

Chitosan Modified by Poly(ethylene oxide): Film and Mixture Properties

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ABSTRACT: Chitosan + poly(ethylene oxide) mixtures and films prepared from these mixtures were studied by rheological, absorption of solvent vapors, SANS, and mechanical testing methods. At a stoichiometric chitosan:poly(ethylene oxide) monomer:monomer composition, the mechanical properties of chitosan + poly(ethylene oxide) film are the best as compared with those of the initial components or of other compositions. This film composition is shown to be less heterogeneous. Chitosan and poly(ethylene oxide) are proved to be slightly incompatible polymers. This is supposed to induce the two components to align and to order at their stoichiometric composition, leading to the improvement in the mechanical properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1114–1122, 2002; DOI 10.1002/app.10319

Key words: blends; compatibility; films; mechanical properties; rheology.

INTRODUCTION

Blending of polymers is used to improve and modify the physicochemical properties of the initial components. For example, by mixing two components in a common solvent and then evaporating this solvent, one can get a product with better mechanical properties than those of the initial components (see, e.g., ref. 1). Such an improvement in the final properties may be caused, for example, by introducing a more flexible polymer acting as a plastificator or by the formation of a new compound due to the chemical reaction between the components or the formation of bonds between them (hydrogen, Coulomb, covalent, etc).

In this work, we studied poly(ethylene oxide) (PEO) + chitosan mixed aqueous solutions and films prepared from these mixtures. Chitosan is a natural nontoxic biodegradable and biocompatible polymer. It is already widely used and it is considered to be a promising material for different applications: in medicine (see, e.g., review in ref. 2 and/or refs. 3 and 4), as a powder, tablets, and gels for the controlled release and as fibers for digestible suture and sheets and membranes or wound dressings; in waste-water treatment^{5,6}; and as separation membranes.^{7,8} However, fibers or films prepared from pure chitosan are rather brittle; therefore, it is very important to improve their ductility. There are several ways to obtain films with better (than the initial component) elastic and strength properties, for example, either to prepare them from blends or to synthesize a chemically modified chitosan. There are several publications where the structure and properties

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Table I Samples' Characteristics

Polymer	M_w	M_n	M_w/M_n	Special Characteristics
Chitosan-13	1.3×10^4	4.5×10^3	2.8	Degree of <i>N</i> -deacetylation 0.96, in chlorhydrate form, polyelectrolyte
Chitosan-400	4×10^5	1.1×10^4	3.8	Degree of <i>N</i> -deacetylation 0.85
PEO-80	8×10^4			
PEO-200	2×10^5			
PEO-600	6×10^5			

of chitosan-based mixtures and films are discussed, for example, where chitosan is mixed with oligomers⁹ or with flexible polymers^{10–13} or when new chitosan derivatives are synthesized.¹⁴

In this article, we show that mixing chitosan with a flexible polymer—PEO—leads to an increase in the tensile strength and elongation at break of the films cast from these mixtures. We report here the solution and film properties of chitosan + PEO blends and discuss the reasons for the observed improvement of the mechanical properties.

EXPERIMENTAL

Materials

Three samples of PEO (see Table I) were used: Two were supplied by the Aldrich Chemical Co. (Deisenhofen, Germany) of $M = 6 \times 10^5$ and 2×10^5 , as given by the manufacturer, and the third one of $M = 8 \times 10^4$ was synthesized at the Institute of Macromolecular Compounds. Its viscosity-average molecular weight was determined using the Mark–Kuhn–Hauwink molecular weight–intrinsic viscosity correlation $[\eta] = 6.4 \times 10^{-5} M^{0.82}$ at $T = 35^\circ\text{C}$ in water.¹⁵

Two chitosan samples from crab shells produced by Aber (Bourg St. Andeol, France; chitosan-13 in the following) and by Sigma (St. Louis, MO; chitosan-400 in the following) were used. The sample characteristics are listed in Table I. The molecular weight was determined by GPC with an RI detector (Knauer) and a small-angle light scattering detector KMX-6 (Chromatix). Two columns, TSK-G6000 PW and TSKG5000 PW, were used. The sample was eluted with a buffer containing 0.23M CH_3COOH and 0.15M $\text{CH}_3\text{COONH}_4$ (pH 4.5). The free amino group content in chitosan was determined by IR spectroscopy on a Perkin–Elmer FTIR spectrometer using

a potassium bromide disc method, described in ref. 16.

