

Application of chitin and chitosan to functional materials; Organo- and water-soluble chitosan derivatives and N-acetyl-D-glucosamine

Sei-ichi Aiba and Hitoshi Sashiwa

Bio-based Polymers Group, Research Institute for Innovation in Sustainable Chemistry,

National Institute of Advanced Industrial Science and Technology (AIST), JAPAN

aiba-seiichi@aist.go.jp



Crab and prawn shells and squid pens

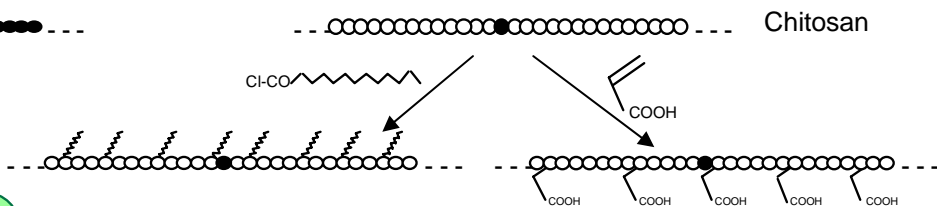
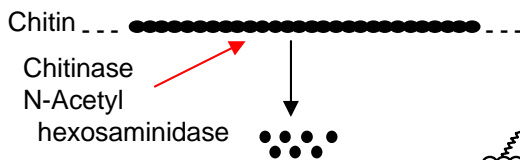
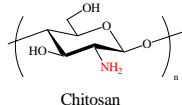
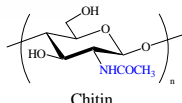
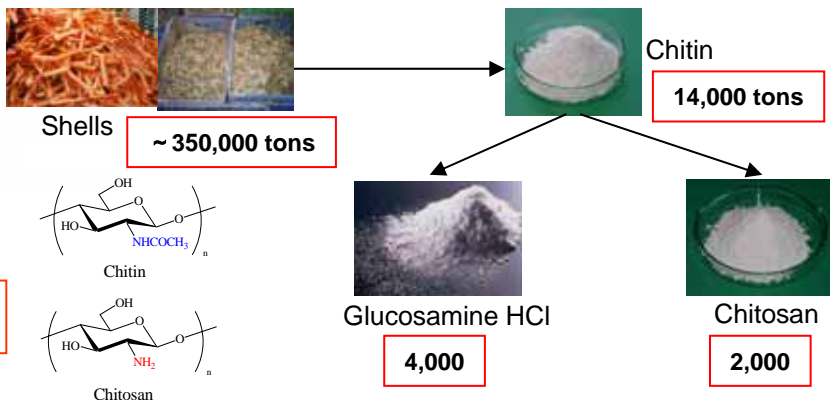
Deproteinization (NaOH with heating)
Decalcification (HCl at room temperature)

Chitin
Deacetylation (conc. NaOH with heating)

Chitosan

Flocculant, cosmetics, wound dressing, food additive, health food, antibactericide, fertilizer

Production of chitin, chitosan, glucosamine in the world



N-Acetyl-D-glucosamine (NAG):
Health food for improvement of osteoarthritis and skin care

Organo-soluble derivatives:
Coating on plastics

Water-soluble derivatives:
Hydrogel for biomedical use

Table 1 Production of NAG from β -chitins^a

Enzyme	Origine	Yield of NAG ^b %
Cellulase T	<i>Trichoderma viride</i>	58
Cellulase A	<i>Acremonium cellulolyticus</i>	59 ^c
Hemicellulase	<i>Aspergillus niger</i>	12
Lipase	<i>Aspergillus niger</i>	16
Pectinase	<i>Aspergillus niger</i>	9

^a β -Chitin: [S]=10 mg/ml; [E]=40 mg/ml; pH=4.0; 37°C; 3 days.

^bYield was calculated from the equation:

Yield (%) = NAG (mmol) / Chitin (mmol) \times 100.

^c(NAG)₂ was detected (Yield=10 %).

