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Thermogravimetric Analysis of Chitosan: A Conceptual Review

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ABSTRACT

The present paper Reviews the thermalgravitational analysis of chitosan. Chitosan is derived from chitin. Chitin is most versatile biopolymer prepared from fish market waste. Government concern over the environment, the depletion of fossil fuels and climate change has promoted the development of biopolymers. Compared to polymeric resources from petroleum, natural polymers from renewable resources have the advantages of biodegradability, biocompatibility, non- toxicity,high reactivity, low cost and ease of availability. The proper utilization of sea food waste and fish market waste not only solves the problem of their disposal but also forms the basis for many potential products used in the fields such as textiles, photography, medicines, agriculture, food processing, Cosmetics etc. therefore, the aim of this investigation is to enhance the utilization of biopolymer and help to minimize the environmental pollution. The investigation of thermal properties of chitosan is required to understand the thermal behaviour of the chitosan. Thermal behaviour of the chitosan determines their fire performance and thermal stability, degradation temperature. Therefore we are working on thermo gravimetric analysis of Narmada Riverside Crab Shells based Chitosan

Keywords:— *Crab shell, chitin, chitosan, TGA, thermal investigation*

I. INTRODUCTION

Thermal properties of chitosan is to improve the fire performance and thermal stability also. Chitin is deacelyted to form chitosan. Chitin can be developed from outer shell of crustaceans and insects. Chitin is also being prepared from fungi, worms, diatoms, etc. [1, 2, 3, 4 and 5]. As a biopolymer chitin has the second place after cellulose [6]. Study on thermal behaviour of crab shell are reported [7, 8 ,9, 10, 11, and 12]. Chitin and chitosan have many important applications in engineering. Food technology, biomedicine, water engineering, agriculture, cosmetics, biotechnology, textile and paper industry, photography, solid state bettetries, chromatographic, ophthalmic technology etc. are the main application areas of chitin and chitosan [13]. chitin is also extracted from Nigerian origin [14 and 15] . Chitin can be prepared by chemical and biological methods. The chemical method has been widely reported [16, 17, 18, 19 and 20]. Chitin and chitosan also extracted from Narmada riverside crab shells [21]. Chitin has more applications when it is partially deacetylation under alkaline conditions [22, 23 and 24]. To prepare chitin and chitosan for the investigation of the thermal properties, generally, two processes are in practice, namely the chemical and biological process. In the exoskeleton tissue or crab shell, protein and chitin combine to form a protein-chitin matrix, which is then extensively calcified to yield hard shells. [25]. A traditional method for the commercial preparation of chitin from crustacean shell consists of two basic steps (a) protein separation i.e. deproteinisation by alkali treatment, and (b) calcium carbonate (calcium phosphate) separation, i.e. demineralization by acidic. Thermal analysis of chitosan [biopolymer] is done by measuring physical properties of the polymer as it is subjected to controlled temperature changes. Thermal analysis performed on condensed matter, specifically solids, glasses, liquids and solutions. Thermogravimetric analysis (TGA) is the most popular method for thermal analysis. Here the thermogravimetric analysis is widely practiced in the polymer and composites industries. Thermal properties are very important to end- use applications and to the processing methods used to make polymer products. There are a number of important thermal transitions that relate to processing. Many polymers degrade or depolymerise when they are heated 100°C or more above their processing temperature.

Thermogravimetric analysis (TGA or TG) is used to measure a variety of polymeric phenomena involving weight change. Typical phenomena include rate of sorption of gases; desorption of volatile contaminants (monomers, solvents, plasticizers and other additives) diffusion and permeation of gases; and polymer degradations in oxidative, inert and vacuum environments. Thermal testing has become easier with appearance of automated equipment for testing small sample. These systems speed the characterization of new and modified polymers, allowing efficient research and development as well as accurate production monitoring. The chemical composition tests are also important, although the chemical compositions of most materials sold commercially are well-known. TGA is useful in determining the composition of unknoun samples or verifying that the expected composition was achieved. They also can be very helpful in identifying impurities, side reactions and additives that can have a big effect on performance properties. TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a material is thermally stable. There will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material beyond this temperature the material will begin to degrade. TGA is used in the analysis of ceramics and thermally stable polymers. Ceramics usually melt before they decompose as they are thermally stable over a large temperature range, thus TGA is mainly used to investigate the thermal stability of polymers. Most polymer melt or degrade before 200°C. however, there is a class of thermally stable polymers that are able to withstand temperature of at least 300°C in air and 500°C in inert gases without structural changes or strength loss, which can analyzed by TGA. Presently we are working on thermal investigation of chitosan prepared from Narmada Riverside Crab Shell.

