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Interactions of anionic polysaccharides with carbon nanotubes

Summary — Agarose, ι-, κ-, and λ-carrageenans, and xanthan gum in aqueous solutions interacted with single-walled carbon nanotubes (SWCNTs) as proven by their wetting in solution and by the microRaman spectroscopy, rheological studies, and differential scanning calorimetry. The investigations provided evidence that the effect of complexation of polysaccharides was independent of the possibility of the formation of helical complexes. Complexation involved, to a certain extent, interactions between hydrophobic surface of nanotubes and hydrophobic sides of the saccharide units of polysaccharides. However, clathration of nanotubes in the polysaccharide matrices was also essential. Formation of the clathrate cages involved intra- and intermolecular hydrogen bonds within polysaccharides.

Key words: agarose, xanthan gum, carrageenans, single-walled carbon nanotubes, polysaccharide-carbon nanotubes, complexes.

ODDZIAŁYWANIA POLISACHARYDÓW ANIONOWYCH Z NANORURKAMI WĘGLOWYMI

Streszczenie — Agaroza, ι-, κ- i λ- karageny oraz guma ksantanowa (wzór I) w roztworze wodnym oddziałują z jednościennymi nanorurkami węglowymi, co potwierdzono analizując widma Ramana oraz wyniki badań reologicznych i skaningowej kalorymetrii różnicowej (tabela 1 i 2). Badania dostarczyły dowodów na to, że efekt kompleksowania polisacharydów nie zależy od możliwości otaczania nanorurek helisami polisacharydowymi. Kompleksowanie polega w pewnej mierze na oddziaływaniach między hydrofobową stroną merów polisacharydów (rys. 2), a hydrofobową powierzchnią nanorurek. Jednakże istotne jest też klatratowanie nanorurek w matrycy polisacharydowej. Klatki tworzą się dzięki zarówno wewnątrz- jak i międzycząsteczkowym oddziaływaniom polisacharydów za pośrednictwem wiązań wodorowych.

Słowa kluczowe: agaroza, guma ksantanowa, karageny, jednościenne nanorurki węglowe, kompleksy polisacharydów z nanorurkami węglowymi.

Complexation of single-walled carbon nanotubes (SWCNTs) with polysaccharides has attracted attention as a potential route to purification of SWCNT from graphite and amorphous carbon [1—5]. Effect of the complexation was observed as a wetting of SWCNT in aqueous polysaccharide solutions and formation of their suspensions from which non-complexed impurities would be either precipitated on the bottom or remained non-wetted. Enveloping of linear amylose around SWCNT to form helical complexes was proposed [1—3, 5] as the result of the complexation. Nature of the complexes of SWCNT with highly branched amylopectin remains unknown [4]. Certainly, the helical complexes could not be formed in the latter case. The formation of the SWCNT complexes with monosaccharides [6] shed light on the possible nature of such complexes. Saccharides, and likely polysaccharides, are oriented with their hydrophobic sides in respect to the hydrophobic surface of SWCNTs.

In our recent paper [7] complexes of four dextrans of molecular weight of 6000, 40 000, 100 000 and 2 000 000 with SWCNTs were characterized and their structures were simulated. The simulations showed that lower molecular weight dextran formed a cradle in which SWCNT was situated. It could not fully envelope SWCNT. Certainly, there was a competition between SWCNT — dextran intermolecular interactions and the dextran intramolecular interactions of the hydrogen bond character within dextran chain. Because the second type interactions dominated, terminals of the dextran chains looped on both sides of the cradle. Only the longest-chain dextran could envelop SWCNT but it took place mainly with involvement of hydrogen bonds formed within a dextran chain, however, with a weak intervention of the SWCNT — dextran chain interactions.

