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Single-walled carbon nanotube–amylopectin complexes

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Abstract

Single-walled carbon nanotubes (SWCNTs) are wetted in aqueous solution of pure potato and waxy corn amylopectins. Formation of weak sorption complexes of amylopectins on carbon nanotubes is postulated based on the micro-Raman spectra, differential scanning calorimetric and thermogravimetric studies as well as scanning electron micrographs and atomic force microscope images. Under an influence of ultrasounds bundles of SWCNTs disintegrated much more readily in aqueous solution of waxy corn amylopectin. In the solid state resulting from evaporation of suspensions to dryness interactions of SWCNTs with waxy corn amylopectin were also stronger than with potato amylopectin.

Keywords: Carbon nanotubes; Nanotechnology; Polysaccharides; Potato amylopectin; Waxy corn amylopectin

1. Introduction

Amylopectin is a branched polymer composed of $1 \rightarrow 4'$ linked α-D-glucose units with branches of similarly built but shorter chains linked to the main chain with $1' \rightarrow 6$ bonds. In waxy corn as well as potato amylopectins branching occurs in every 8–12 glucose units. The outer branches consist of 8–12 glucose units. Red staining of amylopectin in reaction with I_2–KI reagent shows that such short-terminal branches of amylopectin can coil around stick of either I_2 or I_3^- ion (Mould, 1954) and energy of binding is low (Mikus, Hixon, & Rundle, 1946). Potato amylopectin distinguishes from waxy corn amylopectin with phosphoric acid moieties, which esterifies every 12–200 glucose unit at the 6-CH_2OH group (Swanson, 1948).

Single-walled carbon nanotubes (SWCNTs) are tubular forms of elemental carbon of 0.4–2.5 nm in diameter. The sp^2-hybridised carbon atoms in the walls have hexagonal arrangement. Therefore, structure of nanotubes may be considered as a sheet of graphene (a single layer of graphite) folded into a tube. Surface and channel of SWCNTs are non-polar, hydrophobic. Therefore, SWCNTs are not wetted by water and do not form aqueous suspensions (Przygocki & Włochowicz, 2001; Saito, Dresselhaus, & Dresselhaus, 1998)

In our former paper (Lii, Stobinski, Tomasik, & Liao, 2002) wetting of SWCNT in aqueous solutions of potato amylose was demonstrated. A coiling of amylose chain around SWCNTs was shown. The complexation was suggested useful in separation of SWCNTS from impurities usually accompanying them and even their segregation into fractions distinguishing from one another in size of complexed SWCNT. In this paper, behaviour of SWCNTs in aqueous solutions of potato and waxy corn amylopectins is described.

2. Materials and methods

2.1. Materials

Potato amylopectin was purchased from Sigma Saint Louis, MO. Waxy corn amylopectin was isolated from waxy

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corn starch by means of complexation or residual amylose with cyclohexane following procedure of Takeda and Hizukuri (1987). SWCNTs, SE (selected grade) of the size varying between 1.2 and 1.5 nm with average size of approximately 1.3 nm were manufactured by CarboLex, Inc., University of Kentucky, Lexington.

2.2. Complex formation

Aqueous solution of any amylopectin (10 mg in 5 ml of re-distilled water) was blended with about 0.5 mg of the SWCNTs. Suspensions were 30 min sonicated (Bransonic Ultrasonic Cleaner 5210R-DT, Branson Ultrasonic Corp., Danbury, CT). Resulting suspensions did not separate on standing. Flocculation in suspension could be observed after about 2 days of storage of these suspensions. Only heavier particles separated whereas small particles resided suspended for over 2 weeks. Thus, the suspensions were transferred to the small polyethylene containers and left for drying in a drybox. Dry samples were subjected to the following tests.

