Rheological characteristics of aqueous solutions of mixtures of chitosan and polyoxyethylene

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Summary

The rheological characteristics of aqueous solutions of chitosan and polyoxyethylene (POE) with molecular weight in the range of 10^5-10^6, as well as of their mixtures are described. It is found that the solutions of each polymer as well as of their mixtures exhibit pseudoplastic non-Newtonian behaviour which is described by the Ostwald-de-Waele model. It is proposed that the chitosan macromolecules determine the rheological behavior of the chitosan/POE mixtures.

Introduction

Chitosan is easily prepared by partial deacetylating chitin, poly[ß-(1→4)-2-acetamido-2-deoxy-D-glucopyranose]. Chitosan (Chit) has attracted much attention, including for biomedical, pharmacological and biotechnological applications. Due to its amino groups, chitosan is soluble in acidic aqueous solutions and is able to form complexes with metal ions. A large number of mono- and dicarboxylic acids form water-soluble salts with chitosan by protonation of its amino groups. Their aqueous solutions are used for the preparation of spherical particles of different size or for casting films (1). A promising method for the preparation of new chitosan-based materials with desired properties is the obtaining of polymer blends with nonionic water-soluble polymers. Previously (2), we have described the possibility to prepare films from mixtures of chitosan and high molecular polyoxyethylene (POE). It was also found that at certain ratios of the two components the crystallization of the POE macromolecules was impeded. This may be assigned to a polymer-polymer interaction through hydrogen bond formation which results in the orientation of the soft POE chains along the chitosan macromolecules. It is of interest to study the rheological behaviour of mixed chitosan/POE aqueous solutions since such solutions may be used for preparation of drug dosage forms. The rheological properties of semi-dilute chitosan aqueous solutions have been described as similar to those of other rigid-chain ionic polysaccharides with ß-(1→4)-glucoside links (3, 4).

In the present work, the rheological characteristics of dilute aqueous solutions of chitosan and high-molecular-weight POE, as well as of their mixtures are reported.

Experimental

Commercial samples of POE with molecular weight 10^5, 6.10^5 and 10^6 obtained from

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Serva were used. Chitosan with 92% degree of deacetylation was prepared from chitin by alkaline deacetylation procedure described in (1). All solutions of chitosan, POE and of their mixtures were prepared in the same manner - in 0.5% acetic acid and at total polymer concentration equal to 0.9% (w/w).

Flow measurements were carried out using a rheometer with concentric cylinders Rheotest-RV2 at $25\pm0.1°C$ and $40\pm0.1°C$. The mathematical interpretation of the relationship between the shear stress, τ, and the shear rate, $\dot{\gamma}$, according to the Ostwald-de Waele model (5):

$$\tau = k\,\dot{\gamma}^{\,n} \tag{1}$$

was carried out by means of a computer program Statgraphics.
According to equation *(2)*, the apparent viscosity, μ, of the solutions examined decreases with the increase of the shear rate.

$$\mu = \tau/\dot{\gamma} = k\,\dot{\gamma}^{\,n-1} \tag{2}$$

On account of this relation, the dependence of μ on chitosan content in the solutions of its mixtures with POE was determined at a constant shear rate equal to $218.7\ s^{-1}$.

The activation energy of the viscous flow, E, was calculated by equation *(3)*:

$$E = \frac{R\,T_1\,T_2}{T_2 - T_1}\,\ln\frac{\mu_1}{\mu_2} \tag{3}$$

where T_1 and T_2 were known temperatures, μ_1 and μ_2 - the apparent viscosity measured at the same temperatures, correspondingly. The above equation was obtained from Arhenius-Frenckel-Eyring equation

$$\mu = A\,e^{E/RT} \tag{4}$$

expressed in a logarithmic form and written for two different temperatures. The coefficient A depends on the molecular weight of the polymer and is measured in viscosity units (8). Therefore, the flow curves of the polymer solutions were determined at two different temperatures in order to calculate the activation energy.

Results and discussion

The flow curves for the aqueous solutions of each polymer and their mixtures (shear stress, τ, versus shear rate, $\dot{\gamma}$), are presented in Figures 1, 2 and 3. The solutions of POE and chitosan, as well as mixed solutions exhibit pseudoplastic non-Newtonian behaviour which is described by the rheological model of Ostwald-de-Waele (equation 1). The obtained values for the parameters, *k* and *n*, are listed in Table 1. There is a good agreement between the obtained results with the predicted ones by Ostwald-de-Waele model (Figure 4). This is an evidence that the rheological behaviour of the aqueous solutions of chitosan and POE and of their mixtures is described by Ostwald-de-Waele model.

