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THERMAL DEGRADATION OF NATURAL POLYMERS

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Abstract

The thermal degradation of sodium hyaluronate, xanthan and methylcellulose was evaluated by thermogravimetric and infrared analysis. Kinetic parameters such as activation energy and pre-exponential factor were determined considering the Ozawa and Freeman–Carroll methods. The results suggest changes in the degradation mechanism with the fraction of mass loss for both the studied polysaccharides. The activation energy values determined by the Freeman–Carroll method are higher than those obtained by the Ozawa method under the same conditions, probably because in the first method a first order reaction was assumed and the thermal history effects were eliminated since only one TG curve was used to determine the kinetic parameters. Low thermal stability was observed for polyanions e.g. sodium hyaluronate (Na-Hy) and xanthan (XT) in comparison with methylcellulose (MC) which is a neutral polysaccharide. By infrared spectroscopy, it was observed that at low temperatures there occured only the scission of the exocyclic groups for both polysaccharides and that the scission of strong links in the backbone occurred at high temperatures, in agreement with the kinetic parameters determined for the degradation reaction.

Keywords: kinetic parameters, polysaccharides, thermal degradation

Introduction

Most practical applications of polysaccharides are based on their ability to drastically change the physical properties in aqueous solutions, either by increasing the viscosity or by creating cohesive intermolecular networks (gels). Because all polysaccharides modify the flow of aqueous solutions, dispersions and suspensions, the choice of appropriate polysaccharide for any particular application depends upon secondary characteristics such as the presence or absence of charge. In general, polysaccharides are neutral, like amylose and metylcellulose, or ionic, like xanthan, sodium hyaluronate and carboxymethylcellulose [1].

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Polysaccharides are submitted to intense heat during the preparation, processing and preservation of the raw materials used for their extraction and application in different fields. For example, the thixotropy of xanthan has been exploited in its use as a stabilizer in ceramic glass and as a foam stabilizer in fire-fighting liquids [2]. Elevated temperatures may initiate the degradation of polysaccharide macromolecules and consequently can affect some rheological and mechanical properties in solution. Comprehensive studies on the physicochemical properties of polysaccharides are necessary for their rational application in the food and pharmaceutical industries, in medicine, and in the manufacture of various products [3].

In the present work, the thermal stability and kinetics parameters for the degradation reaction of sodium hyaluronate, xanthan and methylcellulose were analyzed. The kinetics parameters, such as activation energy and pre-exponential factor, were determined by the Ozawa [4, 5] and Freeman–Carroll [6] methods.

Experimental

Materials

Sodium hyaluronate (Na-Hy), a charged polysaccharide formed by repeating oligosaccharide units of *D*-glucoronic acid and N-acetyl-*D*-glucosamine linked by a β 1-4 glycosidic bond. Shiseido Basic Research Lab. (Yokohama, Japan) provided this polysaccharide with molecular mass (M_w) of $1.40 \cdot 10^6$ g mol^{-1}. Xanthan (XT) consists of a pentasaccharide repeating unit with a (1→4)-β-*D*-glucopyranan (cellulosic) backbone with O-β-*D*-mannopyranosil- (1→4)-O-β-*D*-glucopyranolsyluronic acid-(1→2)-6-O-acetyl-α-*D*-mannopyranosil side chains 3-linked to alternate glucose residues [7]. The molecular mass was $8.58 \cdot 10^5$ g mol^{-1} and was provided by SKW Brosystems (Baupte, France). Methylcellulose (MC) is a non-ionic polysaccharide, in which some of the hydrogen atoms of the cellulose hydroxyl groups are replaced by methyl groups. The degree of substitution was 1.8 and the $M_w = 3.68 \cdot 10^5$ g mol^{-1}. The MC was received from Shin-Etsu (Tokyo, Japan). Methylcellulose was used without further purification, Na-Hy and XT were purified according to the method of Akasaka *et al.* [8].