2.3. Micro-Raman spectroscopy

A Dilor XY 800 (Lille, France) instrument was used. All Raman spectra were taken at room temperature using 514.5 nm incident photons from a Ar^+ ion laser (Spectra Physics Model 2017). The linearly polarised light was focused on the sample through an 100 × optical microscope objective (0.95 NA) with a spatial resolution of <2 μm in a backscattering geometry. Several locations of each sample were probed to ensure reproducibility of the data. The laser power used was less than 1.5 mW. The possible effect of local heating was checked by varying the excitation power and no appreciable change in the Raman spectra was observed for powers up to $\sim$5 mW. The scattered light without polarisation analysis was collected and dispersed using a Dilor XY 800 triple spectrometer equipped with 1800 grooves/mm gratings and a liquid-nitrogen cooled 1024 pixel wide charge-coupled detector (Jobin Yvon Model Spectrum One). The spectral resolution with these instruments was typically better than 1 cm^{-1}. The model of optical microscope is BH-2, manufactured by the Olympus Company.

2.4. Optical microscopy

Optical microscope with Olympus Vanox (Melville, NY) AHMT 3 was applied.

2.5. Scanning electron microscopy

Scanning electron microscope (SEM) with Field Emission Scanning Electron Microscope HITACHI S-4200 (Hitachi Instruments, Inc., San Jose, CA) was used.

2.6. Atomic force microscopy

An atomic force microscope (AFM) with Digital Instrument Vecco Metrology Group (Santa Barbara, CA) Dimension TM 3100 was used. Observations were performed using silicon wafer as a substrate.

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using an Du Pont 910 DSC System (Willmington, DE) with scanning from 20 to 200 °C at 10°/min. Samples were analysed either in solid state or $\sim$10 mg samples were placed in 30 mg of water and sealed in pans.

2.8. Thermogravimetry and differential thermogravimetry

Du Pont Instrument 951 Thermogravimetric Analyser (Willmington, DE) was used. Analysis was performed with scanning from 20 to 400 °C at 10°/min. Analyses were performed for commercial SWCNT and for those after conditioning in water followed by drying in a drybox. Potato and waxy corn amylopectins were analysed as delivered and for their films formed on evaporation of their aqueous solutions. Complexes were analysed after evaporation and drying in a drybox.

3. Results and discussion

After blending aqueous solutions of either potato or waxy corn amylopectins with SWCNTs and sonication a grey–black suspension was formed. Disintegration of SWCNT proceeded more readily in solution of waxy corn amylopectin. Storage of suspensions for few days resulted in flocculation of heavier particles (larger size) of SWCNTs on the bottom of containers but lighter (smaller) SWCNTs remained in solution. Wetting of nanotubes in solution of surfactants (Ebbesen, 1996) and aqueous solution of amylose (Lii et al., 2002) is known and both amylopectins could act in such case as surfactants. Colloidal and crystalline graphite, being a contamination of applied SWCNT, readily precipitated from solution of amylose (Lii et al., 2002) but such fast fractionation could not be observed in solutions of potato and waxy corn amylopectins. It is commonly known (Greenwood, 1956) that solutions of amylopectin are less viscous than solutions of amylose of comparable concentration. Thus, lack of fast fractionation of SWCNTs and formerly mentioned differences in disintegration of SWCNTs in both amylopectins might be linked to their branched structure and molecular weight as involved factors. Among others, particles of SWCNT and graphite could be trapped between branches of amylopectins. It is well known (see for instance Mazurkiewicz (1997a–c)) that α-D-glucose has two regions distinguishing from one another in their hydrophilicity/hydrophobicity. α-D-Glucose