From the results given in Table 1 it is also seen that, in the mixed chitosan/POE solutions, the increase of the chitosan content causes small changes in the value of the rheological n-parameter (less than 6.8%), while the value of the consistency coefficient, *k*, grows considerably. At weight ratio chitosan/POE=4:6 (POE with molecular weight 10^6), the consistency coefficient attains a value tenfold higher than the one for the corresponding POE solution. Such tendency is observed also for chitosan mixtures with
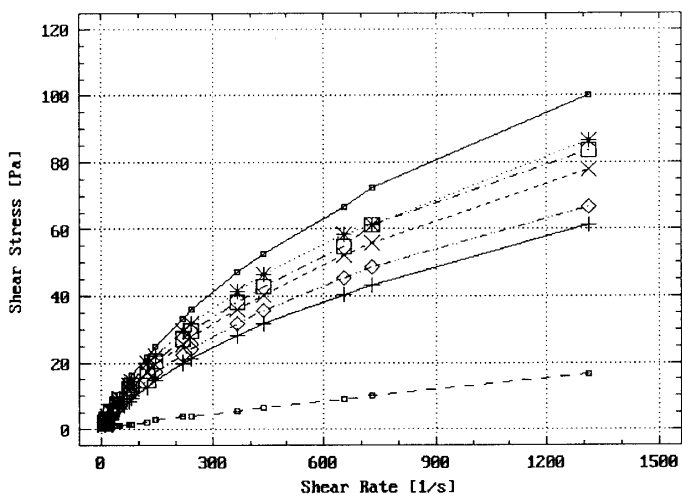
Figure 1. Shear stress, τ, versus shear rate, $\dot{\gamma}$, for the aqueous solutions of: POE, MW 10^6 ($\square$), chitosan MW 10^6 ($\blacksquare$) and their mixtures at weight ratio [Chit]:[POE] = 8:2 ($\ast$), 7:3 ($\square$), 6:4 (**x**), 5:5 ($\Diamond$) and 4:6 (+); temperature 25^0C; total polymer concentration 0.9% (w/w).
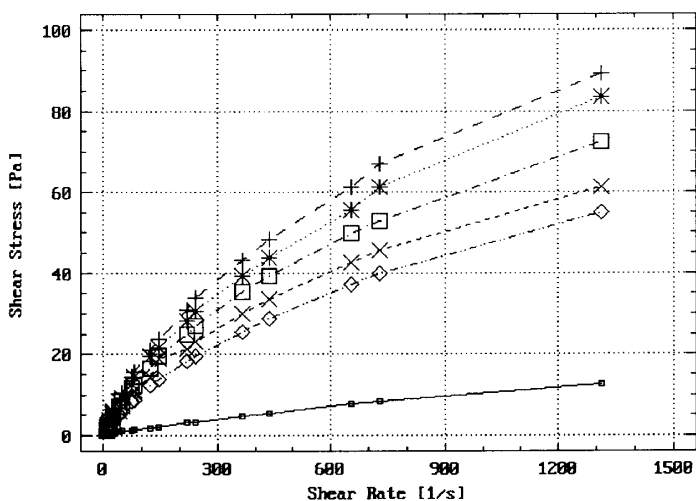

Figure 2. Shear stress, τ, versus shear rate, $\dot{\gamma}$, for the aqueous solutions of: POE, MW 6.10^5 ($\square$) and its mixtures with chitosan at weight ratio [Chit]:[POE] = 8:2 (+), 7:3 ($\ast$), 6:4 ($\square$), 5:5 (**x**) and 4:6 ($\Diamond$); temperature 25^0C; total polymer concentration 0.9% (w/w)
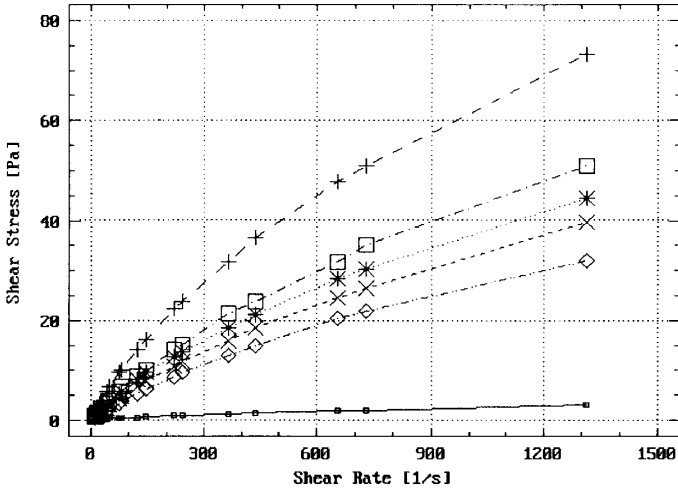
Figure 3. Shear stress, τ, versus shear rate, $\dot{\gamma}$, for the aqueous solutions of: POE, MW 10^5 (□) and its mixtures with chitosan at weight ratio [Chit]:[POE] = 8:2 (+), 7:3 (□), 6:4 (✳), 5:5 (x) and 4:6 (◊); temperature 25^0C; total polymer concentration 0.9% (w/w).

