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Metal complexes of crosslinked chitosans: Correlations between metal ion complexation values and thermal properties

K.D. Trimukhe, A.J. Varma *

Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008, India

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ABSTRACT

A series of heavy metal complexes of crosslinked chitosans were evaluated by thermogravimetric studies. The metal complexes with Cu, Cd and Hg ions exhibiting the highest complexing ability to chitosans (Hg 354–364, Cu 100–112, and Cd 121–160, in mg/g chitosan), had the lowest onset of degradation temperatures (range 194–210 °C) and the lowest final degradation temperatures (generally less than 294–304 °C for Hg, 296–338 °C for Cu, and 305–368 °C for Cd complexes). Mn ion, with the lowest binding to chitosans (Mn 5–7 mg/g), showed the reverse behavior, having onset (240–248 °C) and final degradation temperatures (range 300–368 °C). Zn (binding 74–87 mg/g) and Pb (binding 39–62 mg/g) ions have a binding ability intermediate to Cu/Cd/Hg and Mn extremes, and therefore the effects on onset and final degradation temperatures are intermediate to these values.

1. Introduction

A key property of functional polymers is their ability to complex with a variety of metal ions in solution. A very large number of publications have dwelt on the complexation ability of chitosan and its crosslinked derivatives with complex transition metals, organic species like dyes, and and enzymes (Bassi, Prasher, & Simpson, 2000; Dobetti & Delben, 1992; Domard & Piron, 2000; Juang, Wu, & Tseng, 2002; Li, Chen, & Liu, 2003; Merrifield, Davids, MacRae, & Amirbahman, 2004; Rhazi et al., 2002; Schmuhl, Krieg, & Keizer, 2001; Taboada, Cabrera, & Cardenas, 2003; Tan, Wang, Peng, & Tang, 1999; Trimukhe & Varma, 2008a; Varma, Deshpande, & Kennedy, 2004). Recently we reported (Trimukhe & Varma, 2008a) our detailed investigation into the heavy metal ion binding (Hg, Cu, Cd, Pb, Zn, Mn) to a series of crosslinked chitosans, using trimelitic anhydride, diisocyanatohexane, and dibromodecane as crosslinking agents. This is the first study on crosslinked chitosan materials, wherein the chitin was first crosslinked and then deacetylated to give crosslinked chitosans retaining all the amino groups, which are crucial functional groups for specific heavy metal ion complexation. We also investigated the morphologies of these metal complexes by a study of SEM and WAXRD (Trimukhe & Varma, 2008b). Morphological information from SEM studies indicate that metal ions like Hg which are very strongly bound to the chitosan and crosslinked chitosans, even to the extent of 364 mg/g chitosan, are not seen as distinct moieties on the surface of the polymer, whereas with decreasing extent of binding, in the order Hg > Cu > Cd > Zn > Pb > Mn, we observed increasing presence of metal on the surface. These results agreed with the morphological information obtained with WAXRD studies, as well as with the metal complexation data of these metals with these same chitosan polymer/crosslinked polymer systems. However, thermal properties of these metal complexes are not reported. Thermal stability data of metal complexes is important to confirm the presence of metal ions present either as inclusion complexes or as adsorbed species on the surface of the polymer. Metals ions present as inclusion complexes are expected to have a greater effect on the thermal properties of the polymer, in addition to specific effects of different metal ions. Therefore this paper investigates the thermal degradation of metal complexes of chitosan and crosslinked chitosan under nitrogen atmosphere in the temperature range 50–600 °C. This paper also attempts to correlate the thermal degradation behavior of metal complexes of chitosans/crosslinked chitosans with the binding abilities of metal ions with chitosans/crosslinked chitosans (expressed as binding mg (metal ion)/g (chitosan)) for a series of heavy metal complexes of chitosans. This appears to be the first such reported correlation between the thermal degradation of metal complexes of crosslinked chitosans and their saturated heavy metal ion complexation values.

2. Experimental

2.1. Materials

The chitin and chitosan used in this study are commercial products of Meron Biopolymers, Cochin, Kerala, India. D-Glucosamine

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* Corresponding author. Tel.: +91 20 25902191; fax: +91 20 25902618.
E-mail address: aj.varma@ncl.res.in (A.J. Varma).

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was obtained from Sigma Chemical Co. (St. Louis, MO). Diisocyanatohexane (HDI) was obtained from Sigma–Aldrich Chemical Co (Bangalore, India), trimellitic anhydride (TMA), and dibromodecane (DBD) was obtained from Merck (Mumbai, India). Dimethylformamide, toluene and sodium hydroxide pellets were AR grade chemicals, obtained from SD fine chemicals, Mumbai. Sodium hydride was obtained from Merck. 4-Dimethylaminopyridine was purchased from Lancaster Company. All metal salts were AR grade materials and used without further purification. The salts $ZnCl_2$, $MnSO_4$, $CdSO_4$, $Pb(NO_3)_2$ were obtained from Loba Chemie, Mumbai, $CuSO_4$ was from SD Fine Chemicals, Mumbai, and $HgCl_2$ was from Merck.