Samples Preparation

Chitosan and PEO were dissolved separately in a 2% aqueous acetic acid solution. Chitosan + PEO mixtures were prepared by the direct mixing of initial solutions in different proportions. Concentrations were calculated in weight percent and the mixture composition is given in weight fractions. The total polymer concentration was kept constant. Chitosan + PEO films were prepared from the 0.5% initial solutions mixed at several compositions and cast into Petri dishes or into a PTFE-coated aluminum pan specially designed for these experiments. The solvent was removed by vacuum drying at 25°C . The thickness of films was from 0.2 to 0.4 mm.

It is important to note that films containing a PEO fraction higher than 0.3 were opaque, while films with a low PEO content were transparent and pale yellow brown. From this simple visual observation, we concluded that films with a low PEO content are likely be less heterogeneous than are films with a high PEO content.

Methods

The rheological tools used were as follows:

- A capillary Ubbelohde viscometer having a solvent (aqueous 2% acetic acid) flow time of 125 s;
- A concentric rotational cylinder rheometer “Rheotest-4” (Germany) with a gap between cylinders 0.78 mm;
- An experimental setup for generating a longitudinal hydrodynamic field between two opposite coaxial capillaries. The capillaries were placed into a vessel with looking windows. The solution was pumped into capillar-

ies and a critical flow gradient $\dot{\gamma}_{cr}$, at which the solution stretched between two capillaries becomes birefringent, was measured. The scheme and detailed description of the setup were given in ref. 17.

All rheological experiments were performed at 25°C.

The absorption of water vapors by chitosan + PEO films of different compositions was studied using an experimental setup with a quartz spring Mac-Ben balance under the pressure of saturated solvent vapors at 25°C. Details can be found elsewhere.¹ First, the kinetics of the vapor absorption by a film was recorded. In the case of pure PEO, the absorption of water vapors was studied for a polymer powder that was put into a special holder having a semispherical shape. Then, when the absorption reached the saturation, the amount of the solvent absorbed by 1 g (specific absorption) of chitosan + PEO film at each composition was calculated. The density of chitosan + PEO films of different compositions was calculated from careful measurements of the weight and dimensions of the films pieces.

Mechanical measurements were performed with an Instron 1185 testing machine. The specimens were cut into long and narrow strips, 5-mm width and 70-mm length. Their thickness was 0.4 mm and was uniform throughout the sample. The gauge length was 40 mm. The samples were tested at room temperature in the stretching regime at a $1.7 \times 10^{-3} \text{ s}^{-1}$ deformation rate. Both tensile strength and elongation at break were evaluated as ultimate (breaking) characteristics of the stress-strain curves. Each experimental point was the arithmetic mean value of at least 10 individual measurements.

Small-angle neutron scattering (SANS) measurements were performed on a Membrana-2 small-angle installation at PNPI, St.-Petersburg. The incident neutron beam had an average wavelength of 0.3 nm and a half-width of the spectrum of 0.35. The experimental scattering patterns were corrected for the detector efficiency, incoherent background, and the transmission coefficient. As deuterated polymers were not available, we used protonated samples. The natural contrast was found to be sufficiently good to record the scattering patterns. However, the incoherent scattering led to a smooth background level which was rather high but angle-independent at large angles. It allows one to perform subtraction of the background from the scattering patterns.