Table 1. Values of **k** and **n** parameters in the Ostwald-de Waele equation for the solutions of chitosan, polyoxyethylene and their mixtures and the corresponding determination coefficient R^2

| Solution	k	n	R^2
chitosan MW 10^6	1.23	0.62	0.995
POE MW 10^6	0.04	0.83	0.998
chitosan/POE = 8/2	0.92	0.64	0.995
chitosan/POE = 7/3	0.77	0.66	0.997
chitosan/POE = 6/4	0.75	0.65	0.997
chitosan/POE = 5/5	0.68	0.64	0.996
chitosan/POE = 4/6	0.54	0.66	0.997
POE MW 6.10^5	0.05	0.77	0.999
chitosan/POE = 8/2	1.06	0.62	0.996
chitosan/POE = 7/3	0.90	0.64	0.997
chitosan/POE = 6/4	0.82	0.63	0.994
chitosan/POE = 5/5	0.76	0.62	0.994
chitosan/POE = 4/6	0.55	0.64	0.997
POE MW 10^5	0.03	0.63	0.983
chitosan/POE = 8/2	0.52	0.69	0.997
chitosan/POE = 7/3	0.26	0.72	0.998
chitosan/POE = 6/4	0.27	0.73	0.997
chitosan/POE = 5/5	0.20	0.74	0.998
chitosan/POE = 4/6	0.16	0.74	0.997
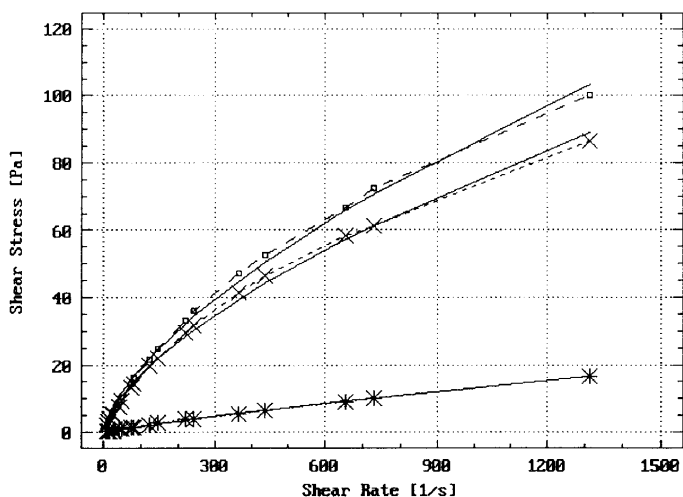
Figure 4. Shear stress, τ, versus shear rate, $\dot{\gamma}$, calculated according to the Ostwald-de Waele model (solid line) and the experimentally determined for the aqueous solutions of: POE, MW 10^6 (✻), chitosan MW 10^6 (□) and their mixture at weight ratio [Chit]:[POE] = 8:2 (×); temperature 25^0C; total polymer concentration 0.9% (w/w).
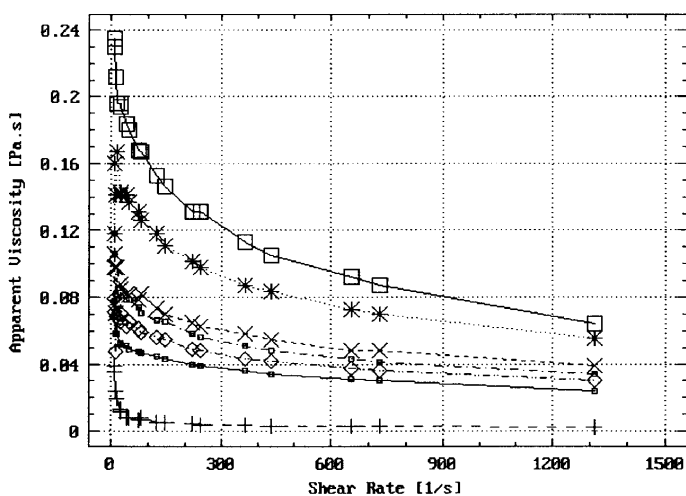

