

Plasticizer Effect on Dielectric and Relaxation Parameters of Xanthan

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The dielectric and relaxation properties of pure and plasticized (with water, glycerol and PPG-200) xanthan were studied by broadband dielectric relaxation spectroscopy. Within frequency range $10\text{--}10^7$ Hz, a solid xanthan and its gels demonstrated two relaxation processes: the β -relaxation and relaxation of gel fragments formed due to xanthan/plasticizer interaction. The relaxation time decreased in the row of plasticizers: PPG-200 > water > glycerol; the segmental dynamics of xanthan respectively grow. The ionic conductivity of gel samples increased in the following sequence: water < PPG-200 < glycerol.

Introduction

Polysaccharides are considered among the most important biopolymers in nature. Being widely spread and easily available from plants, animal and microbial sources, they are prospective materials for chemical synthesis. In particular, cellulose, chitosan, xanthan, cyclodextrines etc. could be a promising base for obtaining new sorbents, drug delivery matrices, flocculants etc. [1-3]. Xanthan is one of the most prospective polysaccharides of microbiological origin due to its biocompatibility, resistance to aggressive chemical media and ability to biodegradation [4]. It is well known that physicochemical properties of polysaccharides considerably depend on bound water, which can work as plasticizer [5]. This article concerns the effects of water and other low-molecular-weight and oligomeric plasticizers such as glycerol and poly(propylene glycol)-200 on dielectric and relaxation parameters of xanthan.

Experimental part

The following substances were used in our study without additional purification: xanthan from “Snork” (China), glycerol and poly(propylene glycol)-200 (PPG-200) from “Merck” (USA). Xanthan gels were prepared by swelling 1 g of polysaccharide in 10 ml of plasticizer (water, glycerol or PPG-200) during 2 days. To obtain the sample of a solid xanthan, the polysaccharide powder contained 10% of moisture was pressed in tablets. Thus, the samples of a solid xanthan, xanthan/PPG-200, xanthan/glycerol and xanthan/water were obtained. Dielectric and relaxation properties were examined by the method of dielectric and relaxation spectroscopy using a Z-1000P impedancemeter (Elins, Russia) within frequency range $10^2\text{--}10^7$ Hz and temperature region from 20 to 120 °C.

Results and discussion

Fig. 1 shows the frequency dependence of $\text{tg}\delta$ for a solid xanthan. The obtained curves

allow identifying two separate relaxation processes: one of them with the maximum at 5×10^2 Hz, which position is shifted to high frequencies at the temperature increase, and the other one which is displayed as an initial part of peak shoulder at the temperatures higher than 60°C and frequencies lower than 10^3 Hz. In the temperature range $20\text{--}120^\circ\text{C}$, the relaxation processes in polysaccharides are usually attributed to the presence of moisture [6] (so-called wet- β -relaxation).

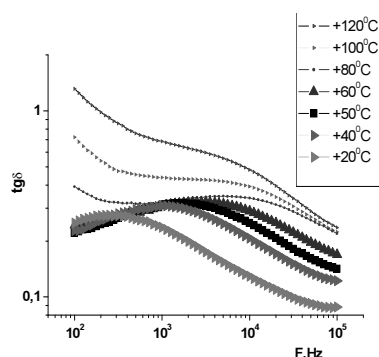


Fig. 1. The frequency dependence of $\text{tg}\delta$ for a solid xanthan within temperature region $20\text{--}120^\circ\text{C}$.

Authors of [5] showed that even small water amount (lower than 1 %wt.) results in the peak appearance at the temperatures lower than 150°C . The shoulder of this peak at $10\text{--}10^3$ Hz and $T > 60^\circ\text{C}$ corresponds to β -relaxation which reflects a local dynamics of main polysaccharide chain (concerning mainly glycosidic bonds of main chain) [5]. For xanthan/water sample (Fig. 2) within the same frequency range, we can observe the only peak, which is evidently the result of overlapping wet- β -relaxation and β -relaxation processes that

was induced by the formation of three-dimensional structure of xanthan hydrogel.

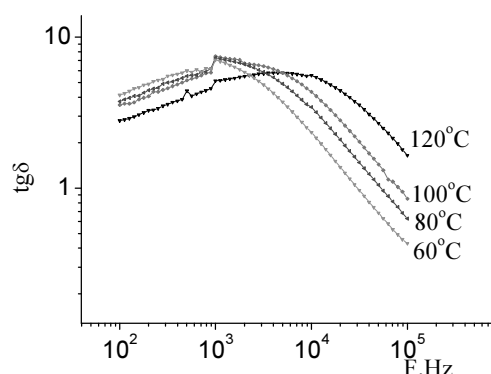


Fig. 2. The frequency dependence of $\text{tg}\delta$ for a water-contained xanthan in the temperature region $60\text{--}120^\circ\text{C}$.

For xanthan samples (gels) contained PPG-200 and glycerol, the appearance of two relaxation processes such as the β -relaxation (as in solid xanthan) and also the relaxation of fragments formed due to xanthan/plasticizer interaction could be observed within the same frequency-temperature range (Fig. 3). Moreover, the last relaxation process shifted into high frequency range for xanthan/glycerol sample as compared to xanthan/PPG-200 one.

Such behavior can be explained by the hydrogen bond formation between glycerol molecules and xanthan functional groups, while PPG-200 does not interact with xanthan in the same way.