2.2. Synthetic procedures

2.2.1. Preparation of different crosslinked chitosan with different metal ions

Detailed Detailed preparation methods crosslinked chitin using diisocyanatohexane (HDI), dibromodecane (DBD) and trimellitic anhydride (TMA) and of deacetylation of chitin have recently been published (Trimukhe & Varma, 2008a). Metal ion complexation studies with Cu^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+} salts has also been published (Trimukhe & Varma, 2008a), along with their morphological properties (Trimukhe & Varma, 2008b).

While the three different crosslinking agents are not expected to produce the same degree of crosslinking in the chitosans, this was not an important aspect since the degrees of crosslinking were designed to be low, and crosslinking was done only to prevent solubility of the material while retaining the maximum surface area.

Further, the degree of deacetylation was measured only for the chitosans so produced (Trimukhe & Varma, 2008a), and not for the crosslinked chitosans, since the degree of crosslinking was low, as evidenced by swelling studies on these materials (Trimukhe & Varma, 2007). Thus, the degree of crosslinking is not expected to change significantly the degree of deacetylation. Due to the low degree of crosslinking, access to the amino groups of chitosan is not affected.

The degree of deacetylation was measured by C-^{13}NMR and XPS (ESCA) studies (Trimukhe & Varma, 2008a).

2.3. Thermogravimetric analysis (TGA)

Thermogravimetry (TGA) and differential thermogravimetry (DTG) were carried out using a Seiko Instruments TG/DTA 32 instrument equipped with a SSC 5100 Disk Station and SP-530 Plotter. The studies were carried out in a nitrogen atmosphere at a heating rate of 10 °C, in the range 50–600 °C.

3. Results and discussion

There are several reports in literature of changes occurring in the thermal degradation behavior of chitosans on crosslinking or on their chemical modification. For example, in one study (Neto et al., 2005) addition of PEO grafts led to a slight increase in thermal stability (from 297.3 to 300.7 °C), whereas crosslinking the chitosan decreased the thermal stability to a small extent (from 297.3 to 288.8 °C). In another report, crosslinking was seen to improve the heat stability of the chitosan (Beppu, Arruda, Vieira, & Santos, 2004). They also found that histidine modified chitosans could bind Cu ions, as a result of which, they inferred, new peaks were observed in the TGA at ~230 °C and 510 °C. Hong et al. found that the thermal degradation can be correlated to the rate of heating the sample, and that the degradation of chitosan is a single stage decomposition (Hong et al., 2007). Modification of chitosan with cyclic oxegenated compounds (Tirkistani, 1998a) as well as with Schiff's bases led to a decrease in thermal stability (Tirkistani, 1998b). Similarly, lactic acid side chains on chitosan decreased its thermal stability (Qu, Wirsen, & Albertsson, 2000).

Thus, it is clear that chemical modifications as well as metal complexations generally lead to a decrease in the thermal stability of chitosans. However, the present report on the correlations of thermal degradation properties of a series of metal complexes of crosslinked chitosans (with unmodified commercial chitosan as a control standard) shows that the decrease in the observed thermal stability is intimately related to the specific type of metal complex. Table 1 shows the TGA results for all samples of chitosans/crosslinked chitosans and their metal complexes, while Table 2 shows the metal binding data of these complexes. Figs. 1–6 show the TGA patterns (single stage and two stage) for all the samples studied. We have ignored the initial water loss stage below 100 °C in our discussions. All the chitosans and crosslinked chitosans (i.e., without any metal ions bound to them) exhibited single stage degradations (the second stage nearly merging with the first stage, i.e., the start temperature of the second stage degradation is the same as the end temperature of the first stage) with the onset of degradation temperature being observed to be in the range 244–250 °C, the range for first step final degradation temperature was 332–350 °C and for the final degradation temperature the range 548–560 °C (sample nos. 1–6 in Table 1). In contrast, all the metal complexes of chitosans showed distinct two stage decomposition curves. The metal complexes with Cu, Cd and Hg ions, which exhibit the highest complexing ability to the chitosans (Hg 354–364 mg/g chitosan, Cu 100–112 mg/g chitosan, and Cd 121–160 mg/g chitosan) (Table 1, sample nos. 7–24), were found to have the lowest onset of degradation temperatures (range 194–210 °C) and the lowest final degradation temperatures (generally less than 294–304 °C for Hg, 296–338 °C for Cu complexes, and 305–368 °C for Cd complexes), as can be seen from the data in Table 1 and Figs. 1–6. Mn ion which has the lowest binding abilities to chitosans (Mn 5–7 mg/g chitosan) (Table 2) showed the reverse behaviour, these complexes exhibited the least effects on the onset (240–248 °C) and final degradation temperatures (range 300–368 °C) (Table 1 sample nos. 31–36)).

