EFFECT OF FERRITE NANOMATERIALS ON THE THERMAL STABILITY OF BIOPOLYMER AND GRAPHENE OXIDE BLEND

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ABSTRACT

The current study focuses on comparative thermogravimetric analysis (TGA) and thermal characterization of Graphene Oxide (GO) and chitin (CH)-based magnetite nanomaterials such as Magnetic Graphene Oxide (MGO), Magnetic chitin (MCH), and Magnetic Graphene Oxide/Chitin (MGO/CH) for the first time. Various thermal parameters such as temperature of maximum mass change rate (Tmax), Crystallization Temperature (Tc), and Melting Temperature (Tm) have been investigated and heat of enthalpy has been calculated for both endothermic and exothermic processes. The pattern of degradation temperature for various percentages of weight loss has also been studied. In addition, the morphological characterization to study the microstructure was performed by scanning electron microscopy (SEM), and the structure, crystallinity, as well as nanoparticle size, were analyzed by XRD studies. From the Degradation patterns, we can infer that the thermal stability of the Magnetite nanocomposites synthesized by us is significantly higher and the corresponding weight loss is much lower than in the pristine material. This enhancement of thermal stability may be due to the intermolecular forces that exist between the polar units of magnetite particles. It is noteworthy that among all the nanocomposites, MCH is found to be the most thermally stable and has the least enthalpy for endothermic as well as exothermic events. With improved heat stability, graphene oxide and chitin-based nanomaterials have a greater potential for use in biomedical, environmental, electrical, catalytic, and food packaging applications.

Keywords: Magnetite, Nanoparticles, Graphene Oxide, Chitin, Thermal stability, Nanocomposites.

Introduction

Inverse spinel nanoparticles (NPs) like magnetite (Fe₃O₄) have been the focus of attention of many researchers and have been extensively explored as a possible source for the development of novel nanomaterials and biomaterials.¹⁻⁵ Due to their multifunctional properties, these materials have been utilized in cancer treatment, biocatalysis, biosensors, tissue engineering-regulated drug delivery, and MRI Studies.⁶⁻¹¹ Recent research reports have also explored the possible applications of Graphene quantum dots.¹² Iron nanostructures when combined with other materials have been reported to display better results.¹³,¹⁴ GO is made up of carbon nano-sheets having a large surface area and an abundance of oxide groups.¹⁵,¹⁶ In this aspect, graphene has demonstrated a strong potential to be a beneficial choice. The diverse range of applications of MgO nanoparticles is attributed to their interesting properties, which include stability, magnetizability, crystallinity, absorptivity, electrical and thermal conductivity, stoichiometry, and reactivity in addition to the simplicity and affordability of preparation methods.¹⁷⁻²⁰ CH nanostructures are used in the formation of bio nanocomposites and provide diverse applications in the field of environmental and biomedical sciences.²¹⁻²⁵ Our work focuses on the preparation of magnetite nanomaterials which include MGO, MCH, and MGO/CH, and their characterization by various techniques. Various characterization techniques viz XRD, SEM, and VSM (Vibrational Sample Magnetometry) were employed to have insight into the materials. The various magnetic parameters like remanence, Coercivity, and type of magnetic sample can be inferred from the VSM data. The thermal stability of the synthesized
samples (Temperature of maximum mass change rate, \( T_{\text{max}} \)) and the decomposition mechanism were investigated by comparing and analyzing their TGA-DTG curves. TGA used in conjunction with DSC is a very useful technique to determine the thermal stability and the chemical kinetics involved at various temperatures. The information obtained allows differentiation between endothermic and exothermic events and consequently melting temperature, crystallization temperature, and heat of enthalpy were also determined. The thermal analysis is particularly useful in tailoring the samples for temperature-dependent specific uses. To the best of our knowledge, a similar comparison on Ferrite added, pristine GO, Biopolymer and GO blend hasn’t been reported earlier.

**EXPERIMENTAL**

**Material and Methods**

Analytical grade reagents were used in the preparation of samples. Iron (III) chloride (FeCl\(_3\), 96.0%), Iron (II) chloride (FeCl\(_2\), 96.0%), Hydrochloric acid (HCl, 35%), Sodium Hydroxide (NaOH, 97%), concentrated Sulphuric acid (Conc. H\(_2\)SO\(_4\), 98%), Hydrogen Peroxide (H\(_2\)O\(_2\), 30%), Chitin (99%), Ethanol and Ammonia solution (NH\(_3\), 25 wt.%), were procured from Merck. Graphite (99%) was purchased from Sigma Aldrich. Sodium Nitrate (NaNO\(_3\), 99%) and Potassium Permanganate (KMnO\(_4\), 99%) were purchased from Hi-media. GO was prepared by the well-known Hummers Method while MGO, MCH, and MGO/CH were synthesized by the methods well reported by other researchers.

