INTRODUCTION
Polymers have attracted an immense research attention due to the wider range of their technical application in several fields. Some of the basic properties of polymers such as; exceptional processability and low production cost necessitate its use in several scientific applications [1, 2]. One of the drawbacks in the field of polymer technology is establishing the application means of such materials and yet, retaining the properties mentioned above. Polymers like Poly(vinyl pyrrolidone) (PVP) are water-soluble synthetically derived vinyl polymers with unique features such as the ability to readily dissolve in water and some organic solvents, considerable ability to react with a wider range of organic and inorganic compounds, non-toxicity to living tissues and biocompatibility.

IMPACT OF DIFFERENT ATMOSPHERIC CONDITIONS ON THE THERMAL DECOMPOSITION BEHAVIOUR OF POLY (VINYL PYRROLIDONE)

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Abstract

The thermal decomposition behaviours of poly (vinyl pyrrolidone) (PVP) was successfully studied using thermogravimetric analysis in the range of 30–1000 °C under different atmospheric condition of nitrogen, oxygen, air and finally at normal condition without passing any gas. Under all the conditions, it was found that the main decomposing agent in PVP is the volatile product from the ester group and the C–C in the polymeric chain. The decomposition under nitrogen atmosphere offers the lowest temperature of 500 °C, while the highest decomposition temperature of 625 °C was observed when the analysis was conducted under normal atmospheric condition. The decomposition under O₂ and air atmosphere recorded final stage at 514 and 568 °C, respectively. The amorphous structure of the PVP was confirmed by the XRD analysis while the FT–IR and Raman analyses were used to confirm the presence of several polymer bonds in the PVP.

PVP is used in the biomedical field as a medical additive or polymeric modifier, and also in food and cosmetics industries [3–6]. Most recently, PVP also plays a significant role as capping agent in the synthesis of semiconductors nanoparticles and magnetic nanocrystals [7–9]. In this instance, the metallic ions are entrapped by ionic–dipole interaction with an amine group in the polymeric chains. The system is followed by a mobility congealment of the metallic cations in the polymer cavity due to the removal of water by drying process [10]. There are limited researches or few findings on the thermal decomposition and degradation behaviors of PVP over the decade. Peniche et al. [11] attributed the formation of pyrrolidone as the main product of the thermal degradation of PVP. On the other hand, Bianco et al. [12] postulated the key volatile components in the thermal decomposition of PVP as those compounds with ester groups, ammonia (NH₃) and hydrocarbons (unsaturated structures). The formation of ester group was due to the scission of N–C=O bond and that of NH₃ depends on the existence of NH₂ groups which undoubtedly made by the protonation of the nitrogen atoms in the PVP [10, 11]. Bogatyrev et al. [13] have reported the thermal decomposition of the PVP to involve the breakdown of both main chains as well as side groups. This procedure comprises removal of the monomer units.
from the ends of the main chain and growing number of the break in the main chain. In this study, we have reported the influence of several gases on the thermal degradation pathways of PVP using thermogravimetry analysis.

**Experimental**

**Materials Preparation**
The Poly(vinyl pyrrolidone), PVP, ($M_w = 29000$ g/mol) used was purchased from Sigma-Aldrich. An aqueous solution was prepared by dissolving 4 g PVP in 100 ml of deionized water in a water bath using a magnetic stirrer. The solution was stirred at 70 °C for 2 h to achieve homogeneity. The PVP solution was placed into glass petri dish and dried at 80 °C for 24 h in an oven. The dried solid was crushed into a powder form. The powdered sample was characterized using various characterization techniques as follow.

**Characterization**
In this work, Thermal degradation of PVP was studied using a Diamond Pyris Perkin Elmer system. The system consists of a thermogravimetric analysis TGA/DTA coupled with Al₂O₃ powder as a reference material in a dynamic pure nitrogen, oxygen, and air atmospheric condition at constant flow rate of 50 ml/min on a temperature range between 30 to 1000 °C and a heating rate of 10°C/ min were used. The sample was also run with the same parameters mentioned above but at normal atmospheric condition only, without the passage of any gas. Thus, the effects of the atmospheric condition were observed. The structural behaviour of the crystalline sample was analyzed by X-ray diffraction spectrometer (XRD Shimadzu model 6000, using Cu kα (0.154 nm) as a radiation source to generate diffraction patterns from the sample at an ambient temperature in 2θ within the range of 10–80°. The bond formation of PVP was studied by infrared spectra (FT-IR, Perkin Elmer model 1650). Horiba Jobin-Yvon LabRam HR high-resolution Micro-Raman spectro-graph with 514 nm of argon ion laser (as the excitation source) was employed to examine the Raman spectra of the samples.

