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## Dextran complexes with single-walled carbon nanotubes

**Summary** — Formation of surface and inclusion complexes of single-walled carbon nanotubes (SWCNT) with dextrans of  $M_w$  6000 to 2 000 000 was proven spectrally, rheologically, and calorimetrically. Band shifts in the Raman spectra, increase in the viscosity of aqueous solutions of particular dextrans after admixture of SWCNT, and enthalpies of melting of those complexes were independent on molecular weight of dextrans. Computational simulations were performed using the HyperChem 7 and Gaussian 03 packages, starting from a model of single, short SWCNT and linear dextran chain made of 12, 18 or 24  $\beta$ -D-glucose units. The simulation indicated that dextran chains composed of 12 or 18  $\beta$ -D-glucose units only partly enveloped SWCNT and the intermolecular interactions in both terminals of the chains prevailed. The dextran containing 24  $\beta$ -D-glucose units fully enveloped SWCNT. However, the role of SWCNT in the envelop formation was limited solely to its hydrophobic interactions with the central part of the dextran chain.

**Key words:** dextrans, carbon nanotubes, complexation, molecular dynamic.

### KOMPLEKSY DEKSTRANÓW Z JEDNOŚCIENNYMI NANORURKAMI WĘGLOWYMI

**Streszczenie** — Metodą spektroskopii Ramana (rys. 1, tabela 1), oraz na podstawie wyników badań reologicznych (tabela 2) i kalorymetrycznych (DSC, tabela 3) potwierdzono powstawanie kompleksów dekstranów o ciężarze cząsteczkowym ( $M_w$ ) z przedziału 6000—2 000 000 z jednościeniowymi nanorurkami węglowymi (SWCNT). Przesunięcia pasm w widmach Ramana, wzrost lepkości wodnych roztworów dekstranów po dodaniu SWCNT oraz wartości entalpii topnienia powstających kompleksów nie zależały od ciężaru cząsteczkowego użytego dekstranu. W odniesieniu do modelowych, krótkich nanorurek węglowych i liniowych dekstranów zbudowanych z 12, 18 lub 24 jednostek  $\beta$ -D-glukozowych wykonano komputerowe symulacje posługując się programami HyperChem 7 i Gaussian 03 (rys. 2—4). Stwierdzono, że dwa pierwsze dekstrany tylko częściowo otaczają nanorurkę, natomiast ich końce zawierają się w wyniku oddziaływań wewnątrzcząsteczkowych o charakterze wiązań wodorowych. Dopiero najdłuższy dekstran całkowicie owija nanorurkę, ale jej udział w tworzeniu otoczki sprowadza się jedynie do hydrofobowych oddziaływań ze środkową częścią łańcucha dekstranu.

**Słowa kluczowe:** dekstrany, nanorurki węglowe, kompleksowanie, dynamika molekularna.

Recently, dissolution of carbon nanotubes (CNT) in aqueous solutions after enveloping them with polysaccharide molecules was reported [1—6]. These molecules coiled around CNT orienting towards the CNT surface with their hydrophobic sides and exposing their hydrophilic sides to the environment. These phenomena have been considered solely on the qualitative basis, that is, they have been related neither to the shape nor size of the enveloping polysaccharide. It has also been shown

[7] that monosaccharides adhered to the surface of single-wall carbon nanotubes (SWCNT) forming weak complexes. This observation might suggest a chance for preparation of SWCNT complexes with dextrans and linking their selected properties with molecular weights of those oligosaccharides.

Thus, in our present work complexes of dextrans of different molecular weight ( $M_w$  from 6000 to 2 000 000) were prepared. The complex formation was proven spectrally, rheologically, and calorimetrically by means of the Raman spectroscopy, rotary viscometry, and differential scanning calorimetry (DSC), respectively.

### EXPERIMENTAL PART

#### Materials

Single-wall carbon nanotubes (as prepared, Carboxex, Lexington, MI, USA), and dextrans of  $M_w$  6000, 40 000, 100 000 and 2 000 000, all chemical grade, were pur-

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chased from Sigma-Poland in Poznań and used as received.

### Preparation of complexes

Dextran (50 mg) was dissolved in deionised water (10 cm<sup>3</sup>) and single-wall carbon nanotubes (10 mg) were added. Solution was agitated or sonicated in an ultrasound bath for 30 min, then allowed to stand for 24 h, decanted from precipitated graphite and left for evaporation in vacuum desiccator.