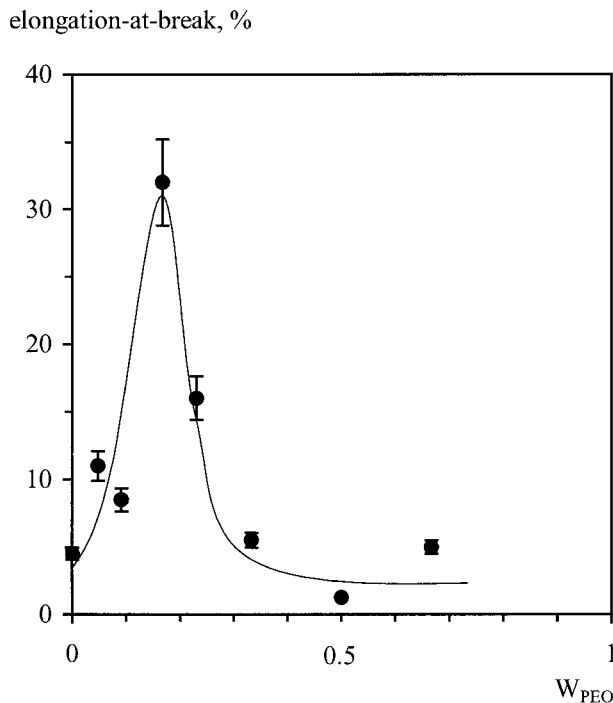


Figure 1 Elongation at break for the chitosan-400 + PEO-600 films as a function of the film composition (PEO fraction W_{PEO}).

RESULTS AND DISCUSSION

Mechanical Tests

The dependence of the elongation at break and of the tensile strength of chitosan-400 + PEO-600 films on the film composition are presented in Figures 1 and 2, correspondingly. Both show a maximum for the film containing a 0.17 wt fraction of PEO. A remarkable feature is that elongation at break increases by a factor of 6 at this composition. This means that this film is the most ductile as compared with those made from pure chitosan and from other chitosan + PEO mixtures. The obtained tensile strength of chitosan + PEO films is 5–10 times lower than that of films prepared from chitosan + cellulose blends,¹⁰ but the elastic properties at the PEO fraction of 0.17 wt fraction of PEO are 1.5–2 times higher.

This film composition corresponds to the stoichiometric ratio between chitosan and PEO monomer units. The following questions arise: What is the reason for such an improvement in the mechanical properties of chitosan + PEO film? Are there any special interactions between the components leading to the formation of interpolymer complexes, as assumed in ref. 13, or are

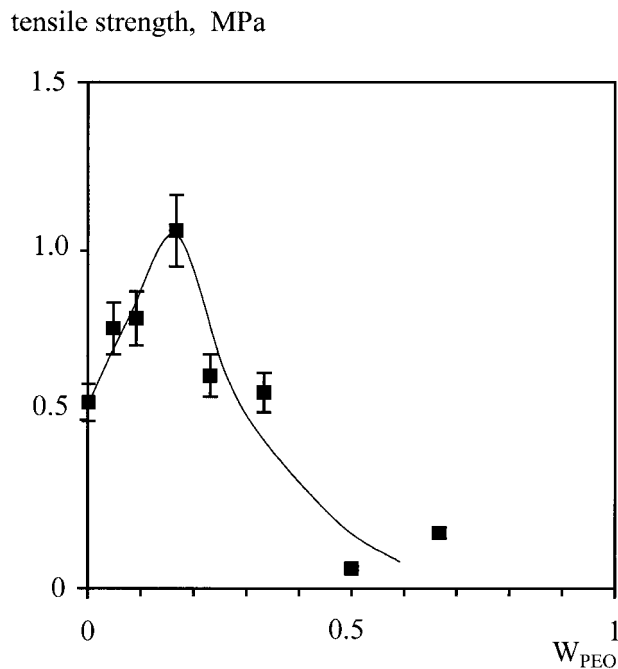


Figure 2 Tensile strength for the chitosan-400 + PEO-600 films as a function of the film composition W_{PEO} .

there any other reasons? To answer these questions, we performed a detailed analysis of films and mixture properties using SANS, the absorption of solvent vapors method, and a rheological study.

SANS Results

The structure of chitosan + PEO films was studied using the SANS technique. SANS experiments were performed on chitosan-400 + PEO-200 and on chitosan-400 + PEO-600 films of different compositions. We used the formalism developed by Debye et al.^{18,19} that describes the scattering from the samples with randomly distributed two phases:

$$I(q) = I_0 / (1 + q^2 R^2)^2$$

where I_0 is a constant determined by extrapolation of the coherent scattering intensity to a zero angle; $q = (4\pi \sin \Theta) / \lambda$ is a scattering vector; and 2Θ is a scattering angle; λ , the wavelength; and R , the correlation length. In our case, where the PEO phase is assumed to be randomly distributed in the chitosan phase, R is a measure of the structural heterogeneity.

