Thermal studies on natural polysaccharide

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ABSTRACT

Objective: To characterize thermal property of natural gums obtained from the seeds of Diospyros melonoxylon (D. melonoxylon) Roxb., Buchanania lanzan (B. lanzan) spreng and Manilkara zapota (M. zapota) (Linn.). P. Royen syn. Methods: Natural gums were thermally characterized using differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermo–gravimetric analysis (TGA) under nitrogen atmosphere. Major thermal transitions as well as activation energies of the major decomposition stages were determined. Elemental analysis was performed in order to determine the composition of carbon, hydrogen, nitrogen and sulfur. Results: DSC traces indicated a major intense exothermic transition (around 200 °C) followed by weaker exotherm(s). Thermogravimetric analysis showed two phase of weight loss. The first phase has minor weight loss in samples is attributed to the loss of adsorbed and structural water of biopolymers or due to desorption of moisture as hydrogen bound water to the saccharide structure. The second weight loss event may be attributed to the polysaccharide decomposition. The initial decomposition temperature (IDT) was calculated from thermograms obtained of TGA, seed Polysaccharide of D. melonoxylon (IDT 221.21 °C), B. lanzan (IPDT 170.4 °C) and M. zapota (IPDT 178.6 °C) were obtained. According to the integral procedural decomposition temperature (IPDT) values calculated based on the TGA thermograms; D. melonoxylon (IPDT 563.3 °C), B. lanzan (IPDT 598.1 °C) and M. zapota (IPDT 600.6 °C) were obtained respectively. The elemental analysis study shows that the isolated natural Polysaccharides consist of certain percentage of carbon, nitrogen, sulphur and hydrogen in all the gums. Conclusions: The results of the present investigation reveal that the natural gums are thermally stable and these gums can be used as release modifiers in various dosage forms.

1. Introduction

Carbohydrates embrace more than 90% of the dry weight of all biomass, and more than 90% of the carbohydrate mass is in the form of carbohydrate polymers (polysaccharides)[1]. Since these biopolymers are copious, come from renewable sources, are relatively inexpensive, are non–toxic, and are amenable to both chemical and biochemical modification, it is not astonishing that they find pervasive and extensive use. For instance, the annual industrial depletion of polysaccharides in the US is ca. 3 000 000 tons with a growth rate of 3% per year. The value of this market is more than 3 trillion dollars[1]. The term ‘gum’ most often specifically denotes a group of industrially useful polysaccharides (glycans) or their derivatives that hydrate in hot or cold water to form viscous solutions or dispersions at low concentrations[2]. When used in foods, gums are sometimes referred to as hydrocolloids[1]. Gums are classified as natural and modified gum[3]. Natural gums include seaweed extracts (e.g. alginates), plant exudates (e.g. Arabic and Tragacanth gums), gums from seed or root (e.g. potato starch), and gums obtained by microbial fermentation (e.g. gum xanthan).

Modified gums include mostly cellulose and starch derivatives, such as ethers and esters of cellulose. Owing to the salable usefulness of gums, physicochemical characterization of these polysaccharides is of substantial importance. According to a literature criticism, no systematic proportional study has been conducted on thermal
characterization of some natural gums obtained from the seed of Diospyros meloxyylon (D. meloxyylon), Buchanania lanzan (B. lanzan) and Manilkara zapota (M. zapota). Capacious studies in this field are mostly focused on cellulose, starch and some of their convenient derivatives[4,5].

The present article deals with thermal characterization of various industrial gums using differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermo-gravimetric analysis (TGA) and elemental composition i.e. carbon, hydrogen, nitrogen and sulfur (CHNS). The thermal stability and transitions were investigated and activation energies of the corresponding thermal degradation were premeditated.

2. Materials and methods

2.1. Materials

Gums were isolated from the seed Polysaccharide of D. meloxyylon (PDM), B. lanzan (PBL) and M. zapota (PMZ), Following AOAC guide line, obtained from the forest of Korba, Chhattisgarh, India. General specifications of the natural polysaccharides are summarized in Table 1.

2.2. Thermal analysis

DSC analysis for various Polysaccharides was performed using a Mettler Toledo Star System, Columbus, USA. Accurately weighed (5 mg) samples were placed into platinum cups and sealed. The temperature range was from 0 to 300 °C under N atmosphere at a heating rate of 10 °C/min[6,7]. Simultaneous thermal analyzer (Stapt-1600, Linseis Germany) was used for DTA and TGA. Derivatograms of the TGA curves (DTG) were also recorded. The thermal analyses were accomplished under atmosphere at a flow rate of 10 mL/min. The heating rate was 15 °C/min till 900 °C. Thermal stability behavior can be investigated in both conditions.