### Methods of testing

#### Rheological measurements

Rheological measurements were carried out for solutions of dextran (500 mg) in water (10 cm<sup>3</sup>) (control samples) and for those solutions to which SWCNT (5 mg) were admixed. The computerized Zim rotary viscometer of own construction [8] was used. The measurements were repeated five times.

#### Differential scanning calorimetry

The solutions prepared previously for rheological measurements were evaporated to dryness by storage in vacuum desiccator. Differential scanning calorimetry (DSC) measurements were carried out in sealed capsules containing a sample of a noncomplexed dextran or a complex (approximately 1 mg) and water (3 mg) by using STA 409C Netzsch (Seib, Germany) apparatus. The measurements were repeated three times.

#### Micro-Raman spectroscopy

Jobin-Yvon LabRam System spectrophotometer equipped with a grating monochromator and a charge-coupled device Peltier-cooled detector (024x256) and 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 1 cm<sup>-1</sup> in the range of 100–3600 cm<sup>-1</sup> 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<sup>-1</sup>. The spectra were taken for five different samples of each particular complex.

### Computations

Computational simulations began from the HyperChem 7 approach for a preliminary SWCNT, dextrans and SWCNT-dextran complexes optimization (Molecular Mechanics, MM) Amber 94 for dextrans, MM+ for SWCNT and SWCNT-dextrans complexes reaching the global energy minima with the manual orientation of molecules. Additional selection of the Molecular Dy-

namics (MD) (Hyper Chem 7.0) at 300 K (run time 1 ps, step size 0.001 ps) approach provided an optimum energy for each system under consideration. Zigzag, open-end SWCNT (12,0) with diameter of 0.93 nm and length of 1.55 nm was composed of 192 carbon atoms and 24 hydrogen at the CNT edges. Dextran molecules consisted of 12, 18 or 24 β-D-glucose units linearly bound by 1 → 6 glycosidic bonds. Their stoichiometry was C<sub>72</sub>H<sub>122</sub>O<sub>61</sub>, C<sub>108</sub>H<sub>182</sub>O<sub>91</sub> and C<sub>144</sub>H<sub>242</sub>O<sub>121</sub>, respectively. This procedure was followed by further computations with the Gaussian 03 package (MM UFF method). In such manner the optimization energy of the system was found. A PC IV with double CPU (2.4 GHz) motherboard, 2 GB RAM and 120 GB HDD was used.

## RESULTS AND DISCUSSION

Single-wall carbon nanotubes were wetted in aqueous solutions of dextrans of different  $M_w$  values. Formation of the complexes was proven, among others, with Raman spectra.

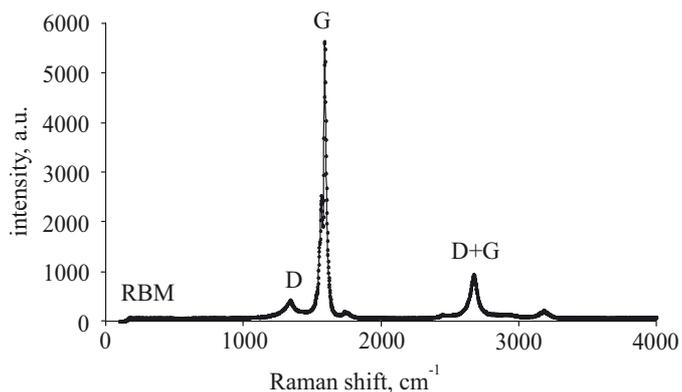


Fig. 1. Raman spectrum of as prepared SWCNT

In the Raman spectrum of non-complexed SWCNT (Fig. 1) particular bands were located at around 146 cm<sup>-1</sup> (RBM — radial breathing mode), 1338 cm<sup>-1</sup> (D band), around 1557 and at 1581.5 cm<sup>-1</sup> (G band), and 2662.5 cm<sup>-1</sup> (D + G band). In the spectra of the SWCNT-dextran complexes (Table 1) the Raman shifts were as follows: bands moved by 1 to 6 (D band), 9 to 10 (G band), and 10 to 17 (G + D band) cm<sup>-1</sup> to the higher wavenumbers, respectively. The magnitude of the shift was independent of molecular weight of dextran. Simultaneously, the RBM modes of the complexes with dextrans of  $M_w = 100\ 000$  and  $2\ 000\ 000$  caused indicating possible tight enveloping of SWCNT.