Zn (binding ability 74–87 mg/g chitosan) and Pb ions (binding ability 39–62 mg/g chitosan) (Table 2) have a binding ability intermediate to Cu/Cd/Hg on the one hand and Mn on the other extreme (see sample nos. 25–30 and 37–42 in Table 1), and therefore the effects on onset and final degradation temperatures are intermediate to these values, i.e. onset temperatures 205–250 °C and final first stage temperatures between 302 and 350 °C. Above 550 °C most of the samples were completely degraded, while the TGA curves above 550 °C for some samples had a tailing effect and were not flat (Figs. 2–6). These samples (samples 9, 14, 17, 21, 25, 26, 29, 31, 33 in Table 1) had final decomposition temperatures in excess of 600 °C, though not much inference can be drawn about this aspect with the present data, and more work needs to be done to understand this aspect.

The TGA results can also be discerned from the DTG peaks observed. DTG data (Table 1) shows that chitosan as well as crosslinked chitosans have only one major peak at ~300 °C (samples 1–6). For the very strongly bound Hg ions, the major peak shifts to 265–268 °C for crosslinked chitosan and 212 and 184 °C for chitosan (samples 19–24); further, a new smaller peak appears at 525–600 °C. For the strongly bound Cu ions, there are generally three peaks seen in the DTG, one major and two minor. The appearance of these additional peaks can be attributed to the metal complexes of the chitosans (Beppu et al., 2004). The major peak appears at 420–450 °C for Cu (samples 7–12) and at 500–545 °C for Cd. The minor peaks for Cu appear in the range 230–278 °C for Cu (except for sam-

Table 1

Thermal analysis of chitosan, deacetylated chitin, HDI-crosslinked chitosan, HDI-crosslinked deacetylated chitin, TMA-crosslinked deacetylated chitin, DBD-crosslinked deacetylated chitin and their metal ions in nitrogen atmosphere in the range 50–600 °C

Sr. No.	Sample name	First stage (°C)		Second stage (°C)		Percentage weight loss (°C)					DTG peaks (Ma = Major Mi = Minor)
		Onset degrade	Final degrade	Onset degrade	Final degrade	200	300	400	500	550	
1	Chitosan	244	332	–	548	11	42	69	86	97	293 Ma
2	Deacetylated chitin	246	350	–	550	10	39	68	89	100	310 Ma
3	HDI-crosslinked chitosan	246	350	406	550	11	38	63	87	98	298 Ma
4	HDI-crosslinked deacetylated chitin	250	350	–	550	13	37	67	87	95	300 Ma
5	TMA-crosslinked deacetylated chitin	248	340	–	552	16	44	69	87	97	302 Ma
6	DBD-crosslinked deacetylated chitin	248	346	–	560	12	39	65	84	96	300 Ma
7	Chitosan–Cu^{2+}	205	322	396	450	15	45	56	88	88	230 Mi 270 Mi 425 Ma
8	Deacetylated chitin–Cu^{2+}	236	338	436	500	18	44	60	89	92	262 Mi 266 Mi 456 Ma
9	HDI-crosslinked chitosan–Cu^{2+}	200	296	400	*	17	65	78	100	100	248 Ma 428 Ma
10	HDI-crosslinked deacetylated chitin–Cu^{2+}	212	308	400	450	17	44	59	90	90	240 Mi 278 Mi 420 Ma
11	TMA -crosslinked deacetylated chitin–Cu^{2+}	208	306	400	450	23	55	67	97	98	240 Mi 270 Mi 450 Ma
12	DBD-crosslinked deacetylated chitin–Cu^{2+}	208	308	400	450	27	55	66	96	97	240 Mi 275 Mi 430 Ma
13	Chitosan–Cd^{2+}	248	322	498	550	14	33	50	60	85	286 Mi 510 Ma
14	Deacetylated chitin–Cd^{2+}	252	368	498	*	11	27	59	67	85	300 Ma 340 Ma 545 Ma
15	HDI-crosslinked chitosan–Cd^{2+}	250	308	500	552	24	44	60	71	94	283 Mi 500 Ma
16	HDI-crosslinked deacetylated chitin–Cd^{2+}	200	350	500	552	29	48	64	76	98	290 Ma 510 Ma
17	TMA-crosslinked deacetylated chitin–Cd^{2+}	248	305	500	*	24	46	59	68	93	290 Mi 520 Ma
18	DBD-crosslinked deacetylated chitin–Cd^{2+}	250	316	500	550	24	43	58	66	92	290 Mi 520 Ma
19	Chitosan–Hg^{2+}	204	304	430	550	13	61	74	89	99	212 Ma 184 Ma
20	Deacetylated chitin–Hg^{2+}	200	302	–	560	10	61	75	88	97	265 Ma 600 Ma
21	HDI-crosslinked chitosan–Hg^{2+}	194	300	498	*	12	59	72	83	91	248 Ma 558 Mi
22	HDI-crosslinked deacetylated chitin–Hg^{2+}	200	300	–	560	11	60	77	90	99	268 Ma 565 Mi
23	TMA-crosslinked deacetylated chitin–Hg^{2+}	210	294	–	600	08	59	72	86	95	268 Ma 525 Mi
24	DBD-crosslinked deacetylated chitin–Hg^{2+}	206	300	–	600	12	61	73	87	95	268 Ma
25	Chitosan–Zn^{2+}	250	306	500	*	18	43	57	66	86	278 Ma 525 Ma
26	Deacetylated chitin–Zn^{2+}	250	350	480	*	12	32	51	66	83	285 Ma 535 Ma
27	HDI-crosslinked chitosan–Zn^{2+}	248	316	500	552	17	39	56	66	90	275 Ma 533 Ma