Methods

Thermogravimetric measurement was carried out on a Shimadzu 50 thermogravimetric analyzer. Non-isothermal experiments were performed in the temperature range from 25 to 900°C at heating rates (β) of 5, 10 and 20°C min^{-1} on each sample. The average sample size was 5 mg and the nitrogen flow-rate was 50 cm^3 min^{-1}. The thermogravimetric data was analyzed using the Ozawa and Freeman–Carroll methods. For the Ozawa method, the parameters were determined using the associated TGA-50 software, and the apparent activation energy was derived from the slope of the dependence of the heating rate upon the reciprocal absolute temperature, at defined mass loss. In the Freeman–Carroll method, the degradation rate (mass loss in function of time: –d*W*/d*t*) is considered to be dependent on temperature and composition. Considering *W* as the remainder mass fraction in a TG curve that represents thermal degradation at a constant heating rate, and assuming the reaction order to be equal to unity, the degradation reaction can be described by Eq. (1), where *A* represents the pre-exponential factor, *E* the apparent activation energy, *R* the universal constant of gases, and *T* the absolute temperature. The slope of the plot of $\ln([-dW/dt]/W)$ *vs.* $-1/RT$ determines the apparent activation energy and the linear coefficient corresponds to the pre-exponential factor.

$$\ln([-\mathrm{d}W/\mathrm{d}t]/W)=E(-1/RT)+\ln A \qquad (1)$$

For the degradation process, the samples were put into TG equipment at a required temperature in the presence of N_2, and after the thermal degradation the residual samples were cooled to room temperature for the FT-IR analysis.

The infrared spectra of unheated polysaccharides, and of the thermally degraded samples, were performed on a Perkin Elmer spectrometer (model 16PC), with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}. KBr technique was applied to all the analyzed samples.

Results and discussion

The thermal degradation was studied in order to evaluate the thermal stability and kinetic parameters such as activation energy and pre-exponential factor. The thermogravimetric (TG) and the derivative (DTG) curves of Na-Hy, XT and MC are shown in Fig. 1. For MC, we observed only one mass loss stage corresponding to the degradation reaction. The Na-Hy and XT showed two mass loss stages, in which the first indicated the water loss and the second the polysaccharide degradation. The maximum degradation temperatures for MC, XT and Na-Hy, determined with regard to the DTG curves, were 376, 298 and 276°C, respectively, suggesting a high thermal stability for MC. In general, neutral polysaccharides (e.g. MC) showed higher thermal resistance than charged polyanions (e.g. Na-Hy and XT). On the other hand, if we consider the residual mass percentage at 600°C, higher values were observed for the Na-Hy (37%) and XT (27%). Under the same conditions, the residual weight value for MC was 12%. The higher values for Na-Hy and XT are due to the presence of Na^+ in the structure, which can form inorganic sub-products in the degradation reaction.

For the kinetics studies, we considered the major processes of degradation as indicated for the maximum temperatures (DTG) in Fig. 1. The apparent activation energy for the polysaccharides determined using the Ozawa method *vs.* the mass loss fraction (α) are shown in Fig. 2. Similarly, *E* increased with the mass loss fraction for both polysaccharides. For Na-Hy and XT, *E* rose to approximately 155 kJ mol^{-1} when α=0.45. On the other hand, for MC, the maximum value was 165 kJ mol^{-1} when α=0.75. The observed behaviour is related with changes in the thermal degradation mechanism, such as those observed in other polymeric systems [6]. Considering that weak link scissions, in general, are associated with *E* values lower than 100 kJ mol^{-1}

[6], the above results suggest that the process occurred by random scission of strong links of the chain.

