Thermal Stability of Biodegradable Plastic Films Produced Using Clay from Pyata, Niger State

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Abstract:- The biodegradable polymers from renewable resources to substitute synthetic polymer products has provided opportunities for the reduction of waste via biological recycling. Starch-based biodegradable composite (plastic) films of varied compositions were prepared using casting techniques. The composite films were characterized for thermal stability using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The TGA results indicated that the sample with glycerol, starch and clay of 17.50 wt. %, 70.00 wt. % and 12.50 wt.% respectively was the most thermally stable, having an onset degradation temperature of 245.68°C and a maximum degradation temperature of 277.96°C. The DSC of the films revealed that the sample also has the highest melting temperature of 119.47°C and a corresponding enthalpy of 163.64 J/g. The films produced can be used for packaging.

Keywords:- Cassava Starch, Clay, Glycerol, Composite Films, Biodegradable.

I. INTRODUCTION

The biodegradable polymers from renewable resources have paved ways for reducing waste through biological recycling to the biosystem (Mishra et al., 2011). Biodegradable polymers synthesized from natural and renewable raw materials decomposed easily by microorganism. They are better alternative for replacement of environmentally unfriendly synthetic polymer. Starch is one of the most studied biodegradable polymers due to its abundant in nature and low cost (Toraleit., 2002, Fariaet al., 2012). For instance, starch as biodegradable polymer is vastly studied as a result of its high availability in nature and effective cost. (Oyaet al., 2000). Starch is completely biodegradable in soil and water, effectively used as packaging material because it is non-expensive and exhibits fast biodegradability (Oyo et al., 2000). Poor melting properties and high viscosity inhibit the processing of starch. Furthermore, products made from starch are hydrophilic and brittle (Bhattacharya, 1998). To overcome this setbacks, modification of starch unto composite form is welcoming (Abdul-Hatiz, 1997).

However, owning to its poor thermal and mechanical properties, starch films are compounded with fillers, especially clay to overcome the shortcomings. During composite formation, the clay is uniformly dispersed in the polymer matrix using in-situ polymerization, melt intercalation or intercalation from solution methods (Giannelis, 1996). In this study, clay from Pyata, Niger State, Nigeria, was used as filler in the production of biodegradable plastic films for consideration in packaging.

II. MATERIALS

The cassava tubers were purchased from Kure ultra-Modern Market, Minna, Niger State. Clay material was obtained from Pyata village, Minna and glycerol (plasticizer) was obtained from Chemistry laboratory, Federal University of Technology, Minna.

III. METHODS

3.1 Starch Extraction

Starch was extracted from cassava as demonstrated by Adejumo et al. (2011).

3.2 Mineral Clay Processing

The raw clay samples were wet refined by sieving in water slurry to remove impurities and particles. The clay was oven-dried at 110 °C for 4 h and ground using mortar and pestle. The sample was sieved using 200 BSS (75.0 µm) sieve. The sieved samples was used prior to analysis.

3.3 Preparation of Starch/clay Biodegradable Film

Different masses of dried cassava starch were dissolved in 15 cm\(^3\) of distilled water. The mixture was heated at 70-80 °C for 2 min and stirred using a magnetic stirrer. The dried clay was dispersed in 10 cm\(^3\) of distilled water and the suspension was added to the aforementioned starch solution. To the solution, glycerol was added while the heating continued at 70-80 °C for the stirring speed for further 1 min. The mixture was casted in a plastic petri dish and then oven-dried at 50 °C for 10 h to obtain starch/clay composite film. The formulations of the biodegradable plastic films are shown thus:
Table 1.0: Formulation of Biodegradable plastic Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glycerol (Constituents wt. %)</th>
<th>Starch</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCF1</td>
<td>25.00</td>
<td>70.00</td>
<td>05.00</td>
</tr>
<tr>
<td>BCF2</td>
<td>20.00</td>
<td>70.00</td>
<td>10.00</td>
</tr>
<tr>
<td>BCF3</td>
<td>17.50</td>
<td>70.00</td>
<td>12.50</td>
</tr>
<tr>
<td>BCF4</td>
<td>10.00</td>
<td>70.00</td>
<td>20.00</td>
</tr>
<tr>
<td>BCF5</td>
<td>17.50</td>
<td>77.50</td>
<td>05.00</td>
</tr>
<tr>
<td>BCF6</td>
<td>12.50</td>
<td>77.50</td>
<td>10.00</td>
</tr>
<tr>
<td>BCF7</td>
<td>10.00</td>
<td>77.50</td>
<td>12.50</td>
</tr>
</tbody>
</table>

3.4 Thermogravimetric Analysis (TGA)
The thermal stabilities of the biodegradable film specimens were carried out using thermogravimetric analysis at a heating rate of 10 °C/min in nitrogen atmosphere at a flow rate of 20 cm³/min and a temperature between 45 °C and 600 °C.