(*continued on next page*)

Table 1 (*continued*)

Sr. No.	Sample name	First stage (°C)		Second stage (°C)		Percentage weight loss (°C)					DTG peaks (Ma = Major Mi = Minor)
		Onset degrade	Final degrade	Onset degrade	Final degrade	200	300	400	500	550	
28	HDI-crosslinked deacetylated chitin–Zn^{2+}	252	320	500	556	16	37	54	64	86	280 Ma 525 Ma
29	TMA-crosslinked deacetylated chitin–Zn^{2+}	250	294	538	*	18	40	54	64	74	285 Ma 540 Ma
30	DBD-crosslinked deacetylated chitin–Zn^{2+}	250	312	494	552	17	38	52	66	90	285 Mi 548 Ma
31	Chitosan–Mn^{2+}	248	350	502	*	11	41	64	73	91	290 Ma 490 Mi
32	Deacetylated chitin–Mn^{2+}	248	346	–	550	13	41	66	93	99	308 Ma 508 Mi
33	HDI-crosslinked chitosan–Mn^{2+}	248	340	406	*	13	41	67	92	100	300 Ma 500 Ma
34	HDI-crosslinked deacetylated chitin–Mn^{2+}	248	350	–	550	14	45	64	91	100	300 Ma 500 Ma
35	TMA-crosslinked deacetylated chitin–Mn^{2+}	248	300	–	550	14	45	64	91	100	300 Ma 500 Ma
36	DBD-crosslinked deacetylated chitin–Mn^{2+}	240	340	–	550	13	39	64	90	95	293 Ma 495 Ma
37	Chitosan–Pb^{2+}	248	302	448	508	12	42	55	93	97	485 Ma
38	Deacetylated chitin–Pb^{2+}	232	308	454	512	13	43	59	93	99	274 Ma 480 Ma
39	HDI-crosslinked chitosan–Pb^{2+}	205	312	448	512	10	41	54	87	93	260 Ma 475 Ma
40	HDI-crosslinked deacetylated chitin–Pb^{2+}	218	312	448	502	11	40	58	93	95	280 Ma 485 Ma
41	TMA-crosslinked deacetylated chitin–Pb^{2+}	226	300	450	512	12	42	56	92	97	268 Ma 483 Ma
42	DBD-crosslinked deacetylated chitin–Pb^{2+}	228	312	m	502	13	42	57	94	96	260 Ma 485 Ma

*, >600 °C.

Table 2
Metal complexation data for different chitosans and crosslinked chitosans [average values of three different analytical methods – atomic absorption spectrophotometer method, UV–vis spectrometry, and titrymetric methods, as in Trimukhe and Varma (2008a)]

Sample name	Cu^{2+} (mg/g)	Cd^{2+} (mg/g)	Hg^{2+} (mg/g)	Zn^{2+} (mg/g)	Mn^{2+} (mg/g)	Pb^{2+} (mg/g)
Chitosan	103	135	354	86	6	43
Deacetylated Chitin	112	121	364	81	5	50
HDI-crosslinked deacetylated Chitin	108	145	359	81	7	46
DBD-crosslinked deacetylated Chitin	108	160	362	83	5	39
TMA-crosslinked deacetylated Chitin	109	134	361	87	7	61
HDI-crosslinked Chitosan	100	133	362	74	6	62