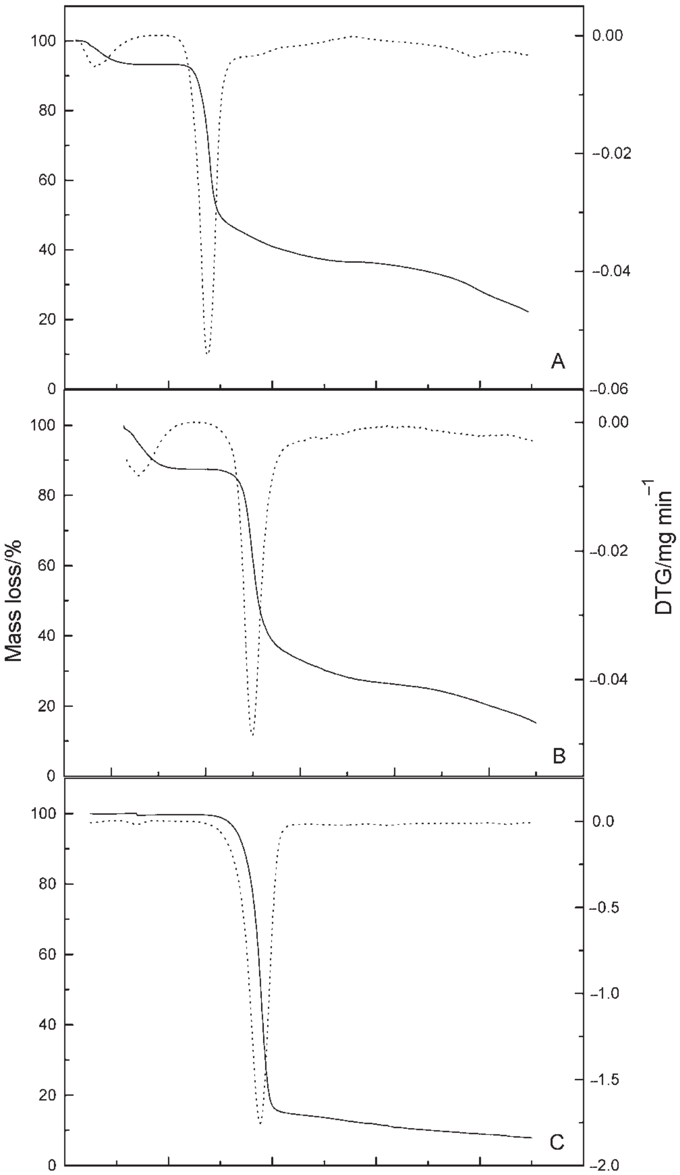

Fig. 1 Thermogravimetric (—) and DTG (- - - -) curves for A – Na-Hy, B – xanthan and C – methylcellulose at a heating rate of 10°C min^{-1} in nitrogen atmosphere

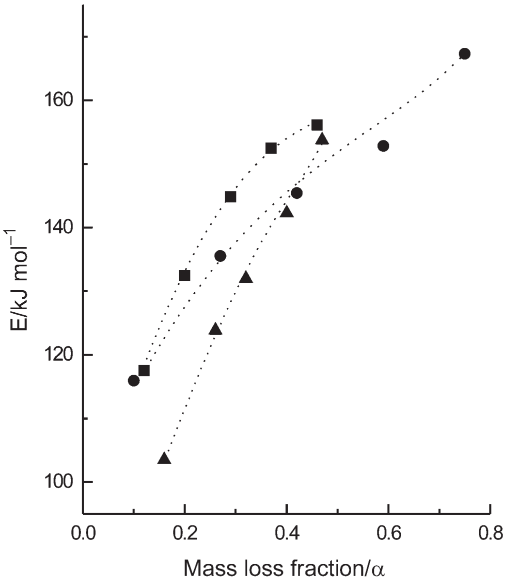

Fig. 2 Plots of activation energy *vs.* mass loss fraction for ■ – Na-Hy, ▲ – xanthan and ● – methylcellulose

The above results were compared with E values obtained using the Freeman–Carroll method, considering the major mass loss stage for each system, as shown in Fig. 1. The plots of $\ln([-dW/dt]/W)$ *vs.* $-1/RT$ for Na-Hy and XT at different heating rates, considering Eq. (1) (first order reaction), are shown in Fig. 3. For the heating rates 5, 10 and 20°C min^{-1}, a curving trend is observed that has been fitted by using two dotted straight lines defining two regions (denoted I and II in Table 1), in which the slopes are equal to the apparent activation energy, E. Apparently, the presence of two linear regions is related with a change in the dominant mechanism of degradation. This change occured at a determined transition temperature which increased with the heating rate for both systems. For MC, the plot such as Eq. (1) (not shown) was similar to that observed fo XT, including the appearance of the two regions, although the transition temperatures varied from 337 to 367°C. E and $\ln A$ values for the three studied systems, considering the two regions and the heating rates of 5, 10 and 20°C min^{-1}, are shown in Table 1. As can be seen, E for XT in each linear region is approximately the same for the three heating rates. However, the changes of E were observed for MC and Na-Hy. The pre-exponential factor ($\ln A$) for the studied systems is related with the activation energy in both regions. E values for XT and MC, considering region I, are almost the same as those observed by the Ozawa method (Fig. 2). For region II, on the other hand, higher values are observed, which are probably related with the scission of the more stable links of the polysaccharide structures. The activation energy values for MC in both regions (I and II) are higher than XT under the same conditions. This behaviour agrees with the values of the maximum degradation temperatures (Fig. 1) which suggest higher thermal stability for the neutral