Figure 3 shows the dependence of the correla-

tion length R as a function of the film composition for both chitosan-400 + PEO-200 and chitosan-400 + PEO-600 films. There is a slight decrease of the correlation length for the films containing 0.17 wt of PEO. This phenomenon was observed for films made of PEO of both molecular weights (2×10^5 and 6×10^5). The decrease in the correlation length means a decrease in the structural heterogeneity of the film, which can be a reason for the improvement of the mechanical properties. Further growth of the correlation length with increase of the PEO content means increase of the film heterogeneity, which proves the visual observation (see the section Samples Preparation).

The question that still remains to be answered is, "What is the reason for such a decrease in the structural heterogeneity at a certain film composition? Is this caused by any special interactions between the components or are there other reasons leading to the improvement in the mechanical properties of films prepared from a mixture but not from a pure component (chitosan)?"

Rheological Properties of Chitosan + PEO Mixtures

A straightforward method for testing any special interactions between the components (formation of interpolymer complexes) is to measure the mix-

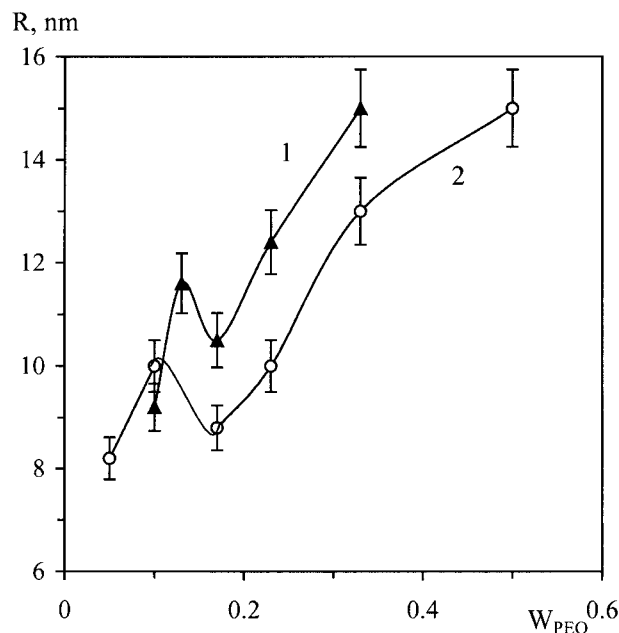


Figure 3 Correlation length R for (1) chitosan-400 + PEO-600 and (2) chitosan-400 + PEO-200 films as a function of the film composition W_{PEO} .

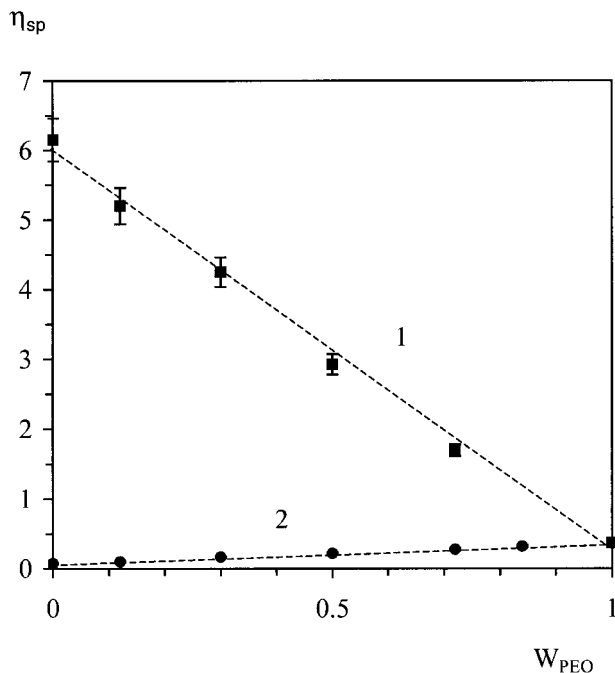


Figure 4 Specific viscosity of (1) chitosan-400 + PEO-600 and (2) chitosan-13 + PEO-600 mixtures as a function of the mixture composition W_{PEO} . Total polymer concentration was 0.1%. Dashed lines correspond to the calculated additive dependence.

ture specific viscosity as a function of its composition in a capillary viscometer and to compare this dependence with the calculated additive curve. This procedure is well known and described in the literature (see, e.g., refs. 20–22).