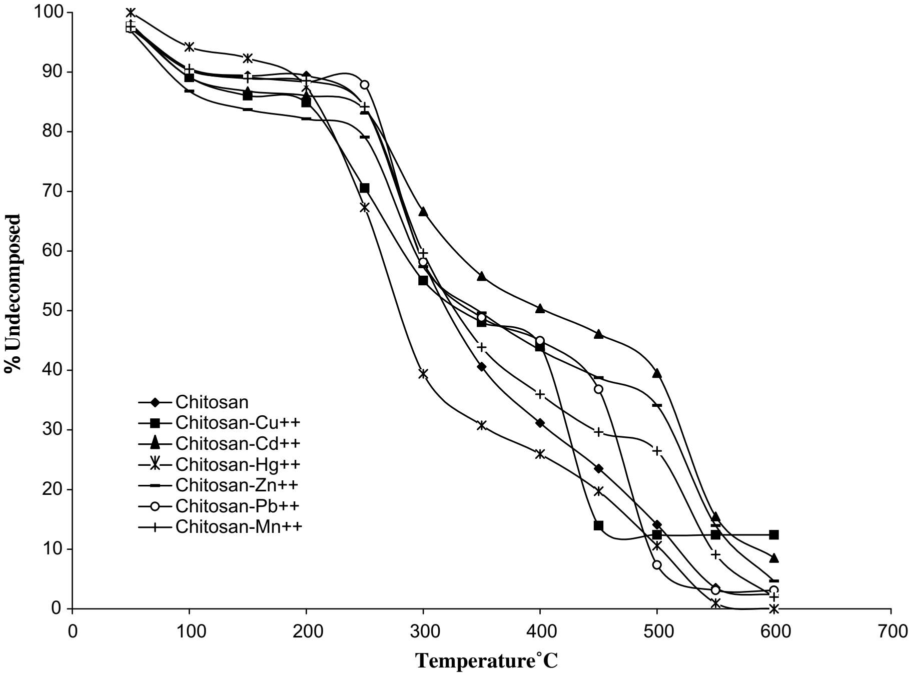

Fig. 1. TGA of chitosan with metal ions.

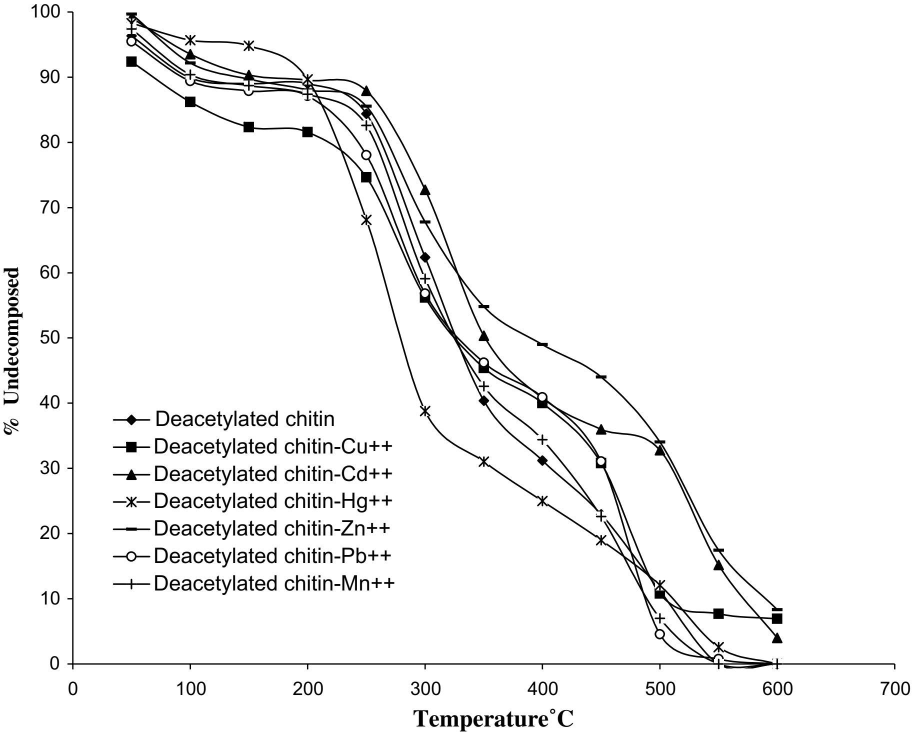

Fig. 2. TGA of deacetylated chitin with metal ions.