3.5 Differential Scanning Calorimetry (DSC)
The differential scanning calorimetry (DSC) was examined to measure the melting temperature (T_m) of biodegradable plastic films at operating conditions; mass of sample (7 mg), nitrogen purge at a flow rate of 20 cm³/min and heating rate (10 °C/min) from 60 to 300 °C.

IV. RESULT AND DISCUSSION

4.1 Thermal Analysis of the Biodegradable Plastic Films
The thermal stabilities of the polymer composites were monitored to determine the weight loss of the materials as a result of the formation of volatile compounds under degradation temperature. As shown in Fig. 4.1, the thermal decomposition of the films occurred in two steps which conforms to the thermal degradation phenomena of starch-based films as reported in literature (Sanyanget al., 2015; Dang and Yoksan, 2015).

Thermogravimetric analysis was conducted on the films to investigate the thermal stability. (Figure 4.1) showed the thermograms of different biodegradable plastic films. It was observed from the thermogram that, BCF3 with 17.50 wt.% glycerol, 70.00 wt.% starch and 12.50 wt.% clay relative to dried starch exhibited a major degradation step at 245.68 °C, indicated the degradation of starch and clay by breaking their polymer network. A minor degradation occurred at 184 °C for glycerol evaporation. The film lost minor weight near 100 °C which represented the loss of bound water from the film. The DTG curve showed one major peak with a total weight loss of 93.436% at 277.96 °C and a corresponding ash content of 6.564%. From the thermal analysis, it is quite clear that the BCF3 was stable up to 184 °C and degradation started at 245.68 °C.

Figure 4.1: Combined TG Thermogram of Biodegradable Plastic Films

BCF2 with 20.00 wt.% glycerol, 70.00 wt.% starch and 10.00 wt.% clay relative to dried starch showed a major degradation step at 208.12 °C, indicated the degradation of starch and clay by breaking their polymer network. A minor degradation occurred at 168 °C for glycerol evaporation. The film lost minor weight near 100 °C which represented the loss of bound water from the film. The DTG curve showed one major peak with a total weight loss of 93.436% at 275.10 °C and a corresponding ash content of 6.564%. It can be seen that BCF2 was stable up to 168 °C and degradation started at 208.12 °C. While BCF4 with 10.00 wt.% glycerol, 70.00 wt.% starch and 20.00 wt.% clay relative to dried starch indicated a major degradation step at 178.52 °C, for polymer network breakage. A minor degradation occurred at 102 °C for glycerol evaporation. The film lost minor weight near 100 °C. The DTG curve showed one major peak with a total weight loss of 99.821% at 269.61 °C and a corresponding ash content of 0.179%. BCF4 was stable up to 102 °C and degradation started at 178.52 °C. This supported the findings of Mittal (2007) who reported that introduction of clay in to polymeric matrices improves thermal stabilities.

Figure 4.2: Combined DTG Curves of Biodegradable Plastic Films.
This was attributed to the clay hindrance of permeability of volatile degradation products off the materials, thus delay the release of thermal degradation products (Mittal, 2007).

4.3 Differential Scanning Calorimetry (DSC)

DSC curves are presented in Figure 4.3 the result showed that, BCF3 with 17.50 wt. % glycerol, 70.00 wt.% starch and 12.50 wt.% clay relative to dried starch exhibited the highest melting temperature of 119.47 °C with an enthalpy of 163.64 J/g, BCF2 with 20.00 wt. % glycerol, 70.00 wt.% starch and 10.00 wt.% clay relative to dried starch that showed a melting temperature of 117.98 °C and a corresponding enthalpy of 154.72 J/g. The least was BCF4 with 10.00 wt. % glycerol, 70.00 wt.% starch and 20.00 wt.% clay relative to dried starch displayed a melting temperature of 63.76 °C with an enthalpy of 78.05 J/g. The formation of intercalated/exfoliated structure subdued the absorbance of water into the starch matrix, reducing free movement of the chains, therefore leading to an increase in the melting temperature (Tang et al., 2008).

![Figure 4.3: Combined DSC Endotherm of Biodegradable Plastic Films](image)

BCF3 with 12.50 wt.% clay and 17.50 wt.% glycerol indicates good dispersion in all clay filled samples in the polymeric matrix and improvement on the surface dispersion activity of clay. This resulted to high adhesion of the clay with the polymer chains, also promoting melting temperature of the composite. Thus, the energy required for any type of phase change increases with better dispersed clay filled samples.

V. CONCLUSION

Biodegradable plastic films were produced with different proportion of starch, clay and glycerol; their thermal stabilities were investigated using Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). From the results obtained, BCF3 with 17.50 wt. % glycerol, 70.00 wt.% starch and 12.50 wt.% clay relative to dried starch was the most thermally stable film, also displayed the highest melting temperature and a higher melting enthalpy. The biodegradable plastic films produced can be considered for packaging.

REFERENCES