Table 2 Chemical structure of chitosan derivatives

Compd.	Yield ^a %	FW	NH ₂	NHAc	NHCOR	OCOR	Protection of NH ₂ ^b
2	65	222	0.59	0.41	-	1.04	69
3	60	211	0.65	0.06	0.29	0.56	76
4	65	281	0.55	0.13	0.32	1.64	65
5	60	256	0.74	0.13	0.13	1.14	87
6	62	292	0.67	0.12	0.21	1.29	79
7	60	248	0.54	0.08	0.38	0.56	64
8	67	306	0.79	0.05	0.16	1.28	93
9	70	353	0.70	0.10	0.20	1.28	82
10	72	447	0.73	0.05	0.22	1.61	86
11	75	490	0.31	0.09	0.60	0.98	36
12	66	624	0.22	0.10	0.68	1.24	26
13	70	647	0.40	0.10	0.50	1.31	47
14	68	335	0.28	0.05	0.67	0.92	33

^aYield was determined by weight recovery and according for change in FW according to the substitution level (MF) determined by ¹H NMR.

^bProtection of % = (A/0.85) \times 100; A = MF of (NH₂)

R = H or C(=O)R'

- 2 R=Me
- 3 R=Et
- 4 R=Pro
- 5 R=iPro
- 6 R=nBu
- 7 R=tBu
- 8 R=(CH₂)₂CH₃
- 9 R=(CH₂)₃CH₃
- 10 R=(CH₂)₄CH₃
- 11 R=(CH₂)₅CH₃
- 12 R=(CH₂)₆CH₃
- 13 R=(CH₂)₁₀CH₃
- 14 R=Ph

Derivatives (6 – 14) are soluble in THF, CHCl₃, and toluene

Table 3 Adsorption of Pd ion to chitosan derivatives^a

Compd.	Pd adsorbed $\mu\text{g}/\text{cm}^2$
7	4.1
8	4.4
9	4.6
9 ^b	0
9 ^c	0
10	3.2
11	4.4
12	4.0
13	2.6
14	0

^aCompd., 4.5 mg; PVB, 4.5 mg; PEG-L, 1 mg.

^bWithout PEG-L. ^cWithout PVB and PEG-L.

^dWithout compd.

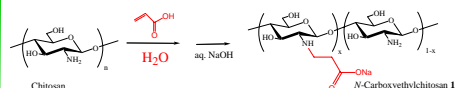


Table 4 Synthesis of N-carboxyethyl (CE) chitosan (1)

Entry	Acrylic acid equiv.**	Temp	Time day	DS /unit	Water solubility*
1	1	50	1	0.09	x
2	1	50	2	0.18	
3	2	25	4	0.06	x
4	2	50	1	0.14	x
5	2	50	2	0.27	
6	2	50	4	0.46	

* , dissolved; x, undissolved **Equivalent / NH₂ of chitosan.

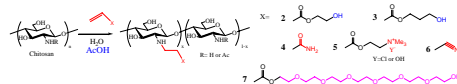


Table 5 Synthesis of various chitosan derivatives (Temp. = 50 °C)

Compd.	Reagent equiv.	Time day	DS	Water solubility
2	2	2	0.44	
3	1	1	0.18	x
	1	2	0.22	
4	2	2	0.09	x
	10	2	0.24	x
5	1	1	0.19	
	2	4	0.48	
6	2	2	0.16	x
	10	2	0.49	x
7	2	1	0.29	
	4	1	0.55	

250g of squid chitin $\xrightarrow{\text{Crude enzyme solution from *Trichoderma viride* (184U)}}$ Total volume, 2.3L (pH 4.1 acetate buffer, 11% EtOH) $\xrightarrow{\text{Incubation at 30°C for 10 days}}$ Ultrafiltration $\xrightarrow{\text{Concentration (0.15L)}}$ Precipitation with ethanol (1.5L) $\xrightarrow{\text{NAG powder (107g, 43%)}}$

Moisture content, 1.0%; Purity, 95% (HPLC), 95%(DMAB); Cl content, 0.42%