1. Dynamic, in which the temperature is increased at a linear rate
2. Isothermal, in which the temperature is kept constant[7,8].

2.3. Elemental composition (CHNS) and heavy metal analysis of polysaccharides

Elemental composition (CHNS) were analyzed by using elemental analyzer (Elemental, Vario E.L, Hanau Germany). Accurately weighed 0.5 g of sample was heated to 1 150 °C and corresponding element was determined by using elemental analyzer[9-14].

3. Results

Table 1.

General specifications of the natural polysaccharides used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PDM</th>
<th>PBL</th>
<th>PMZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Reddish brown</td>
<td>Off white</td>
<td>Brown</td>
</tr>
<tr>
<td>Solubility</td>
<td>Warm H₂O</td>
<td>Warm H₂O</td>
<td>Warm H₂O</td>
</tr>
<tr>
<td>Swelling index</td>
<td>32.17</td>
<td>67.20</td>
<td>16.00</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>219.1</td>
<td>112.9</td>
<td>234.6</td>
</tr>
<tr>
<td>Microbial count</td>
<td>Bacteria: -ve</td>
<td>Fungi: -ve</td>
<td>Fungi: -ve</td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
<td>6.5</td>
<td>6.8</td>
</tr>
<tr>
<td>Melting point</td>
<td>170.4</td>
<td>75.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Charring (°C)</td>
<td>86.0</td>
<td>103.1</td>
<td>159.2</td>
</tr>
<tr>
<td>Loss on drying (%)</td>
<td>6.48</td>
<td>5.00</td>
<td>2.88</td>
</tr>
</tbody>
</table>


Table 2.

Technological TGA characterization of polysaccharides.

<table>
<thead>
<tr>
<th>Mucilage</th>
<th>Decomposition stage</th>
<th>Temperature range (°C)</th>
<th>DTG peak (°C)</th>
<th>Enthalpy (J/g)</th>
<th>Heat change (VVs/mg)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDM</td>
<td>1</td>
<td>221.2 – 334.7</td>
<td>70.1</td>
<td>−177.720</td>
<td>−54.495</td>
<td>36.57</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>334.7 – 394.3</td>
<td>304.7</td>
<td>225.865</td>
<td>109.387</td>
<td>6.64</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>394.3 – 563.3</td>
<td>475.4</td>
<td>7641.322</td>
<td>2483.341</td>
<td>31.99</td>
</tr>
<tr>
<td>PBL</td>
<td>1</td>
<td>170.4 – 367.8</td>
<td>352.6</td>
<td>3641.322</td>
<td>237.968</td>
<td>40.55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>367.8 – 698.1</td>
<td>506.8</td>
<td>1845.965</td>
<td>423.308</td>
<td>33.09</td>
</tr>
<tr>
<td>PMZ</td>
<td>1</td>
<td>178.6 – 359.7</td>
<td>350.3</td>
<td>315.873</td>
<td>138.435</td>
<td>41.17</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>359.7 – 600.6</td>
<td>614.4</td>
<td>3624.787</td>
<td>1082.215</td>
<td>30.06</td>
</tr>
</tbody>
</table>


Table 3.

Technological thermal stability characterization of polysaccharides

<table>
<thead>
<tr>
<th>Mucilage</th>
<th>IDT a (°C)</th>
<th>IPDT b (°C)</th>
<th>Char yield at 900 °C (%)</th>
<th>Overall Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDM</td>
<td>221.2</td>
<td>563.3</td>
<td>91.9</td>
<td>75.36</td>
</tr>
<tr>
<td>PBL</td>
<td>170.4</td>
<td>598.1</td>
<td>86.8</td>
<td>73.77</td>
</tr>
<tr>
<td>PMZ</td>
<td>178.6</td>
<td>600.6</td>
<td>88.2</td>
<td>71.20</td>
</tr>
</tbody>
</table>

*aInitial decomposition temperature (TGA curve on-set); bIntegral procedural decomposition temperature. PDM: Polysaccharides of D. meloxyylon; PBL: Polysaccharides of B. lanzan and PMZ: Polysaccharides of M. zapota.
Table 4.
Technological CHNS & heavy metal characterization of polysaccharides.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>WC/N</th>
<th>S (mg/kg)</th>
<th>Arsenic</th>
<th>Lead</th>
<th>Cadmium</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDM</td>
<td>78.8</td>
<td>12.2</td>
<td>0.63</td>
<td>124.290</td>
<td>681</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBL</td>
<td>4.3</td>
<td>80.7</td>
<td>10.10</td>
<td>0.428</td>
<td>1319</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PMZ</td>
<td>80.9</td>
<td>10.1</td>
<td>1.58</td>
<td>51.202</td>
<td>512</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: Not detectable. PDM: Polysaccharides of *D. melo*xylon; PBL: Polysaccharides of *B. lanzan* and PMZ: Polysaccharides of *M. zapota*.