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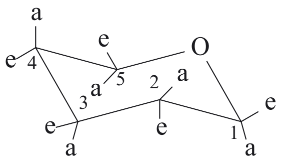
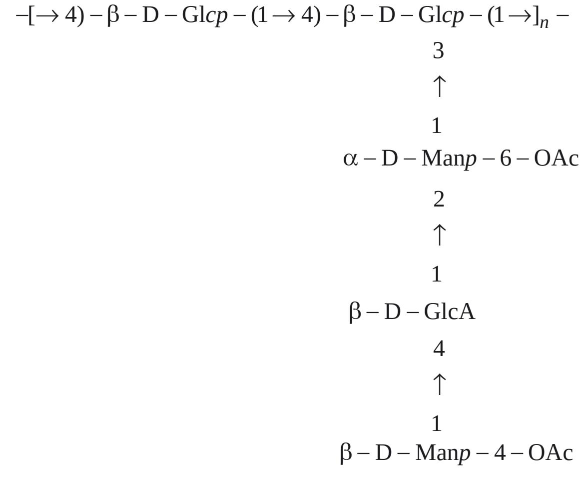


Monosaccharide	Abbreviation	1a	1e	2a	2e	3a	3e	4a	4e	5a	5e
β-D-Galactose	β-D-Gal*p*	H	OH	H	OH	H	OH	OH	H	H	$\mathrm{CH_2OH}$
α-D-Glucose	α-D-Glc*p*	OH	H	H	OH	H	OH	H	OH	H	$\mathrm{CH_2OH}$
β-D-Glucuronic acid	β-D-GlcA	OH	H	H	OH	H	OH	H	OH	H	COOH
α-D-Mannose	β-D-Man*p*	H	OH	OH	H	H	OH	OH	H	H	$\mathrm{CH_2OH}$

Fig. 1. Structures of monosaccharide units occurring in the polysaccharide molecules

In order to check the structural effects of polysaccharides on the formation of the complexes with carbon nanotubes, formation of complexes of the latter with agarose, xanthan gum and ι-, κ- and λ-carrageenans was attempted. Agarose is typically composed of linear agarose and branched agaropectin (up to 10 %) being the polymer of β-D-galactopyranose (Gal*p*). Structures of both polysaccharide components are irregular. The -[→4)-β-D-Gal*p*-(1→4)-β-D-Gal*p*-3,6-Anh-(1→]-$_n$ fragment, where β-D-Gal*p*-3,6-Anh is 3,6-anhydrogalactose unit, is the unit of agarose. Agaropectin is additionally esterified, approximately at every tenth unit, with pyruvic acid moieties. Formation of the agarose-SWCNT complex has been proven by microRaman spectroscopy, rheological tests and differential scanning calorimetry, the latter providing information about the stability of the complex. Xanthan gum is a branched polysaccharide with weak anionic properties as demonstrated by not too willingly formed complexes with proteins [8, 9]. Structure of xanthan gum is presented by formula (I), where Glc*p*, Man*p* and GlcA stand for glucopyranose, mannopyranose and glucuronic acid units, respectively.



$$\begin{array}{c} -[\to 4)-\beta-\mathrm{D}-\mathrm{Glc}p-(1\to 4)-\beta-\mathrm{D}-\mathrm{Glc}p-(1\to]_n- \\ 3 \\ \uparrow \\ 1 \\ \alpha-\mathrm{D}-\mathrm{Man}p-6-\mathrm{OAc} \\ 2 \\ \uparrow \\ 1 \\ \beta-\mathrm{D}-\mathrm{GlcA} \\ 4 \\ \uparrow \\ 1 \\ \beta-\mathrm{D}-\mathrm{Man}p-4-\mathrm{OAc} \end{array} \qquad (\mathrm{I})$$

In 40 % of the total, the originally acetylated 6-$\mathrm{CH_2OH}$ group is acylated with the pyruvic and acid residue instead acetylated. The pyruvic acid moiety cyclizes with the 4-OAcetyl (Ac) group into -6-$\mathrm{CH_2O}$-C(COOH)(Me)-O-4-.

Three carrageenans: ι {[→3)-β-D-Gal*p*(4-$\mathrm{SO_3K}$)-(1→4)-β-D-Gal*p*(2-$\mathrm{SO_3K}$)-(1→]$_n$}, κ {[→3)-β-D-Gal*p*(4-$\mathrm{SO_3K}$)-(1→4)-β-D-Gal*p*(3,6-Anh)-1→]$_n$}, and λ [→3)-β-D-Gal*p*(2,6-di-$\mathrm{SO_3K}$)-(1→4)-β-D-Gal*p*(2,6-di-$\mathrm{SO_3K}$)-1→]$_n$} are typical anionic algal gums with sulphate groups, neutralised preferably with potassium cation. Fig. 1 presents full structures of particular monosaccharide units occurring in the polysaccharide molecules and Fig. 2 shows location of the hydrophilic and hydrophobic sides of the monosaccharide units.