**General Procedure**

X-ray powder diffraction spectra were recorded on a Bruker D8 Discover instrument (X-ray source Cu, 3 kW). SEM images were captured using a JEOL Japan JSM 6610LV setup. The magnetic moment and other parameters were determined at room temperature using a Vibrating sample Magnetometer (Microsense Model ADE- EV9). The Thermogravimetric scans were obtained by heating the powder samples in an alumina pan in TGA HiRes 1000 thermal analyzer. A heating rate of 10\(^\circ\)C/min was maintained in N\(_2\) gas (20 ml/min). DSC analysis for studying crystallization and melting behavior of nanocomposites was conducted by using Waters (TA Instruments) Make Q200 modulated DSC thermal analyzer. The samples (3 mg each) were heated at 5\(^\circ\)C/min from Room temperature to 400\(^\circ\)C in N\(_2\) gas (50 ml/min). Care was taken to take precise sample weight for accurate enthalpy measurements.

**RESULTS AND DISCUSSION**

**XRD Analysis**

From Fig.-1, it is seen that the intense peak of GO at 10.5\(^\circ\), is amorphous and broadened in the obtained XRD pattern of MGO and subdued in the MGO/CH Curve. Liu et al. too have reported similar behavior in their sample. The characteristic peaks corresponding to the cubic inverse spinel structure of Fe\(_3\)O\(_4\) nanoparticles appear at 30.36\(^\circ\), 35.57\(^\circ\), 43.12\(^\circ\), 57.36\(^\circ\), and 62.82\(^\circ\) corresponding to (220), (311), (400), (422), and (440) crystal plane reflections of pure Fe\(_3\)O\(_4\) (JCPDS CARD 19-0629) in MGO, MCH and MGO/CH nanocomposites. The peaks of CH at 9.10\(^\circ\)and 22.94\(^\circ\) are visible in MCH and MGO/CH samples as reported by Elsayed et al. too. The average size of the Fe\(_3\)O\(_4\) nanoparticles was calculated from the major diffraction peak of (311) in MGO, MCH, and MGO/CH using Debye–Schererrer equation and were found to be in the range of 8 – 22 nm. The dimension of nanoparticles was estimated by analyzing the full width at half maximum of the referred peak.

Fig.-1: XRD Curves of GO, MGO, MCH, and MGO/CH
SEM Analysis
The SEM images of GO, MGO, MCH, and MGO/CH NM with different magnifications are represented in Fig.-2. The smooth surface of GO is roughened due to the addition of magnetite Fe₃O₄ in our samples as clearly indicated in the image for MGO. The smooth surface of CH is also destroyed by Fe₃O₄ NPs which is seen in the relevant SEM image. Fe₃O₄ particles are nano-sized and can be seen deposited on the chitin surface. A dense microstructure is seen in the morphology of the MGO/CH NC.

VSM Analysis
It is seen that Magnetization increases with an increase in an applied magnetic field and an S-shaped hysteresis curve is obtained for MGO, MCH, and MGO/CH at room temperature in Fig.-3. No hysteresis loop was observed in our samples. The absence of any magnetic behavior as in the case of GO shows that pristine GO is nonmagnetic in nature. The absence of coercivity and permanence suggests that all samples are superparamagnetic. The values of saturation magnetization in our samples were low in comparison to the reported results.

TG Analysis
The TGA and DTG curves of the four samples GO, MGO, MCH, and MGO/CH are shown in Fig.-4 and Fig.-5 respectively. It is observed that barring GO; the rest of the samples exhibited a multistep degradation pattern. Details of the thermal degradation of the four samples are given below in Fig.-4 and 5.
natural state, caused by decreased van der Waals interactions. The pyrolysis of the functional groups that results in the production of CO, CO$_2$, and steam also causes a significant drop in the onset temperature. DTG graphs were also generated from TGA curves displaying mass loss peaks at 97°C and 205°C. The temperature of the maximum rate of mass degradation ($T_{\text{max}}$), occurs at about 205°C. Likewise, the DSC curve has a prominent exothermic peak centered at a temperature of 197.5°C. Kyzas et al. too have reported the occurrence of similar peaks between 200-250°C. The removal of more stable functional groups is responsible for a slower, yet continuous mass loss of 5% between 400 and 800°C.

Thermal Analysis of MGO
A mass loss of 10% is observed due to water loss or any absorbed moisture from room temperature to 80°C and from 100 -190 °C there was a mass loss of 14%, which was due to the destruction of loosely bound oxygen-containing compounds. The major weight loss as seen by the DTG peaks occurs at 805°C ($T_{\text{max}}$) which was due to the destruction of graphene nanosheets. The final residual weight was roughly double (44%) than GO (20%) at 800°C. This enhanced stability may be attributed to lower defect density.