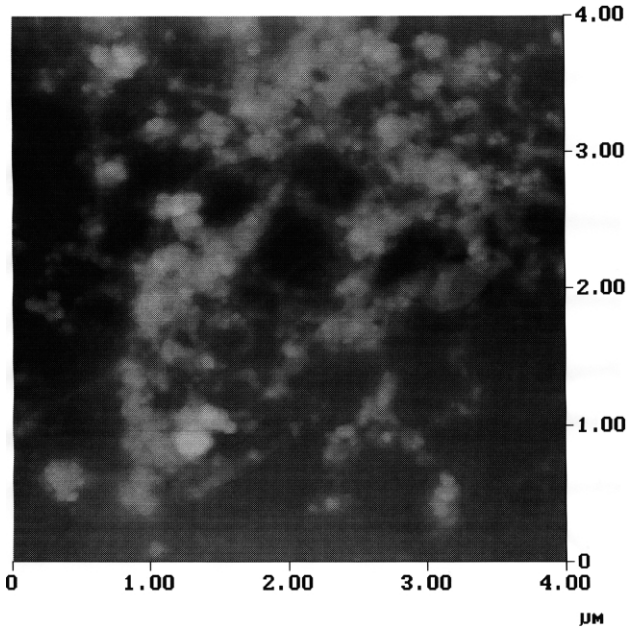

Fig. 1. The AFM image of the waxy corn amylopectin–SWCNT film after evaporation of the aqueous suspension.

units of amylopectin chains oriented in respect to the SWCNTs surface with their hydrophobic side could engage van der Waals and dispersion forces to held the carbon species by a weak complexation. It could be a main factor holding SWCNTs and graphite suspended in solutions of potato and waxy corn amylopectins.

Optical and scanning electron micrograms of dried blends of both amylopectins with SWCNTs presented folded black films of amylopectins with included carbon species forming irregular in their form islands. No specific organisation of folds and hills containing SWCNTs inside could be observed. Also AFM images of dried films did not show anything more than lack of any organisation (e.g. randomly distributed hills with a maximum roughness of the 250 nm) (Fig. 1).

One could notice that SWCNTs did not initiate crystallisation of amylopectins by nucleation. Assumption that amylopectins could form sorption complexes with SWCNTs found its support in results from the Raman spectroscopy. Table 1 presents results of this investigation.

Both pure thin dried films of amylopectins did not exhibit any vibration in the region of 110–220 cm^{-1} where breathing modes of SWCNT were observed nor in the region of 1300–1600 cm^{-1} where D- and G-bands appeared, respectively. There was only a very flat, broad band around 950 cm^{-1} which could be tentatively assigned to glucose unit C–C stretching modes based on such assignment for the doublet at 943.6–956.3 in the Raman spectrum of amylose (Phillips, Corke, Jie, Liu, & Chong, 1998) to glucose unit C–C stretching modes. The band at 1657 cm^{-1} found by Phillips et al. (1998), Phillips, Jie, Chong, Liu, and Corke (1999a) and Phillips, Jie, Liu, Pan, and Corke (1999b) in the Raman spectrum of amylose remained invisible in our spectra because they could overlap with side bands of the G_2-band of SWCNT.

Interaction of both amylopectins with SWCNTs produced always anti-Stokes–Raman scattering with summation of molecular vibrational transition frequency (MVTF) and original energy of scattering photon. The MVTF term and its contribution to the ω_D modes could not be distinguished whereas for ω_G modes they did not exceed $+6.5$ cm^{-1} for potato amylopectin and $+2.5$ cm^{-1} for waxy corn amylopectin for G_2-band and $+8$ and $+4$ cm^{-1} for G_1-band, respectively. Corresponding shifts of the bands in the spectrum of SWCNT with potato amylose (Lii et al., 2002) were approximately twice as high as these reported above. The shifts of vibrational modes due to interaction with amylopectins reflected changes in vibration symmetry from E_{1g} (1585 cm^{-1}) and A_{1g} (1587 cm^{-1}) into E_{2g}

Table 1
Positions of selected modes (ν in cm^{-1}) in Raman spectra of SWCNT and their complexes with potato and corn amylopectins

Species and sample number	Breathing modes			Type of mode (cm^{-1})		
				Diamond (ω_D)	Graphite I (ω_{G1})	Graphite II (ω_{G2})
SWCNTs						
1	148.85	163.6	170.7	1342.03	1564.26	1589.16
2				1347.52	1562.79	1587.77
Potato amylopectin–SWCNTs						
1	148.85	161.7	170.7	1344.78	1568.78	1592.90
2				1346.76	1572.39	1595.10
3				1343.31	1572.39	1595.10
4				1345.87	1570.76	1595.64
5				1346.42	1570.22	1595.10
6				1345.33	1572.93	1594.56
Waxy corn amylopectin–SWCNTs						
1	150.13	163.0	–	1344.76	1566.51	1590.96
2				1345.87	1567.58	1590.43
3				1347.52	1568.12	1591.49