For the mixtures of PEO-600 with chitosan-13 and chitosan-400, the dependence of the mixture specific viscosity on its composition is presented in Figure 4. The concentration of the initial polymer solutions was 0.1% for all mixtures; thus, the total polymer concentration was kept constant at 0.1%. The dashed lines show the additive dependence of the viscosity of each mixture η_{add} on its composition, which in the first approximation corresponds to the absence of the special interactions between the components. To avoid any uncertainties in the determination of the additive curve, we used a procedure developed for mixtures where at least one of the components is a polyelectrolyte: we measured the viscosity–concentration dependence for each component by diluting it with a solvent (aqueous 2% acetic acid) and then calculated the additive mixture viscosity as follows^{20–22}:

$$\eta_{\text{add}} = \eta_{\text{sp}1}(C_1) + \eta_{\text{sp}2}(C_2)$$

$\eta_{\text{sp}1}(C_1)$ and $\eta_{\text{sp}2}(C_2)$ are the specific viscosity of each polymer at a concentration at which it is in the mixture, and C_1 and C_2 are polymer concentrations in the mixture; $C_1 + C_2 = 0.1 = \text{const}$.

Figure 4 shows that for the mixtures studied there is no difference between the experimental and calculated values of the mixture viscosity. It is known that if compact interpolymer complexes are formed in a mixture of two polymers in a common solvent [e.g., interpolymer complexes based on poly(methacrylic acid) + PEO] the mixture viscosity should be lower than the additive viscosity.²³ If a “gel-like” complex with a branched structure is formed, the mixture viscosity should be higher than the additive one.^{21,22} As far as that, in our case, the mixture viscosity coincides with the calculated additive values, we concluded that there are no strong interactions between PEO and chitosan.

The result obtained is not consistent with the one reported for chitosan + PEO mixtures¹³ where a positive deviation from the additive dependence was observed, implying the interpolymer complex formation. First, those experiments were performed on solutions that are far from a dilute regime (5–6%); thus, it is not correct to judge the polymer–polymer interactions. Then, as was demonstrated in ref. 13 and what we shall show in the following paragraph, a pure chitosan solution and all mixtures exhibit a shear-thinning effect which makes the comparison between the measured and additive viscosity also questionable. In any case, a viscometric test even performed for mixtures in a dilute concentration range without other physicochemical analysis (light scattering, velocity sedimentation, IR analysis, etc.) cannot give a clear answer on polymer–polymer compatibility or interactions.²⁴

As shown by the viscometric test and by SANS, within the studied range of component molecular weights (1.3×10^4 to 4×10^5 for chitosan and 2×10^5 to 6×10^5 for PEO), the result does not depend on the molecular weight of either chitosan or PEO and on the state of chitosan (charged or not, see Table I). The following rheological studies were performed for the system chitosan-400 + PEO-80: We studied the shear flow of this mixture at several mixture compositions and of the initial components (Fig. 5). Here, the total polymer concentration was 2.9%, which is a semidilute regime. As far as chitosan is a semirigid polymer, it shows a clear shear-thinning phenomenon as well as chitosan-containing mixtures. The dependence of the mixture viscosity on its compo-