**Results and Discussion**

**TGA Analysis**
PVP, when subjected to a different atmospheric condition, offers an essential information of the influence of gases on its decomposition behaviour. This goes along way to predict and choose the appropriate temperature to commence the calcination process that leads to the decomposition of PVP. The
thermogravimetric measurement and its derivative (TGA–DTG) presented in Figure 1 designates the percentage of weight–loss as a function of the temperature for PVP subjected to a nitrogen atmosphere. The spectra reveal three different decomposition paths. The earlier one was the weight loss observed at 77 °C which was supposed to be the moisture content entrapped in the sample. The second point or the slight weight loss detected approximately at a temperature of 205 °C was ascribed to the volatile components in the ester group [1]. The third stage of the decomposition was the peak observed at 423 °C which implies that significant amounts of the organic source in PVP (C–C in the polymeric chain) has been decomposed [2]. The curve reveals no further weight loss on the peak as the temperature reached 500 °C; this was attributed to the entire decomposition of PVP, thereby turning into a carbonaceous product [3].

Figure 1. Thermogravimetric (TG) and differential or derivative thermogravimetric (DTG) curves for the decomposition of PVP at a heating rate of 10 °C/min under nitrogen atmosphere.

On the other hand, the degradation pattern of PVP under oxygen atmosphere on the TGA–DTG curve presented in Figure 2 reveals more complex peaks with at least five distinct stages: In the first stage, the PVP begins to lose weight at 77 °C which was due the water content absorbed by the sample in the cause of
preparation [4], [5]. The second weight loss was at about 329 °C, this gives rise to the volatilization of degraded products of the ester group, and the presence of O2 which could cause the formation of peroxide residues [6]. The third and fourth peaks sighted at 416 and 432 °C was decomposition of the significant part of the C–C in the polymeric chain. It is imperative to note that under the influence of oxygen atmosphere, there is higher tendency of peroxide residue formation which simply can decompose at moderately low temperature. This implies that the under oxidative conditions, active radicals formation is favoured. Nevertheless, at high temperatures between 400-500 °C, the amount of degradative free radicals is higher and the formation of peroxides under this condition does not promote adequately to the rise of this parameter. But the presence of oxygen provides a better condition to reduce the amounts of active degradative active species as compared to the process under N2 condition. This is due to the ability of oxygen acting as an inhibitor or deactivating agent of radicals [6]. The fifth peak at 514 °C was the indication of complete decomposition of the PVP. The curves exhibit no further decomposition behaviour beyond 620 °C as all the PVP has to turn into a carbonaceous product.

Figure 2. Thermogravimetric (TG) and thermogravimetric derivative (DTG) curves for the decomposition of PVP at a heating rate of 10 °C/min under oxygen atmosphere.
However, the TGA–DTG curve presented in figure 3, for the PVP under an air atmosphere, the spectra exhibits five distinct decomposition steps. The first was sighted at temperature of 74 °C due to weight loss caused by moisture content in the sample [2], [7]. The second stage which occurs at 195 °C was associated with low molecular weight ester group [8]. Whereas the third and fourth decomposition step occurs at temperature range of 437 to 443 °C with weight loss of 78.96% that represents the decomposition of organic source (C–C in the polymeric chain) [9], [8], [10]. The fifth decomposition stage which occurs at 568 °C was the temperature where the entire PVP is decomposed [10]. There is no further decomposition beyond 715 °C on the curve, as the spectra exhibit linear approach [10].

Figure 3. Thermogravimetric (TG) and thermogravimetric derivative (DTG) curves for the decomposition of PVP at a heating rate of 10 °C/min under air atmosphere.

The decomposition behaviour of PVP at normal atmosphere without passing any gas was presented in Figure 4 which shows the weight loss percentage as a function of the temperature. The spectra exhibit three different decomposition patterns. The earlier one was weight loss at a lower temperature of 74 °C and
presumed to be the moisture entrapped in the PVP [4], [5]. The second stage was weight loss observed at 434 °C which was due to decomposition of most of the organic source (C–C in the polymeric chain) from PVP (Al-Hada et al., 2014). The decomposition curve recorded at 625 °C was due to complete conversion of PVP into a carbonaceous product [10].

FT-IR Analysis
In this study, spectroscopy was applied to aid in examining the molecular bond and the kind of several bonding existing in PVP. The FT-IR spectrum of PVP presented in Figure 5 was conducted at room temperature. The result indicates the presence of various organic sources related to PVP. To make the classification more easily, the vibrational band and their assignments were given in Table 1. The wavenumber 1646, 2945, and 3414 cm⁻¹ were ascribed to the vibrational band of C=O, N-H, and C-H stretching vibration [14]. The vibrational band at 1429 cm⁻¹ was assigned to C-H bending created from methylene group [7].