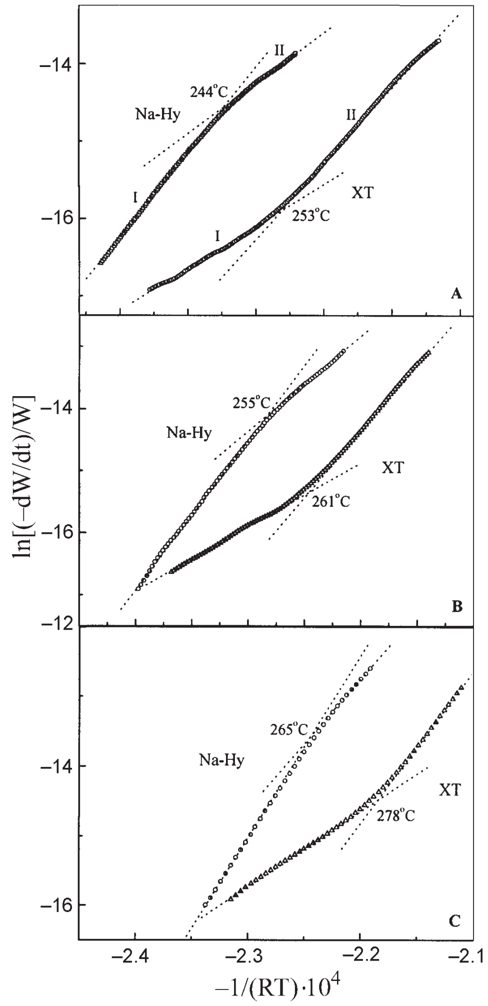

Fig. 3 Plots of ln[(–d*W*/d*t*)/*W*] *vs.* –1/*RT* using the Freeman–Carroll method for Na-Hy and XT at heating rates of A – 5, B – 10 and C – 20°C min^{-1}

polysaccharide (MC) in comparison with Na-Hy and XT that are charged polyanions. For Na-Hy, region I showed higher *E* values than those observed for XT and MC. This behaviour is probably related with the more compact helical and stable structure in the solid state for Na-Hy, in comparison to the other studied polysaccharides [10]. The analyses of TG and DTG curves (Fig. 1) and the transition temperatures (Fig. 3) indicated that less than 10% of each polysaccharide sample was degraded in region I. This fact suggests that the energy in region I is related also with changes in the polysaccharide conformation before the degradation reaction, justifying the higher *E* values observed for region I in the Na-Hy system.

Table 1 Kinetic parameters obtained by Freeman–Carroll method

System	β/°Cmin^{-1}	Region I			Region II		
		E/kJ mol^{-1}	ln$A$	r^a	E/kJ mol^{-1}	ln$A$	r^a
Na-Hy	5	215.6	35.5	0.9995	128.3	15.3	0.9991
	10	234.7	39.4	0.9995	155.6	21.4	0.9992
	20	251.7	42.8	0.9999	196.2	30.4	0.9992
XT	5	104.8	8.0	0.9990	195.9	28.8	0.9993
	10	107.1	8.7	0.9995	208.4	31.5	0.9994
	20	108.8	9.3	0.9996	210.8	31.6	0.9995
MC	5	209.8	14.5	0.9999	339.8	20.9	0.9996
	10	143.8	22.8	0.9999	222.1	37.9	0.9994
	20	160.2	23.9	0.9997	265.4	43.7	0.9997