Figure 1. Differential scanning calorimetry (DSC) Characterization of PDM, PBL and PMZ.

Figure 2. Differential thermal analysis (DTA) Characterization of PDM, PBL and PMZ.

Figure 3. Thermo gravimetric analysis (TGA) characterization of PDM.

Figure 4. Thermo gravimetric analysis (TGA) characterization of PBL.
3.1. Differential scanning calorimeter and differential thermal analysis

DSC and DTA has emerged as powerful physical tools to monitor physical and chemical changes that occur in the Polysaccharide during thermal processing and these methods yield curves that are unique for a given Polysaccharide. The outcome of DSC and DTA analysis of PDM, PBL and PMZ reveals the transition temperature to be 78 °C, 89 °C and 138 °C. Figure 1 and 2 shows the DSC and DTA curve of the gum.

3.2. Thermo–gravimetry analysis

TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of polymers. Table 2 gives the details of thermal behavior according to the primary thermograms and derivative thermograms of mucilage’s. The representative plot results of thermo gravimetric analysis carried out on the mucilage’s under lean oxygen (5% oxygen in nitrogen) atmosphere are shown in Table 3 and Figure 3, 4 & 5.

3.3. Elemental composition (CHNS) and heavy metal analysis of polysaccharides

The results of CHNS and heavy metal Characterization tabulated in Table 4. From the elemental analysis a general molecular formula (C\textsubscript{n}H\textsubscript{i})\textsubscript{NS}, (CH\textsubscript{n})\textsubscript{NS} and (C\textsubscript{n}H\textsubscript{i})\textsubscript{NS} respectively for PDM, PBL and PMZ respectively derived.

4. Discussion

Structural and functional group differences in polysaccharide gums influence the thermal behavior and affect the transition temperature. The major intense peak recorded in the DSC and DTA thermograms is an endothermic transitions (at around 200 °C) followed by weaker exotherm(s). Generally, dehydration, depolymerization and pyrolytic decomposition are involved in these high temperature stages resulted in the formation of H\textsubscript{2}O, CO and CH\textsubscript{4}. However, because of the difference in structures and functional groups, either the degradation routes or the resulting fragments will be different. The most of polysaccharides are comprised of carboxylate or carboxylic acid functional groups. Therefore, thermal scission of the carboxylate groups and evolution of CO\textsubscript{2} from the corresponding carbohydrate backbone may be a probable mechanism for the thermal transitions. Accurate assigning of the thermal transitions is very difficult\cite{15}.

The details of thermal behavior and thermal stability data according to the primary thermograms and derivative thermograms for the gum show that heating at a rate of 10 °C per min from 0 °C to a maximum of 900 °C results in two mass loss events. The early minor weight loss in samples is attributed is attributed to the loss of adsorbed and structural water of biopolymers as related\cite{15,16}, or due to desorption of moisture as hydrogen bound water to the saccharide structure. The second weight loss event may be attributed to the polysaccharide decomposition\cite{8,17} and is described by a weight loss. The weight loss onset (representing the onset of oxidation or decomposition) of suggests that Polysaccharide good thermal stability.

The elemental analysis study shows that the isolated natural Polysaccharides consists of certain percentage of carbon, nitrogen, sulphur and hydrogen in PDM, PBL and PMZ, possibly suggests the presence
of S-containing protein amino acids like cysteine, also conforms the formation of bond (primary strong covalent bonds, weak secondary hydrogen bond and Vander Waal’s forces) of polysaccharides with mucosa in a short duration of time in case of mucoadhesive drug delivery system.

In this paper, thermal characteristics of various industrial gums are reported. The different polysaccharides exhibit different thermal behavior due to structural and functional group differences. PDM shows the highest initial decomposition temperature, it exhibits a fast degradation (low Ea) to yield char residue at 900 °C (75.36%). In contrast, PDM and PBL start to decompose slowly at 250-280 °C and produce high char (86.8% and 88.2%) at the final temperature.

According to the values of integral procedural decomposition temperature (IPDT) calculated based on the TGA curves, the overall thermal stability of the investigated gums may be concluded to be in order. The elemental composition indicates that Polysaccharides can be used in mucoadhesive drug delivery system as it contains the sulfur and hydrogen in abundant quantity.

Conflict of interest statement

We declare that we don’t have conflict of interest.

Acknowledgement

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References