



REFERENCES

- Averous, L., Moro, L., Dole, P., and Fringant, C. (2000). Properties of thermoplastic blends starch/polycaprolactone. Polymer, 41, 4157-4167.
- Bezwada, R.S., Jaminolkoski, D.D., Lee, I., Agarwal, V., Persivale, J., Trenka-Benthin, S., Ermeta, M., Suryadevara, J., Yang, A., and Liu, S. (1995). Monocryl[®] suture, a new ultra-pliable absorbable monofilament suture. Biomaterials, 16(15), 1141-1148.
- Chen, D.R., Bei, J.Z., and Wang, S.G. (2000). Polycaprolactone microparticles and their biodegradation. Polymer Degradation and Stability, 67, 455-459.
- Chiu, F.C. and Min, K. (2000). Miscibility, morphology and tensile properties of vinylchloride polymer and poly(ϵ -caprolactone) blends. Polymer International, 49, 223-234.
- Corden, T.J., Jone, I.A., Rudd, C.D., Christian, P., and Downes, S. (1999). Initial development into a novel technique for manufacturing a long fibre thermoplastic bioadsorbable composite *in situ* polymerization of polycaprolactone. Composites: Part A, 30, 737-746.
- David, N. and Hon, S. (Eds.). (1996). Chitin and chitosan: medical applications. Polysaccharides in Medical Applications. New York: Marcel Dekker.
- De Kesel, C., Lefèvre, C., Nagy, J.B., and David, C. (1999). Blends of polycaprolactone with polyvinylalcohol: a DSC, optical microscopy, and solid state NMR study. Polymer, 40, 1969-1978.
- Grant, S., Blair, H.S., and McKay, G. (1990). Deacetylation effects on the dodecanoyl substitution of chitosan. Polymer Communications, 31, 267.
- Hirano, S. and Noishiki, Y. (1985). Journal of Biomedical Review, 19, 413.
- Hirano, S., Usutani, A., Yoshikawa, M., and Midorikawa, T. (1998). Fiber preparation of N-acylchitosan and its cellulose blend by spinning their aqueous xanthate solutions. Carbohydrate Polymer, 37, 311-313.
- Hirotsu, T., Ketelaars, A.A.J., and Nakayama, K. (2000). Biodegradation of polycaprolactone/polycarbonate blend sheets. Polymer Degradation and Stability, 68, 311-316.

- Huatan, H., Collett, J.H., and Attwood, D. (1995). Journal of Microencapsulation, 12(5), 557- 67.
- Kim, C.H., Choi, E.J., and Park, J.K. (2000). Effect of PEG molecular weight on the tensile toughness of starch/PCL/PEG blends. Journal of Applied Polymer Science, 77, 2049-2056.
- Krister, G., Cassarlas, G., and Bergounhon, M. (2000). Structural characterization and hydrolytic degradation of solid copolymers of D,L-lactide-co-caprolactone by raman spectroscopy. Polymer, 41, 925-932.
- Koenig, M.F. and Huang, S.J. (1995). Biodegradable blends and composites of polycaprolactone and starch derivatives. Polymer, 36(9), 1877-1882.
- Kubota, N., Tatsumoto, N., and Sano, T. (2000). A simple preparation of half N-acetylated chitosan highly soluble in water and aqueous organic solvents. Carbohydrate Research, 324(4), 268-274.
- Kumar, M.N.V. (2000). A review of chitin and chitosan applications. Reactive and Functional Polymers, 46, 1-27.
- Lee, K.Y., Ha, W.S., and Park, W.H. (1995). Blood compatibility and biodegradability of partially N-acylated chitosan derivatives. Biomaterials, 16(16), 1211-1216.
- Lee, V. F. (1974). Solution and shear properties of chitin and chitosan. Ph.D. Dissertation, University of Washington, University Microfilms, Ann Arbor, Michigan, USA, Microfilm 29-74, 446.
- Muzzarelli, R.A.A. (1997). Human enzymatic activities related to the therapeutical administration of chitin derivatives. Cell Mol. Biol. Life Science, 53, 131.
- Ng, C.S., Teoh, S.H., Chung, T.S., and Hutmacher, D.W. (2000). Simultaneous biaxial drawing of poly(ϵ -caprolactone) films. Polymer, 41, 5855-5864.
- Nishimura, S.I., Kohgo, O., and Kurita, K. (1991). Chemospecific anipulation of rigid polysaccharide: syntheses of novel chitosan derivatives with excellent solubility in common organic solvents by regioselective chemical modifications. Macromolecules, 24, 4745-4748.
- Olabarrieta, I., Forsstrom, D., and Gedde, U.W. (2001). Transport properties of chitosan and whey blended with polycaprolactone assesed by standard permeability measurements and microcolorimetry. Polymer, 42, 4401-4408.