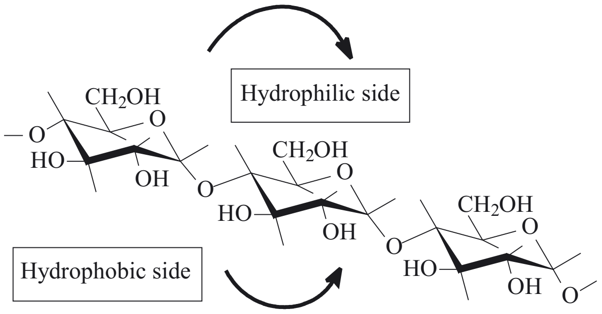


Fig. 2. Hydrophilic and hydrophobic sides of the saccharide pyranose units

The anionic $\mathrm{COO^-}$ and $\mathrm{SO_3^-}$ groups of xanthan gum and carrageenans, respectively, should cause repulsion of those saccharides from the hydrophobic SWCNT surface, perturbing their mutual, specific orientation required for the formation of complexes with involvement of van der Waals and dispersive interactions.

EXPERIMENTAL

Materials

Single-wall carbon nanotubes were purchased from Carbolex, Lexington, MI, USA. They were used as received.

Bacteriological agar (agar-agar) (12 % of humidity, 4 % of ash with Mg and Ca) was purchased from BTL Sp. z o.o. in Łódź, Poland (lot no. S-0001). Its power of gelation was 800—950 g/cm^2. Temperature of gelation was 35 °C, melting point above 85 °C. It was completely water soluble up to 2 wt. % concentration. The solution was neutral.

Carrageenans and xanthan gum were purchased from Sigma Co. St.Louis, Mo, USA, and used as received.

Formation of complexes

A polysaccharide (50 mg) was dissolved in deionized water (10 cm^3) and single-wall carbon nanotubes (10 mg) were added. Solution was agitated for 30 min at room temperature then allowed to stand for 24 hours, decanted from precipitated fraction and left for evaporation in vacuum desiccator.

Methods of testing

Raman spectroscopy

The spectra were recorded for solid samples resulting from evaporation (a steam bath) of solutions. Prior to the measurements, solid samples as well as pure polysaccharides were stored in a deep freeze. SWCNTs dispersed in water and isolated from that dispersion by evaporation to dryness served as controlled sample.

Jobin-Yvone LabRam System spectrophotometer equipped with a grating monochromator and a charge-coupled device Peltier-cooled detector (024x256) and comprising an Olympus BX40 confocal microscope was used. The incident laser excitation was provided by an air-cooled argon laser source operating at 514.4 nm with a power lower than 1 mW at the sample in 0 degree geometry. The spectra of the samples were recorded with a resolution of 4 cm^{-1} in the range of 100—3600 cm^{-1} of the Raman shifts. Before the measurements, a routine calibration of the monochromator was carried out using Si wafer and employing the Raman scattering line at 520.7 cm^{-1}. Average of 10 runs is discussed.

Rheology

Rheological measurements at 20±0.5 °C were carried out for solution of a polysaccharide (50 mg) in water (10 cm^3) (control samples) and for those solutions to which SWCNT (5 mg) were admixed. The computerized Zim rotary viscometer of own construction [10] was used. Measurements were repeated five times.

Differential Scanning Calorimetry

The solutions prepared for rheological measurements were evaporated to dryness by storage over P$_2$O$_5$ in a vacuum dessicator. Differential scanning calorimetry measurements with 5 K/min rate of the temperature increase were carried out in sealed capsules containing a sample of a complex (approximately 1 mg) and water (3 mg) using the STA 409C Netzsch (Seib, Germany) apparatus. Measurements were repeated three times.

RESULTS AND DISCUSSION

After introducing SWCNTs into an aqueous solution of agarose, a suspension was formed. Thus, hydrophobic SWCNTs were wetted, and formation of their complexes with agarose was responsible for it. The behavior resembled that noted in case of amylose [3], amylopectin [5], monosaccharides [6], and dextrans [7].