Rheological measurements revealed statistically significant increase in viscosity of aqueous dextran solutions after admixture of SWCNT (Table 2). This direction in changes reflected better ordering of the structure of solutions, possibly due to enveloping of SWCNT with dextrans oriented to the SWCNT surface with their hy-

drophobic sites. In this manner the hydroxyl groups of particular units of dextran were to a higher extent exposed to the water molecules. That ordering resulted in ordering in the bulk of solution. Again, increments of the increase in viscosity relative to viscosity of SWCNT-free dextran solutions were independent on  $M_w$  of dextrans.

**Table 1.** Positions of the bands in Raman spectra of dextran-SWCNT complexes

Dextran	Bands, $\text{cm}^{-1}$ )				
	RBM	D	G		D + G
None	146.30	1337.90	1557.60	1580.80	2661.80
6000	144.84	1343.45	1569.75	1592.25	2675.75
40 000	142.68	1339.25	1566.95	1589.45	2672.85
100 000	—	1342.05	1568.35	1589.45	2674.35
2 000 000	—	1346.35	1569.75	1591.25	2677.15

<sup>\*)</sup> Symbols — see text.

**Table 2.** Viscosity of aqueous solutions containing 500 mg of dextran in  $10 \text{ cm}^3$  water prior to and after admixture of 5 mg of SWCNT

Dextran, $M_w$	Viscosity, cPa	
	dextran	dextran + SWCNT
6000	$1.168 \pm 0.009$	$1.230 \pm 0.050$
40 000	$2.064 \pm 0.015$	$2.122 \pm 0.034$
100 000	$2.009 \pm 0.0015$	$2.123 \pm 0.083$

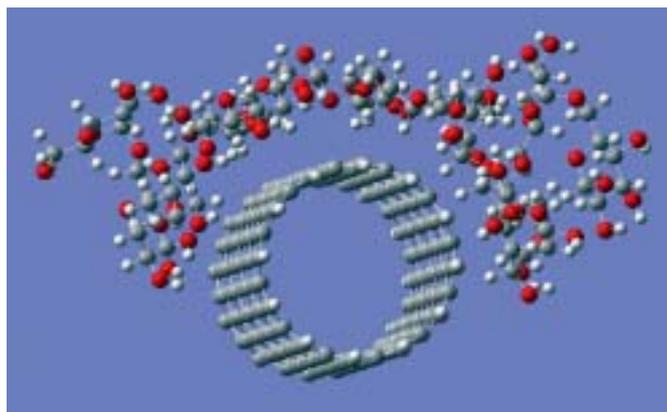
Scanning differential calorimetric measurements revealed that the SWCNT-dextran complexes were formed. After the complex formation, the melting enthalpy decreased by almost one order in respect to the melting enthalpy of corresponding non-complexed dextrans. However, complexes were, generally, weak based on the melting enthalpy values (Table 3).

**Table 3.** Results of DSC studies of dextrans and their complexes with SWCNT

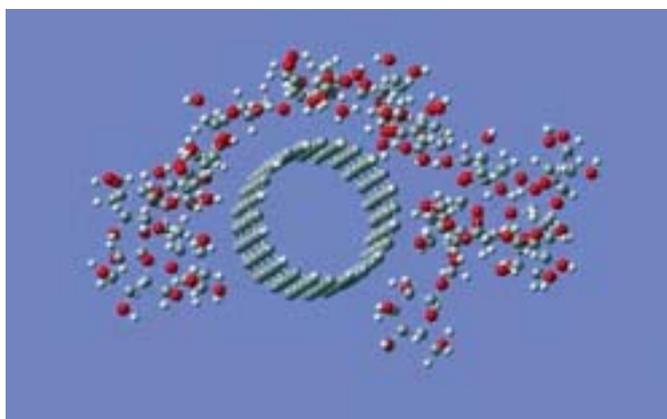
Sample	$T_o^a$ , °C	$\Delta H^b$ , J/g
Dextran 6000	77.1	32.48
Dextran 6000 + SWCNT	118.8	6.69
Dextran 40 000	124.5	21.78
Dextran 40 000 + SWCNT	117.2	5.86
Dextran 100 000	88.4	29.41
Dextran 100 000 + SWCNT	108.4	6.87
Dextran 2 000 000 + SWCNT	125.0	4.25

$T_o^a$  — onset temperature,  $\Delta H^b$  — enthalpy of melting.