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- Rathke, T.D. and Hudson, S.M. (1994). Review of chitin and chitosan as fiber and film formers. Review Macromolecule Chemical Physic, C34(3), 375-437.
- Ratto, J.A., Chen, C.C., and Blumstein, R.B. (1996). Phase behavior study of chitosan/polyamide blends. Journal of Applied Polymer Science, 59, 1451-1461.
- Sanford, D.A. and Stinnes, A. (Eds.). (1991). Biomedical applications of high purity chitosan-physical, chemical and bioactive properties. ACS Symposium Series, 467, 430.
- Sannan, T., Kurita, K., Ogura, K., and Iwakura, Y. (1978). Studies on chitin: 7.Ir.spectroscopic determination of degree of deacetylation. Polymer, 19, 458-459.
- Sashiwa, H. and Shigemasa, Y. (1999). Chemical modification of chitin and chitosan 2: preparation and water soluble property of N-acylated or N-akylated partially deacetylated chitins. Carbohydrate Polymer, 39, 127-138.
- Seo, T., Ohtake, H., Unishi, T., and Iijima, T. (1995). Permeation of solutes through chemically modified chitosan membranes. Journal of Applied Polymer Science, 58, 633-644.
- Shilton, S.J., Bell, G., and Ferguson, J. (1996). The deduction of fine structural details of gas separation hollow fibre membrane using resistance modeling of gaspermeation. Polymer, 37(3), 485-492.
- Shimahara, K. and Takigushi, Y. (1988). Biomass part B: Ligtin, Pectin, and Chitin, New York: Academic Press.
- www. Biopolymer.com.
- Xu, D., McCarthy, S.P., Gross, R.A., and Kaplan, D.L. (1996). Chitosan film acylation and effects on biodegradability. Macromolecules, 29, 3436-3440.
- Yalpani, M. and Hall, L.D. (1998). Some chemical and analytical aspects of polysaccharide modifications 3. Formation of branched-chain, soluble chiosan derivatives. Macromolecules, 3, 8142-8148.

- Zhang, L., Xiong, C., and Deng, X. (1995). Biodegradable polyester blend for Biomedical applicaton. Journal of Applied Polymer Science, 56, 103-112.
- Zong, Z., Kimura, Y., Takahashi, M., and Yamane, H. (2000). Characterization of chemical and solid state structure of acylated chitosan. Polymer, 41, 899-906.

APPENDICES

Appendix A Characterization of Chitosan and H-Chitosan

Table A1 Viscosity-average molecular weight of chitosan

Conc. (g/100ml)	Time (sec)				η_{rel}	η_{sp}	η_{sp}/c
	1	2	3	average			
0	122.57	122.54	122.51	122.54	-	-	-
0.0063	128.88	128.99	128.78	128.88	1.0518	0.0518	8.2167
0.0125	134.96	134.86	134.91	134.91	1.1009	0.1009	8.0757
0.0250	148.42	148.58	148.97	148.66	1.2131	0.2131	8.5251
0.0500	177.85	177.89	177.87	177.87	1.4515	0.4515	9.0305
0.1000	242.53	242.54	242.55	242.54	1.9793	0.9793	9.7927

Conc. (g/100 ml)	$\ln \eta_{rel}$	$\ln(\eta_{rel})/c$
0.0063	0.0505	8.0752
0.0125	0.0962	7.6936
0.0250	0.1932	7.7281
0.0500	0.3726	7.4523
0.1000	0.6827	6.8273