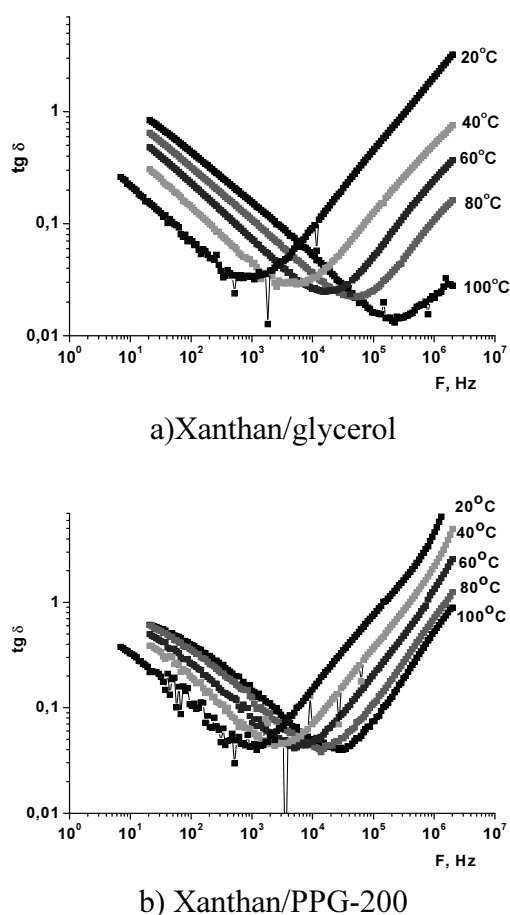


Fig. 3. The frequency dependence of $\text{tg}\delta$ for xanthan/PPG-200 and xanthan/glycerol gels within temperature region 20–100 °C.

This supposition is confirmed by a significant activation energy growth of this relaxation process for xanthan/glycerol gel ($E_A=22,7\text{kcal/mol}$) compared to xanthan/PPG-200 one ($E_A=6,9\text{ kcal/mol}$).

The plasticizer influence is also well seen from the calculated relaxation time (τ). The data in Fig. 4 confirm that for all plasticizer-containing samples τ value is lower than for solid xanthan and decreases with the temperature rise. This is evidence for growth of the segmental dynamics of xanthan. The

relaxation time decreases in the row of plasticizers: PPG-200 > water > glycerol.

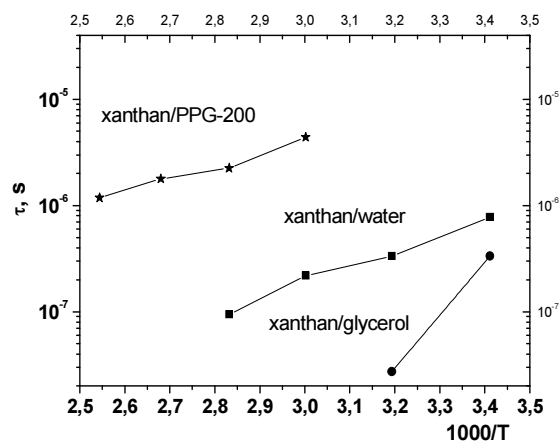


Fig. 4. The temperature dependence of the relaxation times for gel samples under study.

Thus, the introduction of low-molecular-weight and oligomeric plasticizers increases the segmental dynamics of xanthan; moreover, the low-molecular-weight plasticizers (glycerol and water), which are able of forming hydrogen bonds with polysaccharide chains, turns out to be more effective than oligomeric plasticizer PPG-200.

The growth of segmental dynamics is accompanied by the increase in the polysaccharide conductivity (Fig. 5). The data of Fig. 5 show that the temperature rising in all gel samples leads to conductivity growth, thus pointing out the ionic character of conductivity.

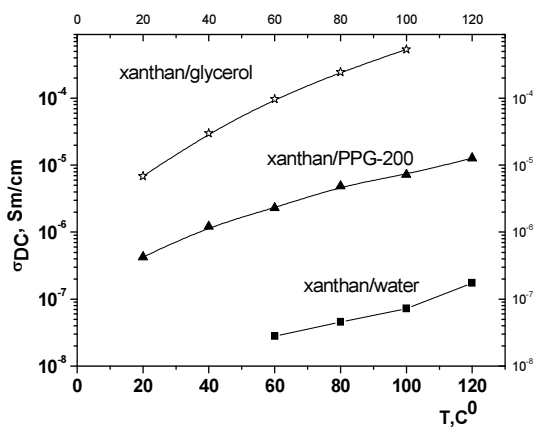


Fig. 5. The temperature dependence of σ_{DC} for all the samples.

The conductivity of gel samples increases in the row of plasticizers: water < PPG-200 < glycerol. This dependence does not correspond to the relaxation time data obtained for these samples. The higher values of σ_{DC} for xanthan/PPG-200 and xanthan/glycerol gels as compared to that for xanthan/water sample can be explained by additional contributions of plasticizer conductivity to the total conductivity of these samples.

Conclusions

In the frequency range $10\text{--}10^7$ Hz, xanthan and its gels demonstrated two relaxation processes: the β -relaxation and relaxation of gel fragments appeared due to xanthan/plasticizer interaction. At the same time, at high water content these processes could not be separated.

The relaxation time decreased in the series of plasticizers: PPG-200 > water >

glycerol; the segmental dynamics of xanthan grew respectively. Thus, glycerol showed the most prominent plasticizing effect among the compounds investigated.

The ionic-type conductivity was characteristic for all gel samples. The conductivity of gel samples increased in the following sequence: water < PPG-200 < glycerol. The highest conductivity ($\approx 10^{-3}$ Sm/cm) was fixed in xanthan/glycerol gel that corresponded to the most plasticizing effect of this compound among others.

References

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