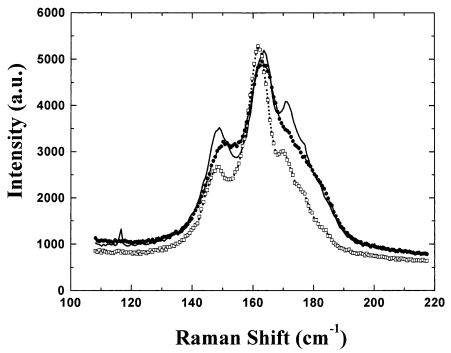

Fig. 2. The Raman spectra of SWCNTs and their complexes with amylopectins in the breathing mode region (110–220 cm^{-1}). Solid line, SWCNTs; solid points, SWCNTS with waxy corn amylopectin; open points, SWCNTs with potato amylopectin.

(1591 cm^{-1}) (Saito et al., 1998). Such relatively weak effects could be rationalised in terms of sorption of amylopectins on SWCNT without coiling, the latter postulated (Lii et al., 2002) in case of amylose. Analysis of effect of amylopectins on the breathing modes of SWCNT confirms SWCNT–amyloses interactions. The interaction with potato amylopectin shifts original absorption band of SWCNT by 1.9 cm^{-1} to lower wavenumber. The effect of interaction of SWCNT with waxy corn amylopectin is reflected by changes in the pattern of side bands. The main band shifted down by 0.9 cm^{-1} and broadened, and the left side band ceased (Fig. 2).

The Raman spectral pattern of the ~1590 cm^{-1} band closely resembled that published, among others, by the Dresselhaus et al. (Jorio et al., 2001). Thus, this band is preceded by another weaker band at 1562.8–1564.3 cm^{-1}. The ratio of the intensities of the long- and short-wavelength bands in this doublet, respectively, in the spectra of SWCNTs varied between 2.22 and 2.36. We recorded several spectra in which this ratio was between 1.71 and 2.11. However, we recorded also some spectra in which this ratio was between 2.22 and 2.55. This effect remains poorly understood.

Formation of complexes of both amylopectins with SWCNTs could be additionally proven by DSC measurements. Results of this study are collected in Table 2.

DSC studies showed that in the solid state as well as in aqueous solution potato amylopectin was more stable than waxy corn amylopectin. All initial temperature, T_o and peak temperature, T_p, for potato amylopectin were higher than for waxy corn amylopectin and enthalpy changes for processes of potato amylopectin were lower than these for waxy corn amylopectin. It could be accounted for differences in molecular weight of both amylopectins and the phosphato group in potato amylopectin, which could stabilise the structure with inter- and intra-molecular hydrogen bonds. Evaporation of aqueous suspension of SWNT in potato amylopectin gave a product DSC analysis of which showed lower T_o and T_p measured in the solid state and in water whereas enthalpy change of corresponding processes remained practically unchanged. In contrast to it, the product of evaporation of SWCNTs suspension in aqueous solution in waxy corn amylopectin had practically unchanged T_o but T_p as well as enthalpy changes of the processes were higher from these of the complex with potato amylopectin. One might suggest that potato amylopectin either did not form complexes with SWCNTs at all or a stabilisation of the product by means of SWCNT interactions with hydrophobic sites of D-glucose units of potato amylopectin was reduced by cancellation of the hydrogen bonds with involvement of the phosphato group.