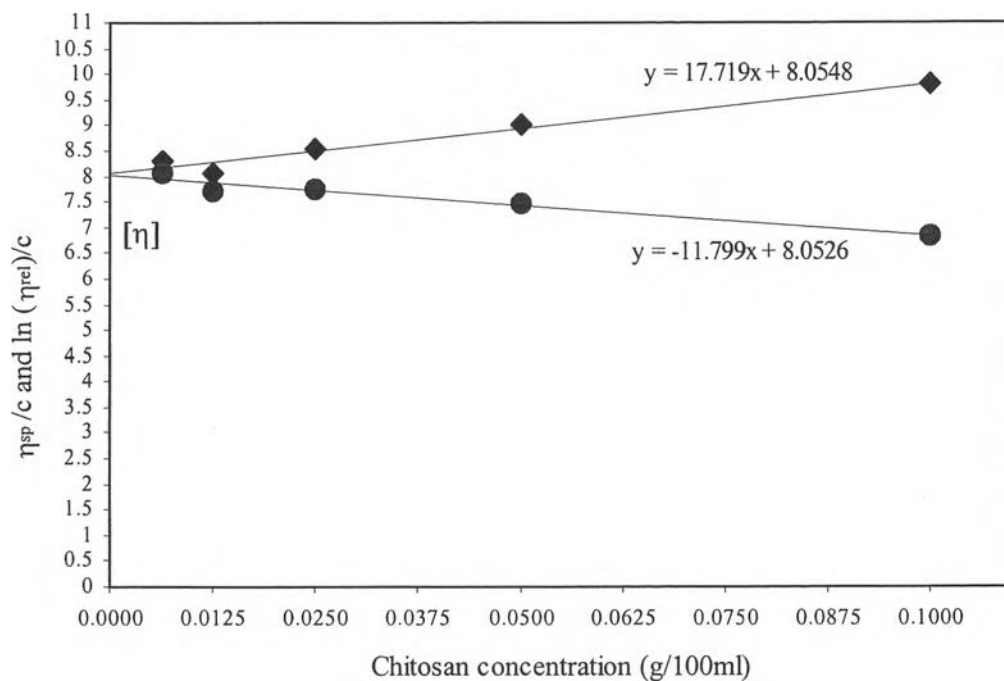


Figure A1 η_{sp}/c and $\ln(\eta_{rel})/c$ against concentration of chitosan solution.

Interception: $[\eta] = 8.0528 \times 10^{-2} \text{ ml/g}$

$$[\eta] = kM^a$$

$$[\eta] = 8.93 \times 10^{-4} M^{0.71}$$

$$M = 3.72 \times 10^5 \text{ g/mol}$$

Table A2 Degree of substitution of H-chitosan from elemental analysis

H-chitosan	specimens	Experiment values			
		%C	%N	%H	C/N
Repeat reaction 1 time	1	65.696	2.395	9.252	
	2	65.710	2.328	9.501	
	average	65.703	2.362	9.377	27.817
Repeat reaction 2 times	1	66.742	2.217	9.604	
	2	66.374	2.309	9.605	
	average	66.558	2.263	9.605	29.411
Repeat reaction 3 times	1	66.831	2.289	9.822	
	2	66.774	2.345	9.960	
	average	66.803	2.317	9.891	28.832

Calculation of degree of substitution of H-chitosan

Assume: Degree of substitution is four.

(Chitosan was fully substituted with hexanoyl groups.)

molecular weight of

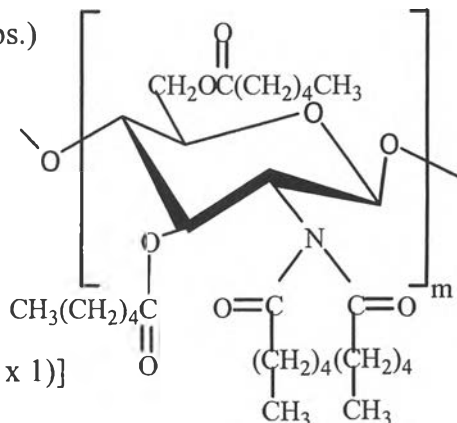
$$\begin{aligned}
 \text{H-chitosan} &= [(\text{no. of C atoms} \times 12) + \\
 &\quad (\text{no. of N atoms} \times 14) + \\
 &\quad (\text{no. of O atoms} \times 16) + \\
 &\quad (\text{no. of H atoms} \times 1)] \\
 &= [(30 \times 12) + (14 \times 1) + (8 \times 16) + (51 \times 1)] \\
 &= 553
 \end{aligned}$$

$$\text{C atoms} = (360 \times 100)/553 = 65.099\%$$

$$\text{N atoms} = (14 \times 100)/553 = 2.532\%$$

$$\text{H atoms} = (16 \times 100)/553 = 9.222\%$$

If degree of substitution is four: C/N 25.711



Appendix B Characterization of H-chitosan/PCL Blend Films**Table B1** Thermal properties of H-chitosan/PCL blend films from DSC

H-chitosan/PCL	Glass transition temperature (°C)	Melting temperature (°C)
0/100	-63.5	63.8
20/80	-62.3	63.4
40/60	-63.5	62.8
60/40	-63.4	62.3
80/20	-63.5	61.5
100/0	-	-

Table B2 Decomposition temperatures of H-chitosan/PCL blend films from TGA

H-chitosan/PCL	Decomposition temperature of PCL (°C)	Decomposition temperature of pyranose ring (°C)	Decomposition temperature of hexanoyl groups (°C)
0/100	391.08	-	-
20/80	387.22	319.92	257.66
40/60	387.85	317.18	249.87
60/40	378.07	307.39	246.82
80/20	385.57	314.19	249.27
100/0	-	321.00	255.38

