirred for 30 min at room temperature. The solutions were cast on clean glass culture dishes, and allowed to stand for almost 2 days. The cast film of $40 \pm 7 \mu\text{m}$ thickness was dried further at 50°C under reduced pressure more an 1 day, after detachment from the glass surface. The initial PEI contents in the blends were 10, 20, 30, 40 wt %. The pure HPC film was prepared by the same procedure.

ATR-FTIR measurements

ATR-FTIR measurements of the blends were made with a Nicolet 6700 FTIR (USA) spectrometer equipped with a smart orbit accessory in the range of $4000\text{--}525 \text{ cm}^{-1}$ at a 45° angle of incidence. The spectral resolution was 4 cm^{-1} .

Mechanical testing

The stress-strain measurements of the blends were performed on an AG-I model mechanical testing apparatus (Schimadzu Co., Japan) and a cross-head speed of 5 mm min^{-1} . The rectangular samples with dimensions at $25 \text{ mm} \times 10 \text{ mm} \times 40 \pm 7 \mu\text{m}$ were analyzed at room temperature. At least 10 samples were used for all mechanical measurements.

Contact-angle measurements

The advancing contact angles of water, ethylene glycol, formamide, and diiodomethane drops were measured with an automatic contact-angle analyzer combined with a flash camera equipment (model DSA 100, Krüss, Germany) at room temperature. The one-liquid method (air-liquid drop-polymer sys-

tem) was used. All the measured contact angles were an average of five measurements.

RESULTS AND DISCUSSION

ATR-FTIR spectra of the blends

ATR-FTIR spectroscopy of as-cast films was carried out to detect any band shifts that could be attributed to weak interactions between the two polymers, such as hydrogen bonding or complexation. The ATR-FTIR spectra of the blend films were characterized by the presence of the absorption bands typical of the pure components. The $-\text{OH}$ and $-\text{C}-\text{O}$ asymmetric stretching bands of HPC are located at $3600\text{--}300 \text{ cm}^{-1}$ and $1075\text{--}1175 \text{ cm}^{-1}$, respectively, as seen in Figure 1(A). For PEI component of the blend, the band at 1565 cm^{-1} corresponding to the $-\text{NH}_2$ groups were detected.

The scale-expanded ATR-FTIR spectra of the blends in the $1800\text{--}1200 \text{ cm}^{-1}$ region are given in Figure 1(B). The presence of hydrogen bonding, which might be formed between the $-\text{OH}$ groups of HPC and the $-\text{NH}_2$ of PEI, can be confirmed by stretching band at 1565 cm^{-1} . As expected, there is a 5 cm^{-1} shift to higher wave number for blends compared with pure PEI. This strongly supports the idea

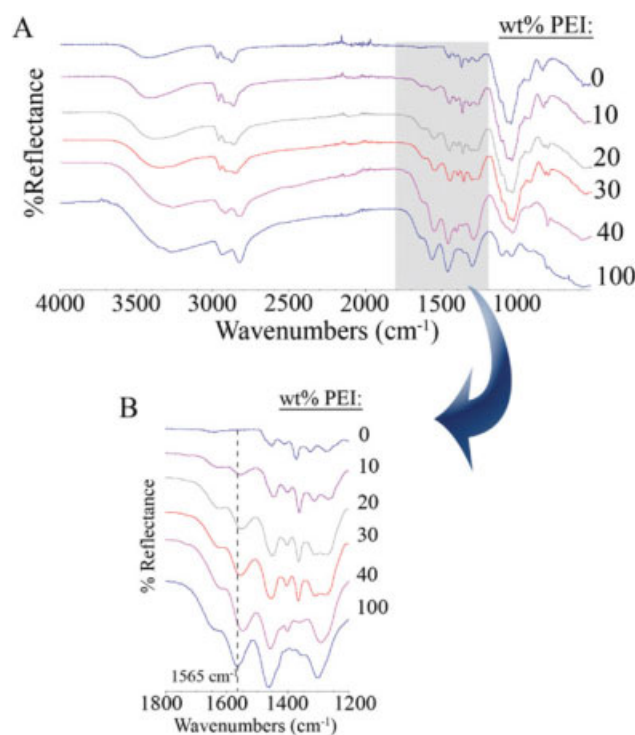


Figure 1 (A) ATR-FTIR spectra of the blends in the $4000\text{--}525 \text{ cm}^{-1}$. (B) SCALE-expanded ATR- FTIR spectra of the blends in the $1800\text{--}1200 \text{ cm}^{-1}$ region recorded at room temperature. [Color figures can be viewed in the online issue, which is available at www.interscience.wiley.com.]