Figure 5. Apparent viscosity, μ, versus shear rate, $\dot{\gamma}$, for the aqueous solutions of: POE, MW 10^5 (+), chitosan MW 10^6 (□) and their mixtures at weight ratios [Chit]:[POE] = 8:2 (✻), 7:3 (✗), 6:4 (□), 5:5 (◊) and 4:6 (■); temperature 25^0C; total polymer concentration 0.9% (w/w).

a lower-molecular-weight POE (molecular weight 6.10^5 and 10^5).

The rheological behaviour of the chitosan/POE mixtures is governed by chitosan. This is illustrated by the viscosity curves (Figure 5) as well as by the dependence of the apparent viscosity, μ, (determined at a constant shear rate) on chitosan content in its mixtures (Figure 6). As seen from Figures 5 and 6, μ values increase with the increase of chitosan content. It is noteworthy that the observed dependence (Figure 6) is not linear
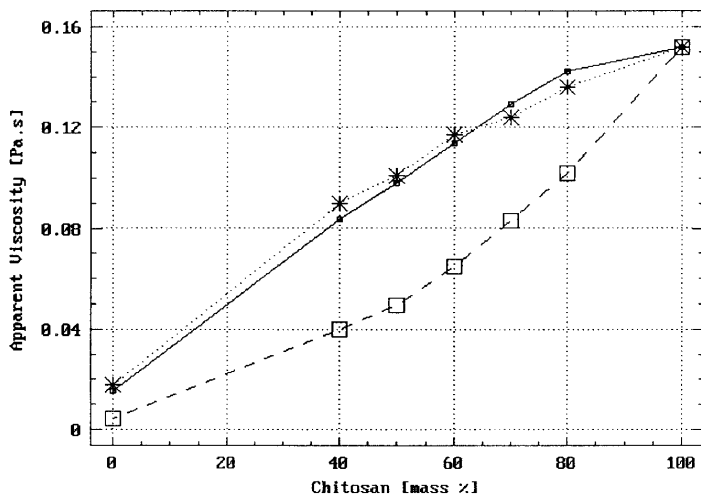

Figure 6. Apparent viscosity, μ, versus chitosan content (% w/w) for the aqueous solutions of mixtures Chit/POE for POE, MW 10^6 (✳), POE MW 6.10^5 (□) and POE, MW 10^5 (☐).

neither for POE of MW 10^6 and 6.10^5 nor for POE with lower molecular weight (MW 10^5). When the content of the latter is about 50% it acts similarly to a lubricant. Further decrease in the POE content to 0% results in a sharp increase of the apparent viscosity. The more pronounced increase of the apparent viscosity of mixtures of chitosan with high-molecular-weight POE may be attributed to the entanglement of the long POE chains with those of chitosan.

In order to estimate the effect of temperature on the rheological behaviour, the activation energy, E, was evaluated. It was found that for the solutions of chitosan, POE and their mixtures E correlates with the shear rates. Thus for the chitosan solution the activation energy values diminishes from 29 to 17.6 kJ.mol^{-1} when the shear rate increases from 121.5 to 1312 s^{-1}. These values are in good agreement with known data (6, 7). For the same range of shear rates and for the POE solution the E values decrease from 36 to 22.4 kJ.mol^{-1}. The higher E values obtained for POE and the fact that the activation energy does not depend on the polymer molecular weight (8) explain the considerable decrease of the apparent viscosity with temperature increase observed for the POE solutions. This tendency is less pronounced for the chitosan solutions because of the lower E values.

From the present study it may be assumed that the rigid chitosan macromolecules

determine the rheological behaviour of the chitosan/POE mixtures. As a result of hydrogen bond formation between the molecules of chitosan, water and POE having molecular weight below a given value (below 10^6), the soft polyether chains can be orientated to a certain extent along the rigid chitosan macromolecules thus facilitating their flow. For mixtures containing higher-molecular-weight POE (MW 10^6 and more) due to entanglement this tendency is rather the opposite.

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