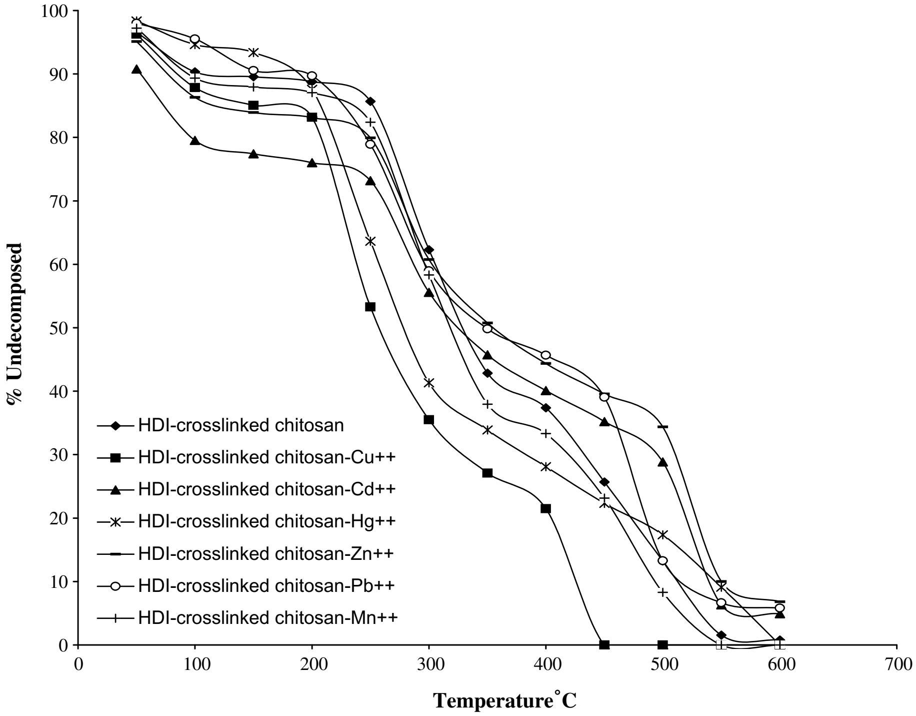

Fig. 3. TGA of HDI-crosslinked chitosan with metal ions.

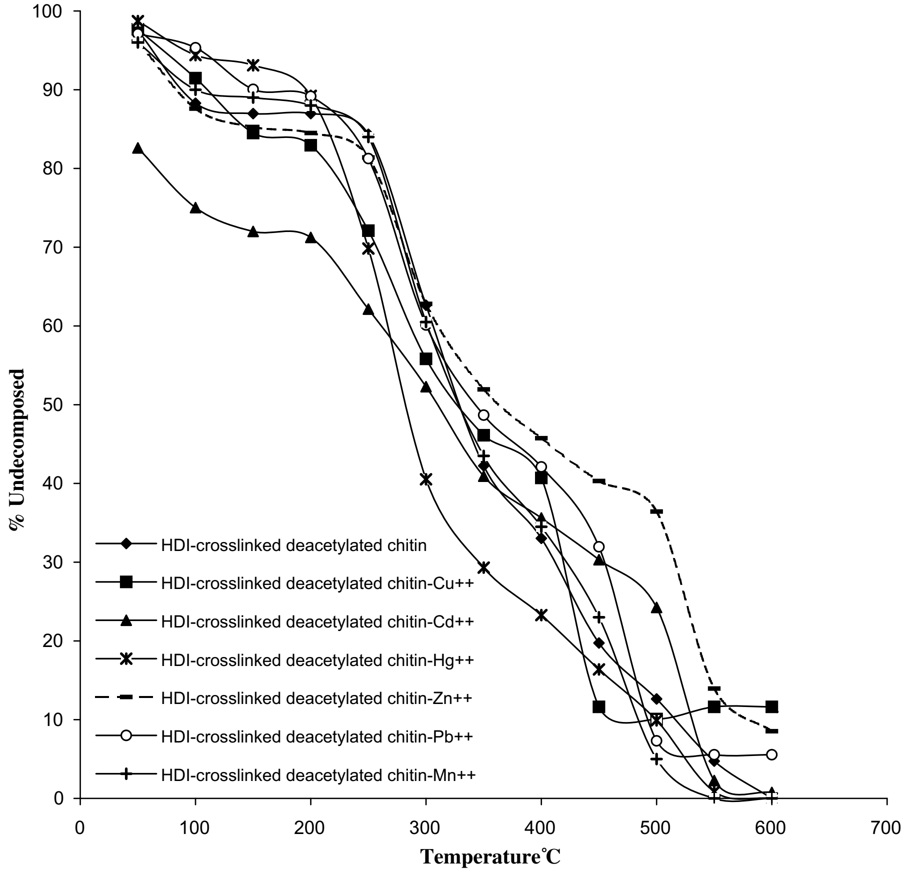

Fig. 4. TGA of HDI-crosslinked deacetylated chitin with metal ions.

ple 9, where the peak at 248 appears to contain both the minor peaks and therefore appears to be a major peak). Cd complexes have mostly two peaks in the DTG.