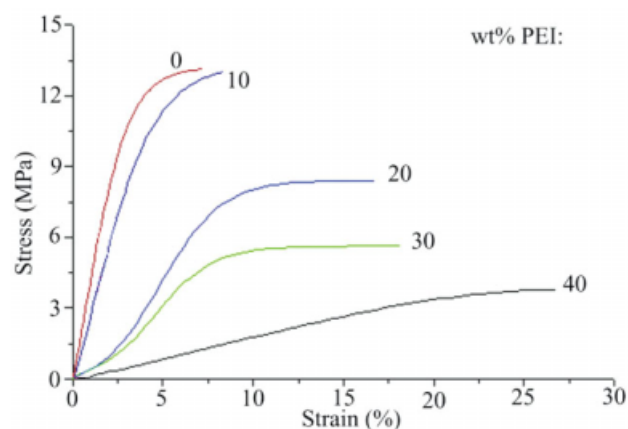


Figure 2 Stress–strain curves of the blend films. [Color figures can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that a hydrogen bond can form between PEI and HPC.

Mechanical properties of the blends

The results of the stress–strain measurements of the pure and blend films were presented in Figure 2. The stress–strain curves in Figure 2 are informative on variation of the pure and blend films resistance to tensile straining under mechanical stress in elongation. The Young modulus can be determined as the slope of the linear region of the stress–strain curves at very small elongations. Since under these conditions, the polymeric film can be regarded as not disturbed from an equilibrium state, the Young module is often considered as material constant characterizing polymer elasticity. Beyond this region, the slope of the stress–strain profiles becomes non-linear and depends not only on the sample elasticity, but also on the deformation condition.¹⁰ The maximum value of the strain appeared when the PEI content in the blend films is 40 wt %. The incorporation of PEI up to 40% made the blend films elastic, with decrease in the Young modulus, in the stress and increase in the elongation at break. The authors claimed that the addition of PEI improved the elasticity of the HPC. Although the natural polymers can be fabricated into highly biodegradable matrices,

TABLE I
Contact-angle Results of HPC and its Blends

Wt % PEI	Diiodomethane	Water	Ethylene glycol	Formamide
0	34.7 ± 0.2	61.1 ± 0.4	49.3 ± 0.3	40.4 ± 0.2
10	42.4 ± 0.2	66.1 ± 0.3	65.5 ± 0.3	56.2 ± 0.3
20	27.3 ± 0.2	76.6 ± 0.5	37.7 ± 0.3	54.8 ± 0.4
30	35.7 ± 0.2	61.3 ± 0.4	53.5 ± 0.4	52.8 ± 0.3
40	34.8 ± 0.1	64.8 ± 0.3	56.7 ± 0.4	54.6 ± 0.3

TABLE II
Surface Free Energy Component Values of Liquids Used
12 (mJ/m²)

Liquid	γ^{TOT}	γ^{LW}	γ^{AB}	γ^+	γ^-
Diiodomethane	50.8	50.8	0.0	0.0	0.0
Water	72.8	21.8	51.0	25.5	25.5
Ethyleneglycol	48.0	29.0	19.0	1.92	47.0
Formamide	58.0	39.0	18.0	2.28	39.6

the main disadvantage of them is their poor mechanical properties and handling inconveniences. The HPC/PEI blend films reported in this work possess both these qualities even in the blend conditions and are hence promising candidates for varied engineering and medical applications.

Surface energetics of the blends

The contact-angle values of diiodomethane, water–ethylene glycol, and formamide drops of the surface of HPC and its blends with different PEI content are shown in Table I. The contact angle measured for the blends gave results very similar to that obtained for HPC film with all the hydrophilic liquids used.