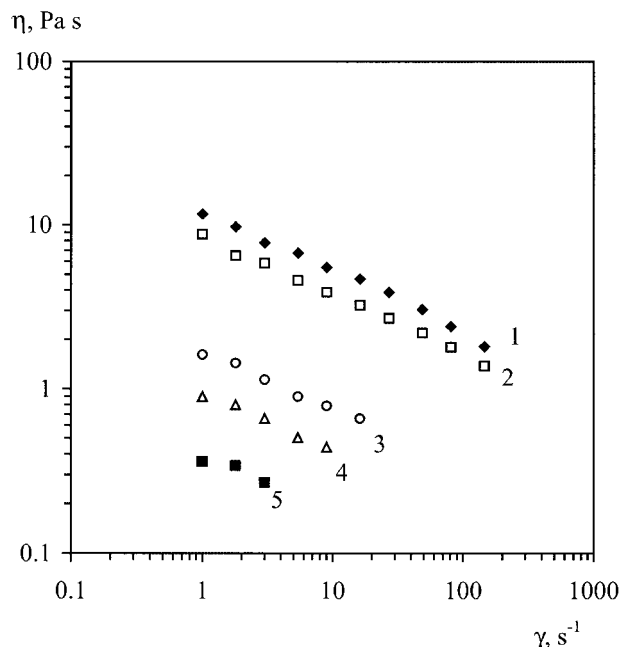


Figure 5 (1) Shear flow of chitosan-400 + PEO-80 mixtures for pure chitosan solution at $W_{\text{PEO}} =$ (2) 0.2, (3) 0.57, (4) 0.8, and (5) pure PEO solution. Total polymer concentration was 2.9%.

sition at a fixed shear rate (27 s^{-1}) is presented in Figure 6. Because the mixtures are in a semidilute region, the additive viscosity should be calculated according to a logarithmic rule:

$$\log \eta_{\text{add}} = \log \eta_{\text{sp}1}(C_1) + \log \eta_{\text{sp}2}(C_2)$$

The same procedure was performed for the mixture viscosities at several shear rates. In all cases, the experimental values of the viscosity were slightly lower than the calculated additive ones. As will be shown later, this means that two polymer components are slightly incompatible, but not because of the interpolymer complex formation.

The elongation flow of chitosan + PEO mixtures was also investigated and compared with the previously studied system, where “gel-like” interpolymer complexes are formed.²⁵ For the solutions flowing in the longitudinal field, the threshold rate gradient $\dot{\gamma}_{\text{cr}}$, leading to considerable uncoiling of a polymeric chain, depends on the time of the deformation relaxation τ of the macromolecule as a whole entity. According to the dumbbell model,²⁶ $\tau = 0.5/\dot{\gamma}_{\text{cr}}$. It was not possible to measure $\dot{\gamma}_{\text{cr}}$ for the PEO solution because the segments of the PEO macromolecule are not op-

tically anisotropic. In our case, this method is sensitive only to the effects connected with chitosan, which has an intrinsic optical anisotropy. Thus, the obtained value of τ is, in fact, the effective relaxation time.

The dependence of τ on the mixture composition is presented in Figure 7. Contrary to the mixture of poly(acrylic acid) + methylcellulose where “gel-like” complexes are formed and, thus, the dependence of the relaxation time on the mixture composition goes through a maximum,²⁵ here τ monotonically decreases without any extremal points. As shown in refs. 25 and 27, this method is sensitive to a complex formation even if one of the components is not optically anisotropic. Thus, we can conclude that the rheological behavior of the chitosan + PEO mixtures in both shear and longitudinal fields does not indicate any presence of interpolymer complexes.

Absorption of Solvent Vapors

The polymer–polymer interactions between two components in the film of chitosan-400 + PEO-

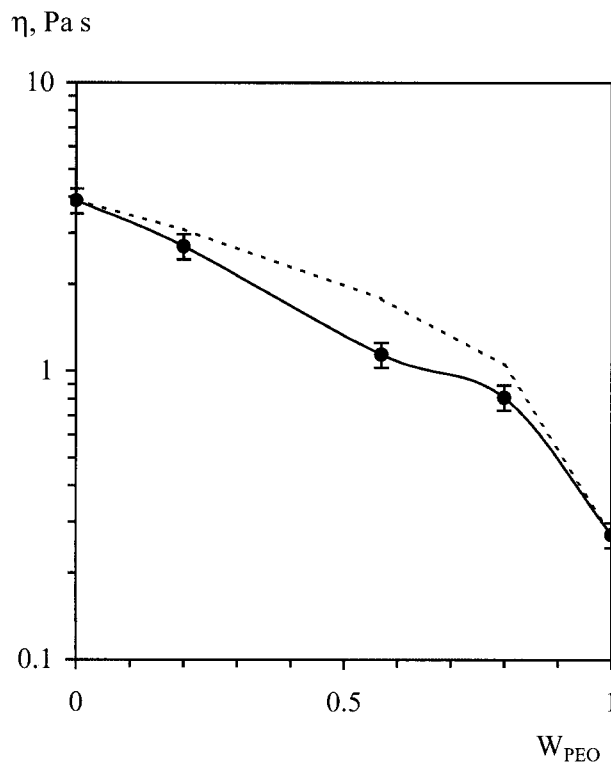


Figure 6 Viscosity of chitosan-400 + PEO-80 mixtures as a function of the mixture composition W_{PEO} . Total polymer concentration was 2.9%. Dashed line corresponds to the calculated additive dependence according to the logarithmic rule.