Fig. 3 presents thermogram of the product of evaporation of the complex of way corn amylopectin with SWCNTs. This diagram resembled very closely that for analogously prepared complex of potato amylopectin with SWCNTs. The sole difference between them was in the DTG peak temperature of the amylopectin decomposition. It was 309.7 °C in the first case and 305.8 °C in the second. The TG line in both diagrams was practically identical what meant that the path of decomposition of both complexes was the same although they were not identical for both amylopectin films. Both diagrams consisted of three DTG peaks. The first peak was assigned to evaporation of water, the second peak corresponded to decomposition of amylopectin and the third peak around 460 °C could reflect degassing of SWCNTs. Thermogram of SWCNTs exhibited a DTG maximum within this temperature region.

Decrease in the decomposition temperature of waxy corn

Table 2
DSC studies of amylopectins and their complexes with SWCNT

Species	Solid state			In water		
	Temperatures (°C)		Enthalpy ($-\Delta H$) (kJ/g)	Temperatures (°C)		Enthalpy ($-\Delta H$) (kJ/g)
	Onset (T_o)	Peak (T_p)		Onset (T_o)	Peak (T_p)	
Potato amylopectin						
Original	67.1 ± 3.0	119.7 ± 9.7	229.5 ± 5.1	105.9 ± 1.9	115.9 ± 2.7	1517.5 ± 35.5
With SWCNT	54.8 ± 7.4	103.0 ± 3.8	230.9 ± 1.6	101.7 ± 0.9	111.5 ± 0.8	1521.7 ± 46.3
Waxy corn amylopectin						
Original	49.4 ± 1.1	88.9 ± 4.2	114.8 ± 6.7	100.9 ± 1.0	106.2 ± 0.4	1450.5 ± 104.5
With SWCNT	50.4 ± 0.4	100.2 ± 3.1	238.0 ± 4.4	101.4 ± 1.7	109.9 ± 5.1	1507.3 ± 30.7