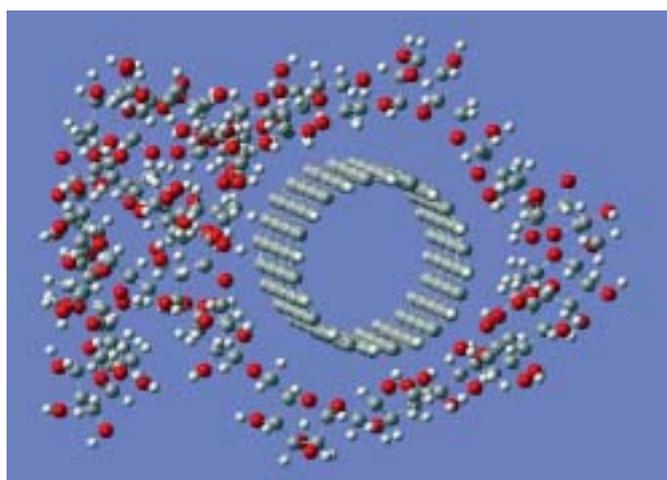
One could see that there were no relationships between the molecular weights of complexed dextrans and melting enthalpies of the complexes. The lack of such relationship might be rationalized in terms of results of computations carried out for linear dextrans composed



*Fig. 2.* Simulated structure of the complex of SWCNT with dextran-12



*Fig. 3.* Simulated structure of the complex of SWCNT with dextran-18



*Fig. 4.* Simulated structure of the complex of SWCNT with dextran-24

of 12, 18 or 24  $\beta$ -D-glucose units (dextran-12, -18, and -24, respectively) interacting with a zigzag (12,0) SWCNT of 0.94 nm in diameter. The ends of linear dextrans curled fairly irregularly on both their ends affect-

ing a regular macrostructures of the solutions to various extents, being responsible for independence of SWCNT-dextran complexes viscosity of the  $M_w$  of dextrans. Also solids left after evaporation of aqueous solutions of complexes should have irregular macrostructures and it could rationalize irregular changes in  $T_o$  and  $\Delta H$  (Table 3) in respect to  $M_w$  of dextrans complexing SWCNT.

In their former papers on complexes of amylose with CNT [2—4], authors assumed that amylose enveloped nanotubes but no evidence for it was given. Energies of intramolecular interactions within dextran chains could be comparable with the energies of the interactions between dextrans and nanotubes. Thus, formerly assumed enveloping of SWCNT with amylose could be false. Formation of complexes of SWCNT with amylopectins [5] showed that enveloping of SWCNT with amylose was no necessary condition for the complex formation. In order to either prove or not the enveloping SWCNT with dextran, molecular mechanics-based computations were performed for SWCNT-dextran systems (for detail — see Experimental Part, Computation).

Preliminary computations performed for linear dextrans-12, -18- or -24 isolated and contacted with SWCNT in vacuum provided an insight into the balance between intra- and inter-molecular interactions in the model systems.

The computations revealed that the shortest (the lowest molecular weight) dextran-12 located the SWCNT inside of a kind of cradle (Fig. 2). The dextran chain fairly smoothly wrapped SWCNT but both terminals of the chain curled as a result of competition between two possible paths of the reduction of the energy of the system. They involve: (i) nonpolar interactions between hydrophobic side of the D-glucose units and the SWCNT surface and (ii) intramolecular hydrogen bond formation within dextran.

A similar cradle for SWCNT was formed by dextran-18 (Fig. 3). The competition between both ways of the lowering energy of the system was more straightforward. The terminals of the dextran-18 chain similarly curled but the partial dextran wrap around SWCNT was not so smooth producing a zigzag pattern. One can observe that also some intramolecular hydrogen bonds were formed among wrapping D-glucose units.

**Table 4.** Gaussian 03 computed total energies of dextrans-12, -18 and -24 ( $E_1$ ), SWCNT ( $E_2 = 1377.39$  kcal/mole), and complexes of SWCNT-dextran ( $E_3$ )

Object	Total energy (kcal/mole) of the object		Energy reduction (kcal/mole) resulting from the complexation ( $E_1 + E_2 - E_3$ )
	dextran ( $E_1$ )	complex dextran-SWCNT ( $E_3$ )	
Dextran-12	358.42	1599.42	136.39
Dextran-18	506.39	1789.53	94.25
Dextran-24	629.52	1935.70	71.21

In contrast to the former dextrans, dextran-24 fully enveloped SWCNT but the D- glucose units of the chain terminals and some such units residing in the central part of that chain formed intramolecular hydrogen bonds (Fig. 4).