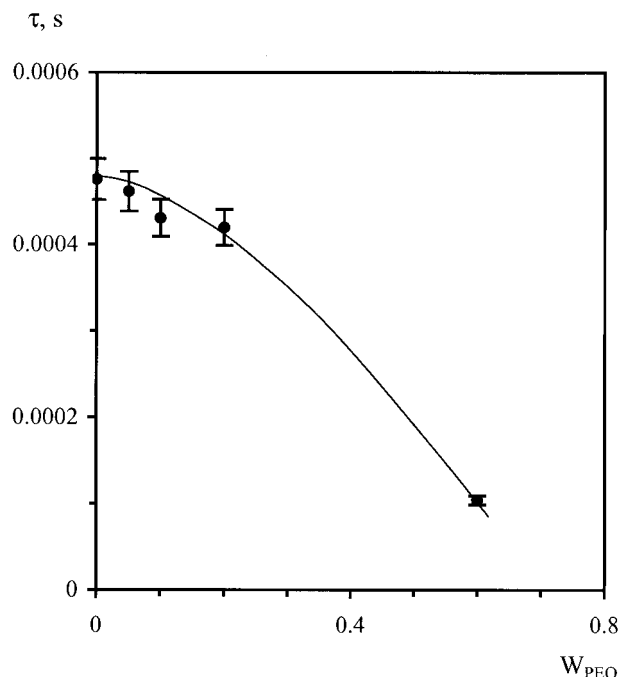


Figure 7 Relaxation time τ of chitosan-400 + PEO-80 mixtures as a function of the mixture composition W_{PEO} . Total polymer concentration was 0.1%.

600 prepared from a mixture of two polymers were investigated using the method of absorption of solvent vapors. The polymer–polymer interaction parameter was calculated as follows¹:

$$\chi_{23} = [\ln \phi_1 + (1 - \phi_1) + (1 - \phi_1)(\chi_{12}\phi_2 + \chi_{13}\phi_3)]/\phi_2\phi_3$$

where index 1 corresponds to the solvent; index 2, to chitosan; and index 3, to PEO; χ_{23} is a polymer–polymer (chitosan–PEO) interaction parameter characterizing the interaction between chitosan and PEO segments; ϕ_1 , the volume fraction of the solvent in the film; ϕ_2 and ϕ_3 , the volume fractions of chitosan or PEO in the film, respectively; and χ_{12} and χ_{13} , chitosan–2% acetic acid and PEO–2% acetic acid interaction parameters calculated from absorption experiments for pure components as follows:

$$\chi_{12} = -(\ln \phi_1 + \phi_2)/\phi_2^2$$

$$\chi_{13} = -(\ln \phi_1 + \phi_3)/\phi_3^2$$

The volume fraction of chitosan + PEO $\phi_{\text{pol}} = \phi_2 + \phi_3$ in the film was calculated using data on

specific absorption and on film density ρ_{pol} , obtained by the gravimetric method:

$$\phi_{\text{pol}} = (1 + A\rho_{\text{pol}}/\rho_1)^{-1}$$

A is the specific absorption value measured for each film composition and ρ_1 is the solvent density.

The dependence of a specific absorption on the film composition is presented in Figure 8. With increase of the PEO fraction in the film, the absorption first decreases and then at $W_{\text{PEO}} > 0.17$ it increases twice. It is this film composition where the improved mechanical properties were detected. The polymer–polymer interaction parameter χ_{23} was calculated for each film composition. The results are presented in Figure 9. It is known¹ that for a thermodynamically stable or compatible mixture, where the interactions between the polymer components are preferable as compared with the polymer–solvent interactions, $\chi_{23} < 0$. In our case, the mixture with a low PEO content ($W_{\text{PEO}} < 0.17$) is compatible, but when $W_{\text{PEO}} > 0.17$, the polymer–polymer interaction parameter is slightly higher than zero, which means that the mixture components are slightly