II. RESEARCH CONTRIBUTIONS FROM RESEARCHERS

Following are the details of research contributions from different researchers in the field of thermogravimetric analysis of chitosan.

2.1 Contributions of Researchers

Diab et al.[28]. According to researcher, thermal study of chitosan. N-(phenylacety) chitosan (NPAC) polymer was synthesized by reaction of phenylacetic acid with chitosan. The chemical structure of the formed polymer was characterized by IR and microanalysis. themogravimetric analysis revealed that the thermal stability of the NPAC polymer was less than that of chitosan, the products of NPAC thermal degradation were identified by the GCMS technique. The TG and DTG curve of chitosan are shown in figure 1. these are two degradation stages in chitosan polimer. In the first stage, weight loss starts at 220°C and continues to 320 with 50% weight loss. The maximum rate of weight loss, shown by the derivative of the curved at 295°C. the second stage reaches a maximum at 470°C with a weight loss percentage of 25%.

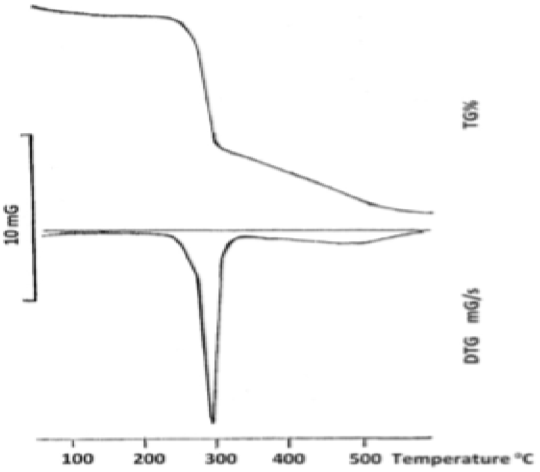


Figure. 1. TG and DTG curves of chitosan

Diab et al. [26] , According to researcher, thermal stability and degradation of chitosan modified by cinnamic acid .the reaction of chitosan with cinnamic acid gave the corresponding N-cinnamoyl chitosan (NCC) polymer. the TG cure of chitosan is shown in figure-2 there are two degradation stages in chitosan polymer. In the first stage, weight loss starts at -220°C and continues to -320°C with -50% weight loss. The maximum rate of weight loss. Shown by derivative equipment associated with TG apparatus. Occurs at -295.C. the second stage reaches a maximum at -470°C with a weight loss percentage of -40%. There are two degradation stages in NCC polymer as shown in figure 3. The first stage starts at-145°C with a weight loss percentage of -50%. The maximum rate of weight loss at -360°C with a weight loss percentage of -44%. TG curves of NCC and chitosan polymer reveal that chitosan is more thermally stable than NCC polymer.