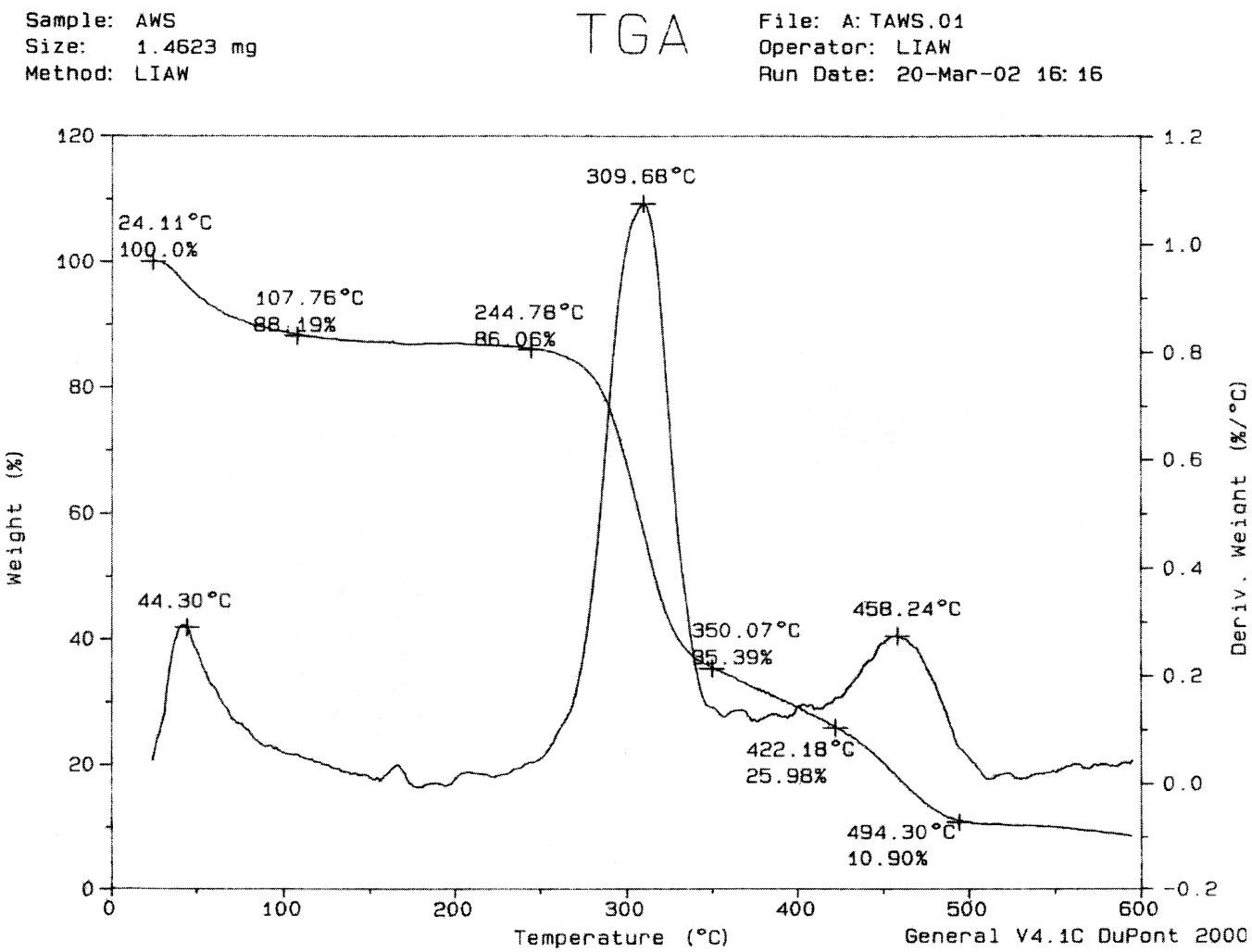

Fig. 3. The thermogram (TGA/DTGA) of the waxy corn amylopectin–SWCNTs complex.

amylopectin after complexation with SWCNTs reached 10.6 °C. This difference could not be accounted for effect of the waxy corn amylopectin structure breaking on its dissolution in water because this procedure rose this temperature by 4.6 °C (Table 3).

However, dissolution of commercial potato amylopectin in water decreased its decomposition temperature by 5.1 °C. Compounding of potato amylopectin with SWCNTs produced further decrease of the decomposition temperature by 4.3 °C. Observed decrease in the decomposition temperature of amylopectins with SWCNTs could be interpreted as changes in the macrostructure of both amylopectins. They were caused by cancellation of certain intra- and inter-molecular hydrogen bonds induced by

Table 3
TGA and DTGA of amylopectins, SWCNTs and their complexes

Sample	TGA water content (%)	DTGA peak temperature (°C)	
		Decomposition of amylopectin	Degassing of SWCNTs
Potato amylopectin			
Commercial	14.9	315.2	
Evaporated from H_2O	11.5	310.1	
With SWCNTs	14.7	305.8	458
Waxy corn amylopectin			
As isolated	17.6	315.7	
Evaporated from H_2O	10.6	320.3	
With SWCNTs	14.0	309.7	465

attempts of such orientation of polysaccharide chains in respect to surfaces of SWCNTs in order to produce the most numerous and efficient mutual hydrophobic interactions. Results from thermal and calorimetric analyses did not fit results from the Raman spectroscopy which indicated stronger band shifts for the potato amylopectin–SWCNTs complexes. It is likely, that potato amylopectin being a salt of amylopectin phosphate ester in aqueous solution was a source of metal cations, which could fill SWCNTs and the species interacting with SWCNTs was polyanion of potato amylopectin. Complexes of SWCNTs with inorganic metal salts have been described in the literature (Ugarte, Stockli, Bonard, Chatelain, & de Heer, 1998; Wilson, 2002) but, thus far, decoration of SWCNTs with metal cations has never been described in the literature.

4. Conclusion

SWCNTs are wetted in aqueous solutions of amylopectins because there are interactions between hydrophobic surface of SWCNTs and hydrophobic sites α-D-glucose units of amylopectins. Interactions with waxy corn amylopectin are stronger than with potato amylopectin. The latter might interact with SWCNT by their decoration with cations originating from dissociation of the phosphato groups.

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