Table B3 Mechanical properties of H-chitosan/PCL blend films

H-chitosan/PCL	specimens	thickness (micron)	load (N)	tensile strength (MPa)	elongation at break (%)
0/100	1	24.70	5.70	8.44	59.15
	2	25.10	7.70	12.47	89.56
	3	21.40	6.80	12.71	57.84
	4	23.40	8.30	14.19	72.30
	5	25.10	8.30	13.23	49.56
average				12.21	65.68
STD				2.20	15.64
20/80	1	29.9	7	9.36	156.2
	2	29.9	9.2	12.31	172.9
	3	23.6	4.8	8.14	119.2
	4	21.2	4.7	8.87	79.55
	5	27.4	7.2	10.51	162.9
average				9.84	138.15
STD				1.63	38.53
40/60	1	26.30	4.6	7.00	187.60
	2	30.00	4.1	5.47	164.30
	3	25.80	4.2	6.51	172.30
	4	30.00	5	6.67	198.60
	5	25.00	3.4	5.44	118.50
average				6.22	168.26
STD				0.72	30.83
50/50	1	28.50	2.80	3.93	77.48
	2	30.00	2.90	3.87	77.48
	3	27.50	3.30	4.80	129.50
	4	27.50	3.00	4.36	97.90
	5	28.50	3.20	4.49	133.50
average				4.29	103.17
STD				0.39	27.21

H-chitosan/PCL	specimens	thickness (micron)	load (N)	tensile strength (MPa)	elongation at break (%)	
60/40	1	30.00	2.2	2.93	37.00	
	2	29.00	2	2.76	32.89	
	3	29.80	2	2.68	24.56	
	4	25.10	1.6	2.87	28.09	
	5	29.00	1.8	2.21	27.88	
	average				2.69	30.08
	STD				0.29	4.87
70/30	1	30.00	2.5	3.39	36.22	
	2	29.00	2.1	2.80	22.89	
	3	29.80	2.2	2.93	24.56	
	4	25.10	2.3	3.07	25.88	
	5	29.00	2.5	3.33	36.49	
	average				3.10	29.21
	STD				0.25	6.61
80/20	1	29.50	2.90	3.93	137.90	
	2	29.50	2.20	2.98	69.56	
	3	30.00	2.50	3.33	61.22	
	4	28.20	2.40	3.40	109.60	
	5	29.70	2.70	3.64	106.20	
	average				3.46	96.90
	STD				0.35	31.42
100/0	1	30.00	3.50	4.67	366.30	
	2	26.30	3.00	4.56	316.20	
	3	30.00	2.90	3.87	346.20	
	4	28.90	2.50	3.46	367.90	
	5	29.80	2.60	3.49	369.60	
	average				4.01	353.24
	STD				0.58	22.77

Table B4 Oxygen permeability measurement of H-chitosan/PCL blend films

H-chitosan /PCL	specimens	T (°C)	films thickness average (μm)	N	G ($\text{cm}^3/\text{m}^2\cdot\text{sec}\cdot\text{bar}$)	\underline{P} ($\text{cm}^3/\mu\text{m m}^2\cdot\text{sec}\cdot\text{bar}$)	
0/100	1	25.6	30.00	1.9818	25179	755379	
	2	25.3	29.00	1.8292	27308	791918	
	3	24.9	30.00	1.8783	26629	798868	
	average					26372	782055
	STD					1087	23362
20/80	1	27.2	30.00	4.6620	10646	319392	
	2	26.8	30.00	4.4543	11158	334728	
	3	26.8	30.00	4.0917	12147	364399	
	average					11317	339506
	STD					763	22881
40/60	1	26.8	30.00	36.3636	1367	41002	
	2	26.8	30.00	35.3357	1398	41943	
	3	28.0	30.00	29.1545	1698	50937	
	average					1488	44628
	STD					183	5484
50/50	1	28.6	27.50	16.1812	3053	83961	
	2	27.6	28.50	10.5485	4699	133922	
	3	28.0	28.50	9.7276	5089	145030	
	average					4280	120971
	STD					1080	32529
80/20	1	25.9	28.50	17.7620	2807	79986	
	2	26.3	29.50	14.1643	3515	103683	
	3	28.3	27.50	12.2699	4032	110872	
	average					3451	98180
	STD					615	16162

H-chitosan /PCL	specimens	T (°C)	films thickness average (μm)	N	G ($\text{cm}^3/\text{m}^2\cdot\text{sec}\cdot\text{bar}$)	\underline{P} ($\text{cm}^3/\mu\text{m}$ $\text{m}^2\cdot\text{sec}\cdot\text{bar}$)	
100/0	1	25.9	27.50	4.7281	10543	289937	
	2	28.0	27.50	11.6550	4247	116799	
	3	28.0	27.50	8.9686	5519	151784	
	average					6770	186173
	STD					3329	91548

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