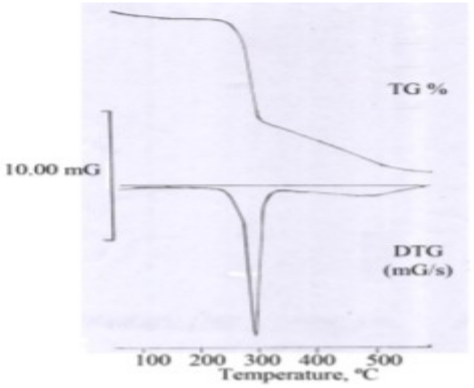


Figure 2. TG curve of chitosan

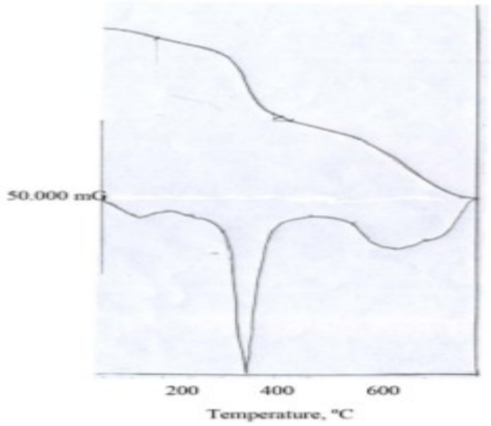


Figure 3. TG curve of NCC polymer.

Zakaria et al. (30), worked on effect of degree of deacetylation of chitosan on thermal stability and compatibility of chitosan polyamide blend, from thermogravimetric analysis (TGA) curves figure 3, it was observed that chitosan showed two steps of degradation (figure 6E). the initial degradation occurred at around 30 to 100°C and displayed 22.33% weight loss. This degradation may correspond to a loss of adsorbed and bound water (Gonzalez et al. 2000; yeh et al. 2006) . the chitosan has a greater capability to form hydrogen bonding as compared to chitin, and chitosan will be more hygroscopic when blended with other materials (Gonzalez et al. 2000). This means that the initial decomposition around 100°C can be attributed to the strong water-adsorptive nature of chitosan. Table 4 displays the degradation temperature and char residue of CS, PA66, and CS/PA66 blends. The second stage of degradation occurred at 210.8°C and continued up to 370.8° C. there was 32.06% weight loss occurring in the second stage due to degradation of chitosan polymer, and the temperature at which maximum degradation occurred (T_{MAX}) was 280.8°C .

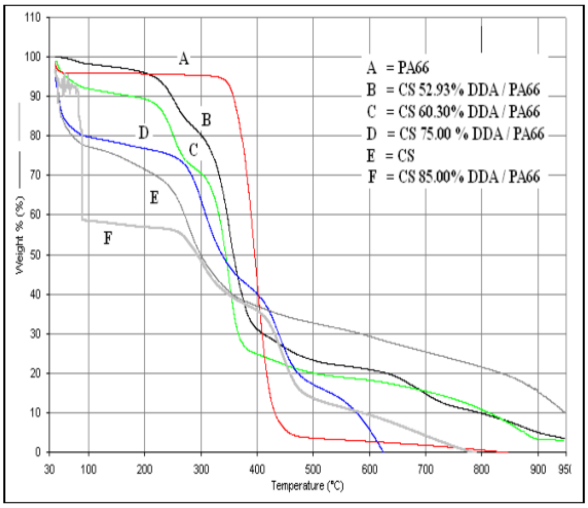


Figure 4. TGA Curve for Chitosan, Polyamide66, and CS/PA66

P.Dhawade and Ramanand N. Jagtap [31], According to the researcher, characterization of the glass transition temperature of chitosan and its oligomsers by temperature modulated differential scanning calorimetry, in differential scanning calorimetry (DSC) remnant moisture loss in sample often overlaps and distort thermal events such as glass transitions. TG curves of chitosan and its oligomers are shown in figure 5. The first stage begins at 80°C with weight loss of 6% . the second stage starts at 260°C and reaches maximum at 380°C with weight loss of 54%. The weight remains after 500°C is 40%. The first stage starts at 60°C with weight loss of 6% for chitosan due to the loss of water . whereas the water loss in oligomers is more during thermal analysis which infers that their thermal stability is less as compared to chitosan. Even from the second stage of thermal analysis it can be observed that weight loss is more as molecular weight decreases.