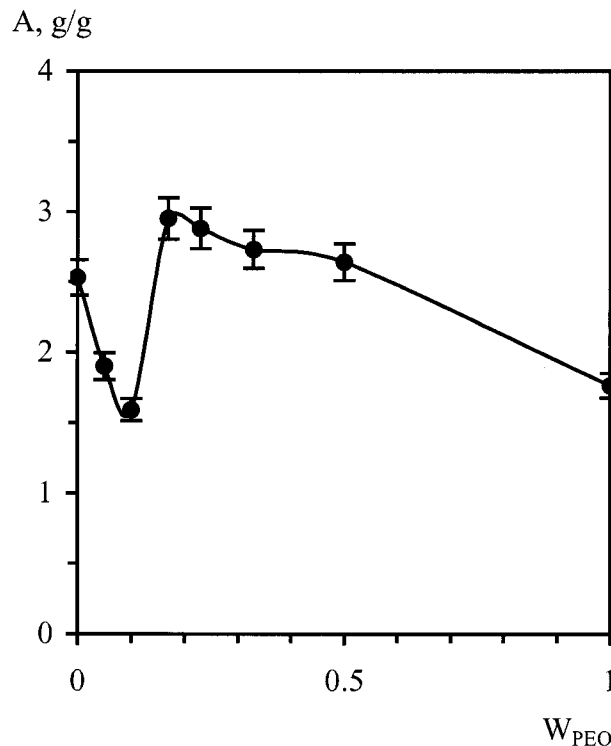


Figure 8 Specific absorption of chitosan-400 + PEO-600 film as a function of the film composition W_{PEO} .

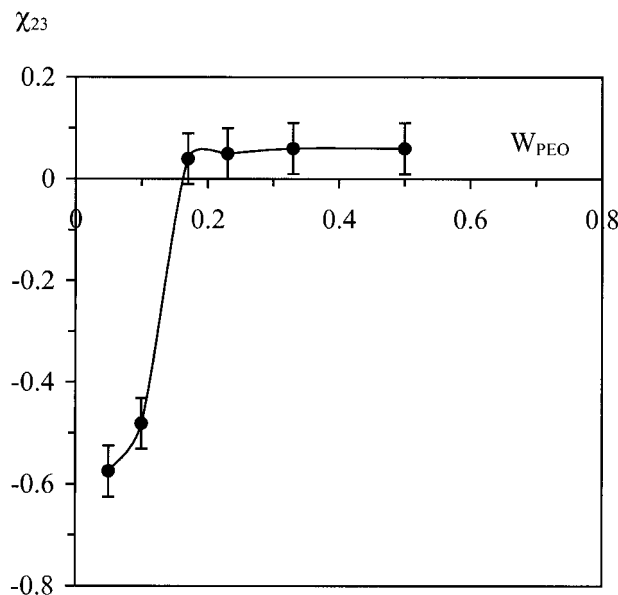


Figure 9 Polymer-polymer interaction parameter χ_{23} as a function of the film composition W_{PEO} .

incompatible. This is the final proof that there is no interpolymer complex formed between chitosan and PEO.

A similar result—the improvement of the mechanical properties of films prepared from slightly incompatible components—was obtained for diacetate cellulose + cyanethyl cellulose mixtures,²⁸ which was explained by the adjustment of polymer chains at a certain composition and, thus, formation of a more perfect structure. We suppose that in the mixture of chitosan + PEO we get the same effect.

CONCLUSIONS

Both rheological and absorption of solvent vapors methods clearly show that the best mechanical properties are achieved when two polymer components start to be incompatible. The incompatibility of PEO and chitosan is not strong; it does not lead to a phase separation. The best mechanical properties were revealed for a 0.83:0.17 = chitosan:PEO film, which is a stoichiometric composition between PEO and chitosan monomer units. At the same composition, SANS showed a decrease in the film heterogeneity.

The example of chitosan + PEO mixtures demonstrates that polymer-polymer compatibility is not necessary for the increase in the mechanical

properties of the films prepared from such mixtures. On the contrary, a slight incompatibility may force the two components to align and to order at their stoichiometric composition. As a result, chitosan + PEO film at this composition shows better mechanical properties than those of the film made from a pure chitosan.

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