Zn, which is not bound strongly to chitosans, has two major peaks in the DTG at 275–285 and 525–548 °C (samples 25–30). Mn which is very weakly bound had one major peak (290–

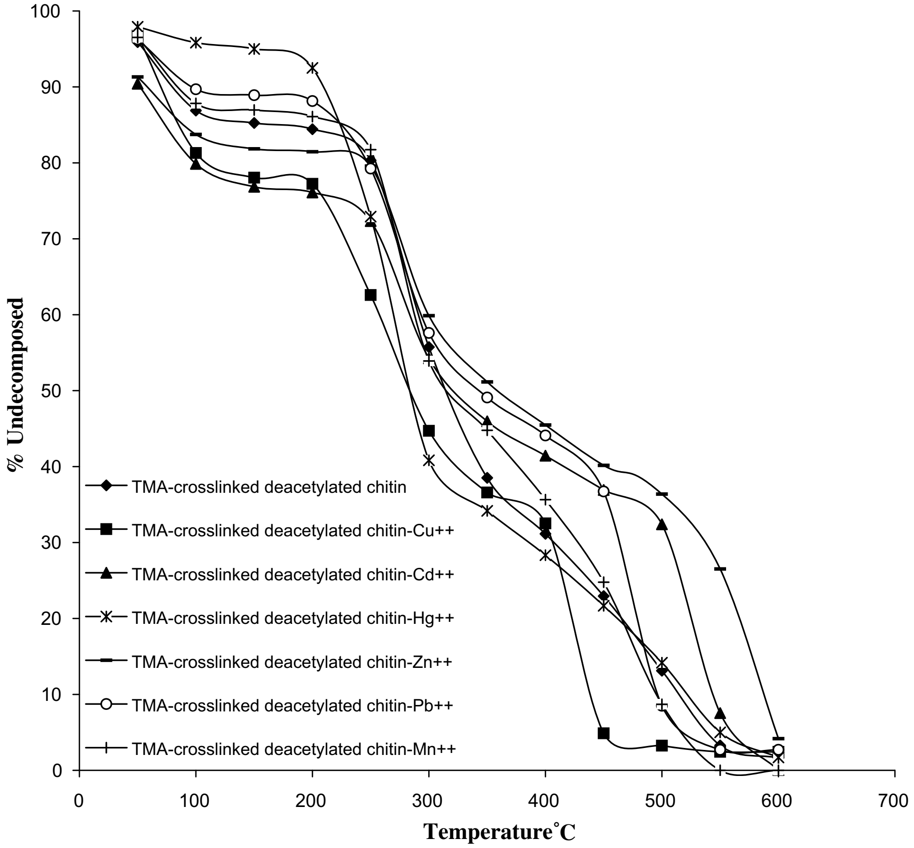

Fig. 5. TGA of TMA-crosslinked deacetylated chitin with metal ions.

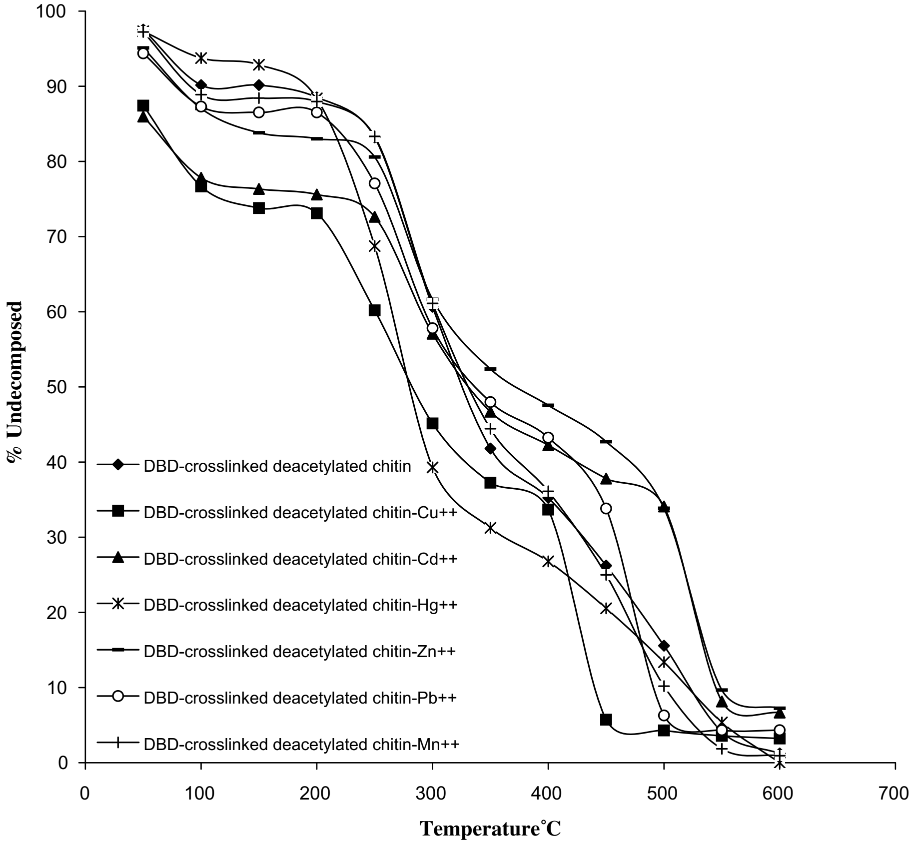

Fig. 6. TGA of DBD-crosslinked deacetylated chitin.