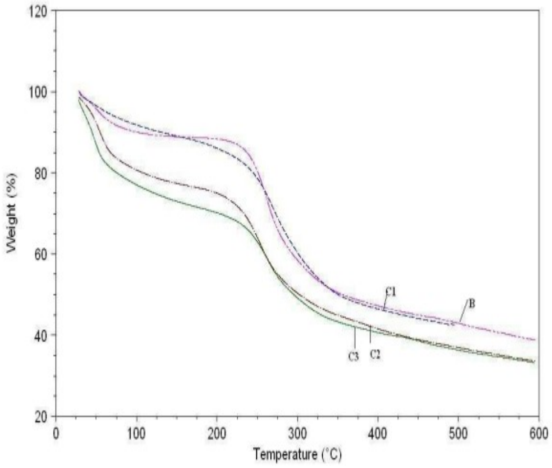


Figure 5. Thermogravimetric Graphs of Pure Chitosan (B) and its Oligomers C_1, C_2 and C_3)

Sanjiv arora et al.[29], revealed that cellulose, chitin and chitosan are the most abundant biopolymer on earth and constitute an important class of biodegradable materials. The decomposition of three major biopolymers viz. chitin, chitosan, and cellulose are studied using simultaneous thermal analysis i.e. thermogravimetry/differential thermal analyzer. Thermal analysis is performed from ambient temperature to 700^{o}C in a flowing nitrogen medium at four different linear heating rates i. e. 2.5, 5, 10 and 20^{o}C /min. thermal stability order of the three biopolymers based on TG followed the order; cellulose> chitin> chitosan.TG curves for chitin, chitosan and cellulose at different heating rates in nitrogen atmosphere are shown in figure, 6-8. The shapes of TG curves are quite similar shifting toward higher temperatures at higher heating rates. The initial decomposition temperature of chitin, chitosan and cellulose are 276.4, 254.6 and 312.9^{o}C and char yield are 20.4, 38.4 and 9.1 at 600^{o}C, respectively. On the basis of Ti, the thermal stability on samples follows the order; cellulose> chitin> chitosan (figure-4).

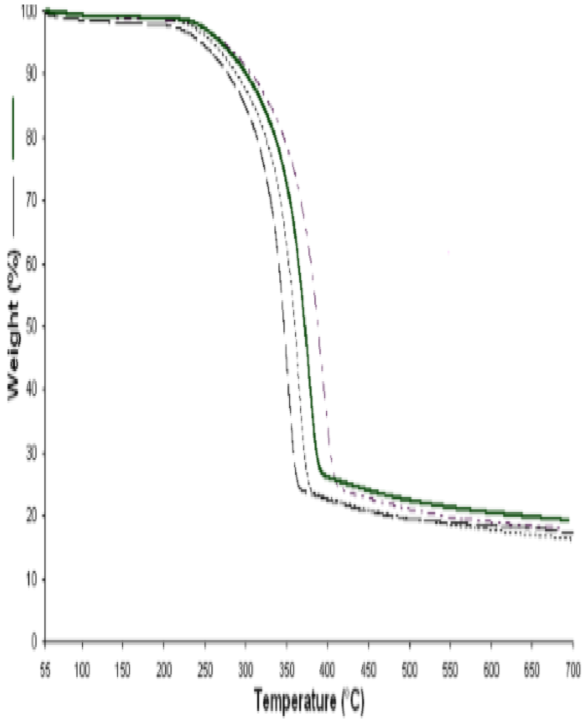


Figure 6: TG curve of chitin at heating rates of (-----) 2.5, (…….)5,(-------)10and (…..)20^{o}Cms

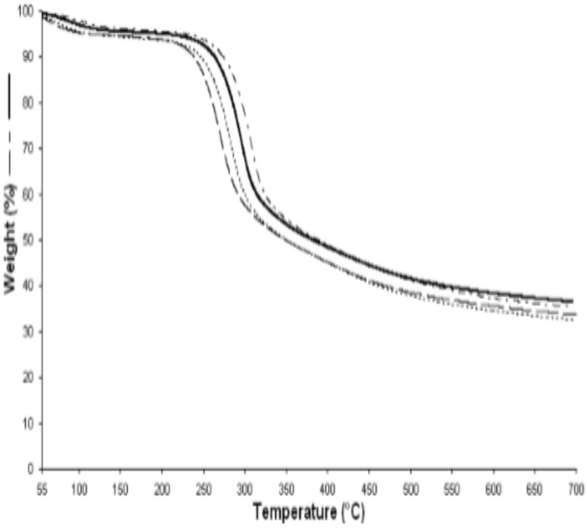


Figure 7: TG curve of chitosan at heating rates of (-----) 2.5, (…….)5,(-------)10and (…..)20^{o}Cmin^{1}