It is well known that contact angles are characteristic constants of liquid–solid systems and provide valuable information on the surface energies of solids. The surface energy components of HPC and its blends were determined from the contact-angle data of polar and apolar liquids by the following complete Young equation comprising both the apolar and polar interactions.^{8,11}

$$\gamma_L(1 + \cos \theta) = 2 \left(\sqrt{\gamma_S^{\text{LW}} \gamma_L^{\text{LW}}} + \sqrt{\gamma_S^- \gamma_L^+} + \sqrt{\gamma_S^+ \gamma_L^-} \right) \quad (1)$$

In the above equation, γ_L is the total surface free energy of the liquid, θ the contact angle of liquid drop on the solid surface. γ_L^{LW} and γ_S^{LW} are the apolar Lifshitz–Van der Waals components, γ_L^+ and γ_S^+ are the electron acceptor surface free energy components, and γ_L^- and γ_S^- are the electron donor surface free energy components of liquid and solid, respectively. Water drop contact-angle values are always used in these blends to avoid large discrepancies

TABLE III
Surface Free Energy Components of HPC and its Blends
(mJ/m²)

Wt % PEI	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S^{TOT}
0	42.20	0.31	17.32	4.63	46.83
10	44.18	0.71	10.27	5.40	49.58
20	45.30	0.16	5.54	1.88	47.18
30	41.70	0.06	19.88	2.18	43.88
40	42.12	0.26	14.59	3.89	46.01

between simultaneous equation solutions.¹² The surface energy component values of the liquids used were taken from Ref. 12 and given in Table II.

For apolar liquid (diiodomethane), $\gamma_L^+ = \gamma_L^- = 0$ and $\gamma_L^{LW} = \gamma_L$; hence, the last two terms of the right hand side of eq. (1) become zero, this equation can therefore be written in the form.

$$\gamma_S^{LW} = \frac{\gamma_L(1 + \cos \theta)^2}{4} \quad (2)$$

The γ_S^{LW} component of the surface free energy of HPC and its blends was first calculated by using eq. (2) and the diiodomethane drop contact-angle values and given in Table III. Then, γ_S^- and γ_S^+ values were calculated by using the general contact-angle equation [eq. (1)], where previously found γ_S^{LW} values were inserted. Water-ethylene glycol, water-formamide sets were simultaneously solved and the average results were added in Table III. The γ_S^- and γ_S^+ components of the surface free energy are combined in a polar component (indicated by superscript AB) caused acid-base interactions.⁸

$$\gamma_S^{AB} = 2 \left(\sqrt{\gamma_S^+ \gamma_S^-} \right) \quad (3)$$

Then, by combining eqs. (2) and (3), the total surface free energy (γ_S^{TOT}) is determined as follows:

$$\gamma_S^{TOT} = \gamma_S^{LW} + \gamma_S^{AB} \quad (4)$$

As a result, all the γ_S^{AB} and γ_S^{TOT} values of HPC and its blends were calculated by using eqs. (3) and (4), respectively and given in Table III. In each case, we recognized minor derivations from the mean values for γ_S^{TOT} . As shown in Table III, the HPC/PEI blend films are characterized by almost the same surface free energy values as that of HPC itself. However, the calculations of apolar Lifshitz-Van der Waals component (γ_S^{LW}) and polar component (γ_S^{AB}) of surface energy have given more detailed information on the surface properties of the samples studied. The γ_S^{LW} values of HPC and its blends are higher than those of the γ_S^{AB} values (Table III). In this case,

it can be said that the HPC and its blends have an apolar character.

CONCLUSIONS

Blend films of HPC and PEI could be easily obtained over the whole composition range from solutions in water by solution blending and casting onto the glass plate. The elasticity properties of the blends were enhanced relative to those of HPC and PEI. The elongation at break of blend with 40 wt % PEI in a dry state was 27%, whereas pure HPC has 8% elongation value. This enhancement is caused by the existence of specific intermolecular interactions between HPC and PEI in the blend. ATR-FTIR analysis revealed this interaction from the shift and change intensity of $-\text{NH}_2$ band. The surface free energy components determined by van Oss-Good contact-angle evaluation methodology of HPC and its blends did not differ so much with the blend composition. However, the γ_S^{LW} values were higher than those of the γ_S^{AB} values.

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