308 °C) and one minor peak (490–508 °C) (samples 31–36). Pb, which is strongly bound only to the surface (Trimukhe & Varma, 2008a), has two major peaks at 260–274 °C and 480–485 °C (samples 38–42), except for the uncrosslinked chitosan–Pb complex (sample 37) having only one peak at 485 °C. All these results correspond to the strength of binding and types of complexes formed with individual metal ions (Trimukhe & Varma, 2008a), and are also supported by both TGA as well as DTG results presented here.

Thus, the thermal behavior of homologous series of metals with chitosans can throw useful new light on the strength and type of metal complex, and whether the metal complex specifically uses the amino functional groups or not. It is well known that the amino group of chitosan has a stabilizing effect on the molecule, proved by the higher thermal stability of chitosan over chitin (Tirkistani, 1998b), therefore those metals which specifically tie up the amino functional groups, such as Cu and Hg ions, cause the maximum thermal instability. Metals which are bound only peripherally on the chitosan/crosslinked chitosan will have minimal effect on the thermal degradation behavior.

References

Bassi, R., Prasher, S. O., & Simpson, B. K. (2000). Removal of selected metal ions from aqueous solutions using chitosan flakes. *Separation Science and Technology, 35*(4), 547–560.

Beppu, M. M., Arruda, E. J., Vieira, R. S., & Santos, N. N. (2004). Adsorption of Cu(II) on porous chitosan membranes functionalized with histidine. *Journal of Membrane Science, 240*, 227–235.

Dobetti, L., & Delben, F. (1992). Binding of metal cations by N-carboxymethyl chitosans in water. *Carbohydrate Polymers, 18*(4), 273–282.

Domard, A., & Piron, E. (2000). Recent approach of metal binding by chitosan and derivatives. *Advances in Chitin science, 4*, 295–301.

Hong, P. Z., Li, S. D., Ou, C. Y., Li, C. P., Yang, L., & Zhang, C. H. (2007). Thermogravimetric analysis of chitosan. *Journal of Applied Polymer Science, 105*, 547–551.

Juang, R. S., Wu, F. C., & Tseng, R. L. (2002). Use of chemically modified chitosan beads for sorption and enzyme immobilization. *Advances in Environmental Research, 6*, 171–177.

Li, H. B., Chen, Y. Y., & Liu, S. L. (2003). Synthesis, characterization, and metal ions adsorption properties of chitosan-calixarenes (I). *Journal of Applied Polymer Science, 89*, 1139–1144.

Merrifield, J. D., Davids, W. M., MacRae, J. D., & Amirbahman, A. (2004). Uptake of mercury by thiol-grafted chitosan gel beads. *Water Research, 38*, 3132–3138.

Neto, C. G. T., Giacometti, J. A., Job, A. E., Ferreira, F. C., Fonseca, J. L. C., & Pereira, M. R. (2005). Thermal analysis of chitosan based networks. *Carbohydrate Polymers, 62*, 97–103.

Qu, X., Wirsen, A., & Albertsson, A. C. (2000). Effect of lactic/glycolic acid side chains on the thermal degradation kinetics of chitosan derivatives. *Polymer, 41*, 4841–4847.

Rhazi, M., Desbrieres, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A., & El Meray, M. (2002). Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste. *European Polymer Journal, 38*(8), 1523–1530 (English).

Schmuhl, R., Krieg, H. M., & Keizer, K. (2001). Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies. *Water SA, 27*(1), 1–7.

Taboada, E., Cabrera, G., & Cardenas, G. (2003). Retention capacity of chitosan for copper and mercury ions. *Journal of the Chilean Chemical Society, 48*(1), 7–12.

Tan, S., Wang, Y., Peng, C., & Tang, Y. (1999). Synthesis and adsorption properties for metal ions of crosslinked chitosan acetate crown ether. *Journal of Applied Polymer Science, 71*, 2069–2074.

Tirkistani, F. A. A. (1998a). Thermal analysis of chitosan modified by cyclic oxygenated compounds. *Polymer Degradation and Stability, 61*, 161–164.

Tirkistani, F. A. A. (1998b). Thermal analysis of some chitosan Schiff bases. *Polymer Degradation and Stability, 60*, 67–70.

Trimukhe, K. D., & Varma, A. J. (2008a). Complexation of heavy metals by crosslinked chitin and its deacetylated derivatives. *Carbohydrate Polymers, 71*, 66–73.

Trimukhe, K. D., & Varma, A. J. (2008b). A morphological study of heavy metal complexes of chitosan and crosslinked chitosans by SEM and WAXRD. *Carbohydrate Polymers, 71*, 698–702.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers, 55*, 77–93.