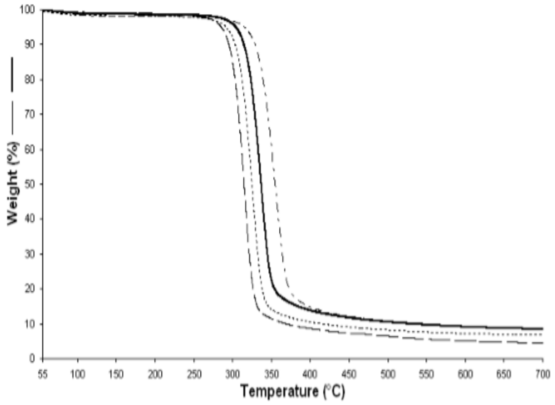


Figure 8: TG curve of cellulose at heating rates of (----) 2.5, (…….)5,(-------)10and (…..)20^{o}Cmin^{1}

A. Nada et al. [32], worked on infrared spectroscopy and thermal analysis of chitosan and its derivatives, chitosan was prepared from crab shell. Different derivatives of chitosan e.g. phosphate, cyanoethyl and carboxymethyl chitosan etric curves of chitosan and its derivatives were shown in figure 9 . after initial loss of moisture at 373-393 K, another loss of weight was carried out. This loss in chitosan and its derivatives was occurred at minor decomposition reaction at 453, 473, 483, and 526K for chitosan, phosphorylated, carboxymethylated, and cyanoethylated chitosan respectively. So the lose in weight % of chitosan itself. This can be attributed to the degradation of chitosan during the reaction of chitosan with different chemicals for incorporation of different function groups. Also the higher lose in weight of phosphorylated and cyanoethylated chitosan is due to the higher minor decomposition temperature. This lose in weight is due to the actual pyrolysis. On the other hand, a major decomposition temperature was proceeded at 553, 753, 743, 603, and 733K for chitosan phosphorylated, carboxymethylated, and chitosan respectively. The lose in weight at these major decomposition temperature was 54, 60, 60 and 75% for chitosan. phosphorylated, carboxymethylated and cyanoethylated chitosan respectively .

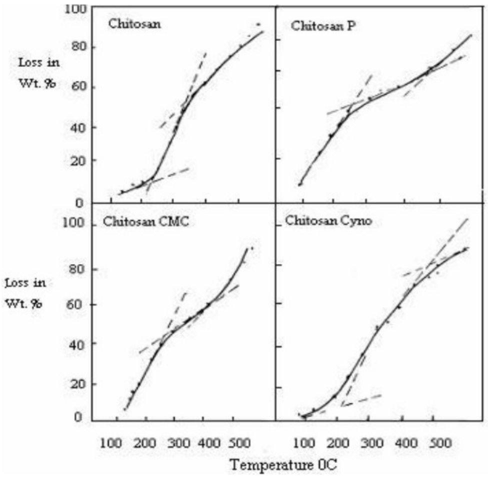
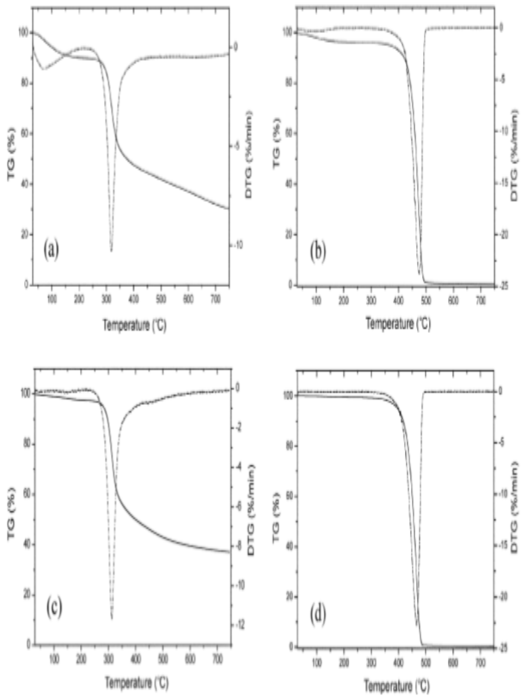