In our former study [7], an increase in viscosity of dextrans was noted after admixture of SWCNTs to the dextran solutions. Such increase by 0.07 to 0.14 mPa · s suggested certain ordering of the solution structure due to complexation. Similar measurement in case of the admixture of SWCNTs to agarose provided hardly 0.022 mPa · s but statistically significant increase in viscosity by 2.2 % (Table 1). It could result from the certain ordering in solution complexation of SWCNT chiefly with linear, non-ionic agarose, as it could be likely assuming that agarose and agaropectin could be mutually incompatible in solution, similarly as were linear amylose and branched amylopectin [11—13].

Table 1. Selected properties of agarose, single wall carbon nanotubes (SWCNT) and agarose-SWCNT complex

Method and property	Agarose	SWCNT	Agarose--SWCNT complex
Rheology:			
viscosity, cPa	1.118±0.005	—	1.140±0.01
Raman spectroscopy:	—		
band position[a], cm^{-1}			
breathing mode		146.0	148.5; 164.3
D		1337.9	1337.9
G$_1$		1557.6	1565.4
G		1580.8	1589.4
D+G		2661.8	2706.4
DSC[b]			
t_o, °C	103.7		101.1
t_p, °C	119.3		130.3
ΔH, J/g	56.0		33.3

[a] The D, G and G$_1$ bands are those called diamond and graphite bands in the spectrum of SWCNTs; they appear in the spectra of pure diamond and graphite, respectively.

[b] t_o and t_p denote onset and peak temperatures, respectively.

A shift of the peaks in the Raman spectrum (Fig. 3, Table 1) of SWCNTs was another evidence of the complexation.

Plain agarose did not provide any clear peak in the region of 60—4000 cm^{-1}. Direction of the shifts of the D (diamond), G (graphite), and combinatory D+G peaks when comparing with SWCNT and SWCNT-agarose system, was substantially the same as noted in case of

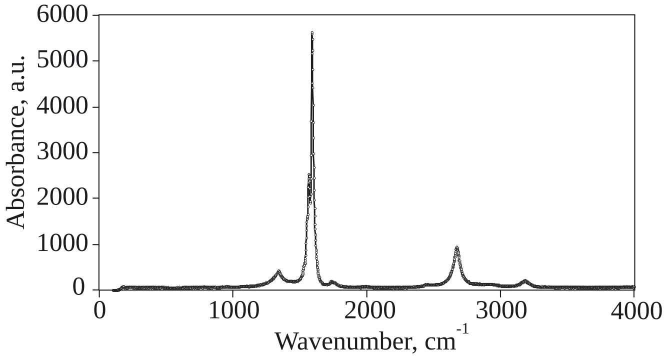


Fig. 3. The Raman spectrum of original single-wall carbon nanotube (SWCNT)

complexes of SWCNTs with amylose [3], amylopectin [4], dextrans [7], and monosaccharides [6]. In case of amylose [3], the complexation caused the shifts of the D, G and D+G bands by 7—13 cm^{-1}, 10—13 cm^{-1}, and approximately 20 cm^{-1}, respectively. In case of amylopectins [4], the shifts of the D and G bands reached 2—4 and 4—8 cm^{-1}, respectively. The shifts of those bands in the spectra of dextran — SWCNT complexes were 2—9 (D band), 8—12 (G band) and 11—16 cm^{-1} (D+G band), respectively, and they were independent on molecular weight of dextran [7]. Thus, one could conclude that vibrations of the SWCNT skeleton were perturbed by the complexation of agarose to a similar extent as in amylopectin. A slightly dependent on the molecular weight of polysaccharide, shift of the spectral bands could be taken as an argument against enveloping of SWCNT with involvement of the SWCNT — polysaccharide interactions. Interaction between the hydrophobic surface of SWCNT and hydrophobic side of β-D-galactose units of agarose could be a driving force of complexation. It could be followed by developing clathrate of a suitable volume of their cavity in order to arrest SWCNT inside it. The formation of the clathrate cages involved intra- and intermolecular hydrogen bonds within polysaccharide. Such possibility was demonstrated in case of dextrans [7].