Figure 4. Thermogravimetric (TG) and thermogravimetric derivative (DTG) curves for the decomposition of PVP at a heating rate of 10 °C/min under a normal atmosphere without passing any gas.
vibrational band that appeared at 1278 cm$^{-1}$ was related to the stretching of C-N, while the two separate peaks at 837 cm$^{-1}$ and 639 cm$^{-1}$ were bands attributed to C-C ring and C-N=O bending vibration, respectively [9].

Figure 5. FT–IR spectra of PVP at room temperature

Table 1. Summary of the FT–IR absorption features and their assignments for PVP

<table>
<thead>
<tr>
<th>Wave Number (cm$^{-1}$)</th>
<th>Assignment of vibration mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>639–641</td>
<td>C-N=O bending vibration</td>
<td>9</td>
</tr>
<tr>
<td>837</td>
<td>C-C ring vibration</td>
<td>9</td>
</tr>
<tr>
<td>1278</td>
<td>C-N stretching vibration</td>
<td>9</td>
</tr>
<tr>
<td>1402–1429</td>
<td>-C-H- bending vibration of methylene group</td>
<td>7</td>
</tr>
<tr>
<td>1648</td>
<td>N-H stretching vibration</td>
<td>14</td>
</tr>
<tr>
<td>2945</td>
<td>C-H vibration</td>
<td>14</td>
</tr>
<tr>
<td>3414</td>
<td>N-H bending vibration</td>
<td>14</td>
</tr>
</tbody>
</table>

Raman Analysis

The Raman analysis of the PVP in this work was used to identify the organic behaviour of the PVP at room temperature. The spectrum shown in Figure 6, exhibited vibrational bands apportioned to quite a lot of organic source associated with the polymer (PVP). For more clarification, the Raman vibrational bands and their assignments were presented in Table 2. The peak at 758 cm$^{-1}$
was due to C–C ring vibration, while the vibrational band sighted at 934 was ascribed to C–C ring breathing [20]. The peak sighted at 1023 cm⁻¹ was due to back bone C–C and the one at 1370 cm⁻¹ was associated to CH deformation [20, 21]. The assignment at 1494 cm⁻¹ was related to CH₂ scissors vibration and C=O (amide) observed at 1665 cm⁻¹ [21].

![Raman spectra of PVP at room temperature](image)

**Figure 6. Raman spectra of PVP at room temperature**

**Table 2. Summary of the Raman absorption features and their assignments for PVP**

<table>
<thead>
<tr>
<th>Wave Number (cm⁻¹)</th>
<th>Assignment of vibration mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>758</td>
<td>Ring C–C vibration</td>
<td>20</td>
</tr>
<tr>
<td>885</td>
<td>C–C stretching vibration</td>
<td>20</td>
</tr>
<tr>
<td>934</td>
<td>C–C Ring breathing</td>
<td>20, 21</td>
</tr>
<tr>
<td>1023</td>
<td>C–C Back bone</td>
<td>20,21</td>
</tr>
<tr>
<td>1370</td>
<td>C–H Deformation</td>
<td>20,21</td>
</tr>
<tr>
<td>1494</td>
<td>CH₂ Scissors</td>
<td>20</td>
</tr>
<tr>
<td>1675</td>
<td>C=O (amide)</td>
<td>20</td>
</tr>
</tbody>
</table>

**X-ray diffraction analysis**

XRD analysis was used to determine the structural form of the PVP at room temperature. Figure 7 gives the XRD spectrum of the PVP sample prepared. The
spectral pattern indicates an amorphous phase due to the broad hump observed and lack of clear pick of crystallinity[7–10]. This is in good agreement with the findings of other researchers, who reported an amorphous behaviour of PVP at room temperature[14,15].

![Raman spectra of PVP at room temperature](image)

**Figure 7. Raman spectra of PVP at room temperature**

**Figure 7. XRD pattern of PVP at Room temperature**

**Conclusion**

The influence of several atmospheric conditions on the decomposition pathway of PVP was reported in this study using thermogravimetry analysis. The main volatile product from the ester group decomposes at the lowest temperature irrespective of the atmospheric condition the PVP was subjected to. The C–C in the polymeric chain is last part of PVP to decompose under any atmospheric condition. The analysis under N\textsubscript{2} atmospheric condition offers the least decomposition temperature for PVP at 500 °C, while the condition under O\textsubscript{2} and air were 514 and 568 °C, respectively. The highest decomposition was at 625 °C when the analysis was conducted under normal condition without passing any gas. PVP was confirmed to be in an amorphous form by the XRD analysis while the FT-IR and Raman analyses revealed the kinds of bond existing in the polymer.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.
Acknowledgments
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