Figure 9: thermogravimetric analysis of chitosan and its derivatives

Liao and hung[27] did a kinetic study of thermal degradations of chitosan / polycaprolactam blends. They have used FT -IR spectra to explain the effects of hydrogen bonding between chitosan and polycaprolactam (PA6). A dynamic mechanical analysis study suggested that the optimum chitosan and PA6 miscibility under the conditions of this experiment were obtained at a blending ratio of 40:60. They studied the thermal degradation of chitosan blended with PA6 by thermogravimetric analysis and kinetic analysis (by the ozawa method). Dry chitosan and PA6 exhibited a single stage of thermal degradation and chitosan/PA6 blends having>20 wt% PA6 exhibited at least two stages of degradation . Chitosan and polycaprolactam (PA6) possess polar groups, so the water is adsorbed onto the polymers while hydrogen bond forming. As the temperature from 30 reach to 120°C, the TG curve indicated a degreed of 12 wt% weight loss of chitosan, implying the presence of water, the weight loss of PA6 was about 4wt% as indicated figure 10(a) and 10(b), following the loss of water, chitosan and PA6 underwent the primery stage of degradation. The primary degradation of chitosan started at about 295°C and completely degraded at about 720°C. after chitosan and PA6 polymers dried at 100°C for 10 min, the TG curves indicated no weight loss of water. As shown in figure 10(c) and (d).

Figure 10. TG and DTG



curve of (a) wet chitosan obtained at a heating rate of 10°C/ min in an atmosphere of nitrogen, (c) dry chitosan at a heating rate of 10°C/min in an atmosphere of nitrogen

Table 1 : Temperature Breaks And Weight Loss of Chitosan in Thermal Gravimetric Analysis (TGA/TG)

S.No	Researchers	1st Degradation		2nd Degradation	
		T(OC)	Weight Loss(%)	T (OC)	Weight Loss (%)
1	Diab et al.(2013)	220-320	50	295-470	25
2	Diab et al.(2012)	220 -320	50	295-470	40
3	Zainoha zakaria et al.(2012)	30-100	22.33	210-370	32.06
4	P.Dhawade and Jagtap (2012)	80	6	260-280	54
5	Sanjiv arora et al.(2011)	254.6-296.3	38.4	270-337	----------
6	A.M.A. Nada et al.(2006)	100-180	14	280	54
7	Liao and hung(2004)	30-120	12	295-720	-------

2.2 Gaps in the research and objectives of proposed research

On the basis of literature survey, following research gaps are being investigated.

1. To the best of our knowledge, there is very limited research based on Investigation of Thermal Properties of chitosan.
2. There is very limited research on biopolymers like chitin and chitosan.

On the basis of above mentioned research gaps, following objectives of the new research are being formulated.

Following are the objectives of the research;

1. To investigation the thermal properties of Narmada riverside crab shell based chitosan.
2. To develop the new novel bio-polymer
3. To analyze the effect of temperature changes on thermal characteristics of chitosan.

III. CONCLUSIONS

The present paper reviewed the thermo gravimetric weight loss of chitosan on the rate of degradation processes by various researchers which took place under the influence of low or at high temperature. Thermal analysis technique (TGA/TG) was used to understand the basic theory and thermal degradation of chitosan and other derivatives. On the basis of first stage and second stage thermal decomposition temperature calculated from TGA curves, the thermal stability of samples follows order; cellulose > chitin > chitosan. Chitosan powder is a stable material at room temperature, although it is hygroscopic after drying. weight loss of chitosan show the results that the process of the polymer thermodegradation depends on its DD value. The most susceptible to therlmal degradation appears to be the sample of the highest DD (unstable amine group), with increasing temperature from 100°C to 200°C more intensive changes of chitosan relative weight are observed.

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