Experimental (DSC) enthalpies of melting (ΔH) of the complexes with dextrans were between 1.1 and 30 J/g for the lowest and the highest molecular weight dextran, respectively, whereas such enthalpy values for the complexes of SWCNT with potato or maize amylopectin were 4.2 and 57 J/g, respectively [3]. Such measurements in case of agarose — SWCNT complexes provided a value of 33.3 J/g (Table 1). Based on these considerations, one could conclude that melting enthalpy of complexes was controlled by the polysaccharide molecular weight, that is, by the number of potential complexation centres and the clathrate formation possibility.

In spite of anionic character of xanthan gum and carrageenans, wetting of SWCNT in aqueous solutions of those polysaccharides was observed, pointing to interactions between them and SWCNTs. This fact was confirmed by shifts of the band positions in the microRaman spectra (Table 2). In contrast to the agarose solutions, the solutions of three carrageenans and xanthan gum became less viscous after admixture of SWCNT (Table 2). The decrease in the viscosity was by 14.6, 15.4, and 8.8 %

Table 2. Selected properties of solutions of carrageenans and xanthan gum prior and after admixture of SWCNT and complexes of those polysaccharides with SWCNT

Method and property	Carrageenan						Xanthan gum	
	ι-		κ-		λ-			
	free	with SWCNT	free	with SWCNT	free	with SWCNT	free	with SWCNT
Rheology: viscosity, cPa	2.33±0.02	1.89±0.03	2.34±0.03	1.98±0.03	2.35±0.02	2.16±0.03	1.81±0.02	1.66±0.02
Raman spectroscopy$^{a)}$: band positions, cm^{-1}								
SWCNT breathing mode		148, 162 —, 166		148, 162 148, 164		157, 173 152, 173		157, 166 —, 166
D		1335 1331		1338 1338		1345 1341		1341 1344
G1		1558 1567		— 1567		1567 1574		1574 —
G		1582 1589		1585 1589		1592 1594		1591 1592
D + G		2662 2672		2662 2666		2684 2674		2673 2684
DSC:								
t_o, °C	105.4—117.4	110.9—111.6	121.1—122.4	111.6—134.1	121.1—127.0	116.6—120.6	122.4—127.9	96.2—114.7
t_p, °C	138.4—139.9	139.6—149.0	139.6—143.1	139.0—149.2	132.1—132.5	142.3—143.7	134.8—137.9	108.2—130.2
ΔH, J/g	59.9—73.6	49.6—74.1	12.0—15.9	4.9—10.3	6.0—11.9	54.1—62.5	11.9—22.8	10.9—14.0

a) See Table 1 for positions of the peaks in the Raman spectrum of original SWCNTs. Data from duplicated measurements are quoted.

in case of ι-, κ- and λ- carrageenans, and by 8.3 % in case of xanthan gum. The differences in the sensitivity of the viscosity to the perturbations caused by admixture of SWCNT should be related to the stability of the polysaccharide networks in aqueous solutions and not to the original viscosity of the solutions. Anyway, in spite of the anionic character of those polysaccharides, there were SWCNT-polysaccharide interactions which obscured the ordering in the macrostructure polysaccharide — polysaccharide interactions. SWCNTs attached by weak interactions to hydrophobic sites of selected monosaccharide units influenced the formation of regular polysaccharide network in solution. Dimensions of polysaccharide cages arresting SWCNTs and, hence, interactions between SWCNT and polysaccharides could vary depending, among others, on size of SWCNTs. That could be a likely reason for observed wide diversity of magnitudes of the parameters recorded (Table 2). Analyses of the Raman spectral data suggested that some nanotubes, particularly with ι- and κ-carrageenans might be left non-complexed. Corresponding band shifts did not exceed 4 cm^{-1} that is, they remained constant within the 4 cm^{-1} precision of that estimation.

However, the shifts of the bands in Raman spectra of SWCNT complexes with non-gelatinizing λ-carrageenan and xanthan gum were remarkable. It suggested that in the case of ι- and κ-carrageenans, the energy of the SWCNT — carrageenan interactions and gel network forming interactions were comparable whereas in case of λ-carrageenan and xanthan gum the SWCNT-polysaccharide interactions predominated.

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