Refined computations with Gaussian provided energetic rationales for the formation of the surface complexes of those three dextrans with SWCNT. Table 4 presents the total energies of the optimized structures of the complexes and the energy reduction resulting from the complex formation.

The total energy of dextran increased with its molecular weight and, obviously, the total energy of the system in which dextran and SWCNT resided without mutual interactions also increased. Computations for the systems in which the objects interacted revealed a considerable energy reduction. The total energy of the system, in which SWCNT interacted with dextran-12, decreased by more than 136 kcal/mole. As the molecular weight of the dextrans increased the energy benefit due to their interactions with SWCNT decreased. This decrease was not proportional to changes in the molecular weights of dextrans. Such non-proportionality could result from the intervention of the intramolecular hydrogen bonds in the dextran chains.

## CONCLUSIONS

Increase in viscosity of dextrans after admixture of SWCNT and associated with it the Raman spectral changes indicate that SWCNT are complexed with the dextrans. Complexes are weak as demonstrated by results of differential scanning calorimetry. Computations indicate that interactions between hydrophobic side of polysaccharide chains and surface of nanotubes as well as intramolecular interactions of the hydrogen bond nature within molecules of polysaccharides are responsible for the results of complexation. Carbon nanotubes are trapped in clathrate-like cages of polysaccharides rather than enveloped with regular helices of polysaccharides.

## ACKNOWLEDGMENT

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## REFERENCES

1. Kim O. K., Je J. T., Baldwin J. W., Kooi S., Phersson P. E., Buckley L. J.: *J. Am. Chem. Soc.* 2003, **125**, 4426.
2. Lii C. Y., Stobinski L., Tomasik P., Liao C. D.: *Carbohydr. Polym.* 2003, **51**, 93.
3. O'Connell M. J., Beul P., Erickson L. M., Huffman C., Wang Y., Haroz E., Kuper C., Tour J., Ausman K. D., Smalley R. E.: *Chem. Phys. Lett.* 2001, **342**, 265.
4. Star A., Steuerman D. W., Heath J. R., Stoddart J. F.: *Angew. Chem., Int. Ed.* 2002, **41**, 2508.

5. Stobinski L., Tomasik P., Lii C. Y., Chan H. H., Lin H. M., Liu H. L., Kao C. T., Lu K. S.: *Carbohydr. Polym.* 2003, **51**, 311.
6. Polaczek E., Stobiński L., Mazurkiewicz J., Tomasik P., Kołaczek H., Hong-Ming Lin: *Polimery* 2007, **52**, 34.
7. Polaczek E., Tomasik P. J., Mazurkiewicz J., Stobinski L., Wrzalik R., Tomasik P., Lin H. M.: *J. Nanosci. Nanotechnol.* 2005, **5**, 479.
8. Mazurkiewicz J., Tomasik P.: *Bull. Chem. Soc. Belg.* 1996, **105**, 173.

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### W kolejnym zeszycie ukaza się m.in. następujące artykuły:

- Jadalne folie oraz powłoki powierzchniowe z polimerów naturalnych stosowane do opakowań żywności. Cz. I. Właściwości
- Badanie przebiegu biodegradacji kompozytów poli(chlorek winylu)/celuloza
- Biodegradowalne mieszaniny kopoliester/skrobia — otrzymywanie, właściwości mechaniczne, zwilżalność, przebieg biodegradacji (*j. ang.*)
- Otrzymywanie i charakterystyka układów na podstawie żywicy epoksydowej i soli srebrowej sulfatazolu (*j. ang.*)
- Charakterystyka reologiczna w zakresie niskich szybkości ścinania stopów polimerów napelnionych włóknami. Cz. II. Badania eksperymentalne (*j. ang.*)
- Wytwarzanie nanokompozytów z zastosowaniem ablacji wymuszanej laserem femtosekundowym w środowisku rozpuszczalników i monomerów (*j. ang.*)
- Holograficzne siatki dyfrakcyjne w funkcjonalizowanych poliamidoimidach
- Zautomatyzowana metoda sekwencyjnego korygowania przebiegu cyklu wtryskiwania tworzyw termoplastycznych. Cz. I. Deterministyczny algorytm korekcji