[a] correlation coefficients considering the $\ln([-dW/dt]/W)$ *vs.* $-1/RT$ plot

Figure 4 shows FT-IR spectra for the residual products corresponding to the degradation reaction of Na-Hy at different temperatures. FT-IR spectra at 280, 350, 450 and 500°C were compared with Na-Hy at room temperature in the 2000 to 400 cm^{-1} region. At 25°C, the main bands are related with C=O stretching at 1653 and

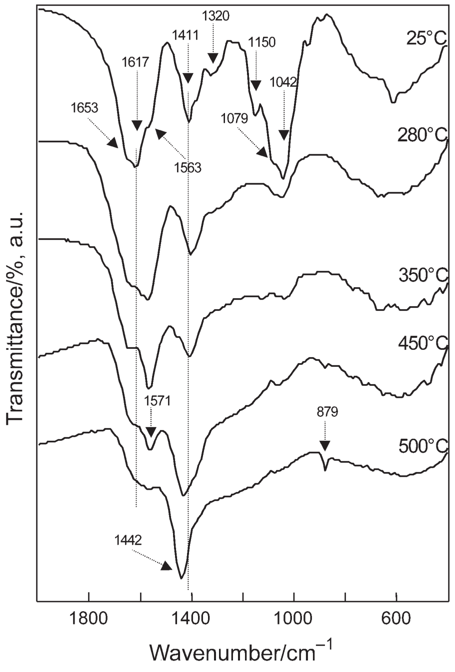

Fig. 4 FT-IR spectra of Na-Hy during thermal degradation at different temperatures

1617 cm^{-1} corresponding to the amide I and acid groups, respectively, NH group at 1563 and 1320 cm^{-1} (amide II and III), C–O group at 1411 cm^{-1} (acid) and C–O–C group at 1150 cm^{-1} (O-bridge), the C–O (exocyclic) and C–C groups at 1079 cm^{-1}, and the C–OH group at 1042 cm^{-1} [10]. FT-IR spectra at 150°C (not shown) present the same bands and intensity observed at room temperature, in agreement with the degradation curves shown in in Fig. 1. At 280°C, the bands corresponding to the exocyclic groups (1150, 1079 and 1042 cm^{-1}) and NH stretching (1320 cm^{-1}) disappeared, indicating the cleavage of the β 1-4 glycosidic bond in the backbone. Apparently, a new band corresponding to the C=N stretching appears at 1571 cm^{-1}, which is stable up to ca 450°C. At 350 and 450°C, the bands corresponding to the carbonyl stretching decreased in intensity. At 500°C, the spectra show the bands' absorption at 1442 and 879 cm^{-1}, which are associated with the formation of cyclic structures. Similar behaviour in terms of the degradation products was observed for the xanthan, probably due to the presence of similar groups in the structures. For MC, on the other hand, the bands corresponding to OH, CH_2, CH_3 and C–O stretching and CH_2 and CH_3 bending observed at room temperature totally disappeared at 500°C. At the same temperature, a new band at 1644 cm^{-1} was observed corresponding to unsaturated structures.

Conclusions

In summary, both methods used for the kinetics analysis suggest changes in the degradation mechanism with the mass loss fraction, for both the studied polysaccharides. Although the Freeman–Carroll method is apparently more effective in determining the exact transition temperature between different mechanism, *E* values are higher than those determined by the Ozawa method, mainly in region II for XT and MC and region I for Na-Hy. The differences are probably related to the assumption of first order reaction and the elimination of thermal history effects, since only one TG curve is used to determine the kinetic parameters by the Freeman–Carroll method. In general, the kinetic parameters determined by the Ozawa method are more precise because multiple constant heating rates are used for the analysis. The activation energy values and the maximum degradation temperature suggest higher thermal resistance for MC when in comparison with Na-Hy and XT. The increase of *E* with the mass loss fraction such as that observed by the Ozawa method, and the *E* values determined by the Freeman–Carroll method, are in agreement with the FT-IR analysis. At low temperatures, only the scission of the exocyclic groups for both polysaccharides occurred. However, at higher temperatures, the scission of strong links in the backbone also took place.

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