Thermal Analysis of MCH
The TGA curve obtained for MCH revealed that the decomposition exhibits a multistep trend from 27°C to 900°C which is different from the two-step degradation pattern of pure CH. The initial slow and small decrease in weight of 5% from ambient temperature to 223°C occurs due to the evaporation of water present in the sample. It is also seen that the maximum weight loss occurs at 340°C owing to polysaccharides decomposition. Thereafter, a gradual loss in weight (4%) is obtained till 665°C. Beyond this temperature, the weight loss is slightly steeper till 900°C. This behavior is different from the high weight loss reported in pure CH samples signifying that CH as a result of adding magnetic nanoparticles becomes more stable thermally. It is also observed that the percentage of residual mass at 800°C in the magnetic sample shows a much higher value of 73%.
Thermal Analysis of MGO/CH

There is a small weight loss of 3.47% up to 200°C. This is due to the evaporation of adsorbed water molecules. A corresponding peak is observed in the DTG curve too. On heating up to 270°C, the pyrolysis of oxygen-containing functional groups causes a large weight loss of 40%. From 270°C to 500°C a reduction in weight of 14% is observed as a result of disintegration of the polysaccharide structure. Another weight loss of 31% is observed henceforth from 500 to 800°C. The DTG peaks conform with the observations. The residual mass at 800°C is around 25% which is much lesser in comparison to MGO alone probably due to the decomposition of CH present in the nanocomposite.

Fig.-6: Onset Temperature of Degradation versus % Wt. Loss for MGO, MCH, and MGO/CH

Fig.-7: DSC Curves of GO, MGO, MCH, and MGO/CH

A Comparison of the weight loss percentage of all 4 samples at 5%, 10%, 25%, and 50% loss is shown in Table-1 wherein it can be seen that the addition of magnetite particles effectively slows down the degradation process in the magnetic nanocomposites as they are very stable even at high temperatures.35,48 For pure CH it is reported that 10% weight loss occurs at 287°C which is significantly enhanced to 330°C in our magnetite-loaded nanocomposite MCH.46 Fig.-6 depicts the bar chart representation showing a comparison of the onset of the temperature of degradation versus % weight loss for all the nanocomposites. It can be seen that amongst the various NCs, the thermal stability of the MCH appears to be far better and decomposes only 25% at the highest temperature of our study. It was observed from the DSC scans (Fig.-7) that barring MGO/CH, all the samples showed both exothermic and endothermic transitions as can be seen by the occurrence of the peak in individual scans. The sharpness of the peak is representative of the rate of transformation in the sample. The area under each peak in the DSC curve for all four samples was calculated by the Simpsons method. The enthalpy, melting temperature, and crystallization temperature for these are listed in Table-2. The enthalpy is maximum for GO and minimum for MCH for both exothermic and endothermic events which is in agreement with the findings of Pandey et al.48

Table-1: Comparison of 5%, 10%, 25%, and 50% Weight Loss of GO, MGO, MCH, and MGO/CH

<table>
<thead>
<tr>
<th>Sample</th>
<th>T5% (°C)</th>
<th>T10% (°C)</th>
<th>T25% (°C)</th>
<th>T50% (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>66.86 - 69.09</td>
<td>91.55 - 97.69</td>
<td>211.51</td>
<td>212.98</td>
</tr>
<tr>
<td>MGO</td>
<td>79.19 - 81.65</td>
<td>113.9 - 118.3</td>
<td>218.24 - 223.72</td>
<td>815.13 - 818.37</td>
</tr>
<tr>
<td>MCH</td>
<td>246.52 - 259.69</td>
<td>330.04 - 333.70</td>
<td>850.52 - 860.96</td>
<td></td>
</tr>
<tr>
<td>MGO/CH</td>
<td>194.72 - 195.68</td>
<td>209.87 - 211.89</td>
<td>252.07 - 252.76</td>
<td>456.82 - 459.71</td>
</tr>
</tbody>
</table>

Table-2: Comparison of Thermal Parameters of GO, MGO, MCH, and MGO/CH

<table>
<thead>
<tr>
<th>Sample</th>
<th>Endothermic event</th>
<th>Exothermic event</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystallization Temperature (°C)</td>
<td>Enthalpy (J/g)</td>
</tr>
<tr>
<td>GO</td>
<td>92.6</td>
<td>-480</td>
</tr>
<tr>
<td>MGO</td>
<td>85.80</td>
<td>-260</td>
</tr>
<tr>
<td>MCH</td>
<td>71.5</td>
<td>-40</td>
</tr>
<tr>
<td>MGO/CH</td>
<td>95</td>
<td>-500</td>
</tr>
</tbody>
</table>
CONCLUSION

In our work, we have successfully synthesized GO, MGO, MCH, and MGO/CH nanocomposites as verified from XRD studies. The SEM images also confirmed the efficient incorporation of the magnetite nanoparticles into the synthesized nanocomposites. This is further evident from the VSM studies which yielded S-shaped hysteresis curves in all the samples, confirming the evolution of superparamagnetic nanomaterials due to the addition of magnetite in otherwise insulating pristine materials like GO and CH. All the samples except GO exhibited a multistep degradation pattern as is evident from the TGA studies. It is seen that the addition of magnetite particles has effectively slowed the degradation process in the magnetic nanocomposites due to the powerful intermolecular interaction between the polar units of magnetite particles and the polar units of the mix chain of GO and CH. The MGO composite with Fe$_3$O$_4$ showed an elevated decomposition temperature of 815°C, whereas pure GO showed a substantial deterioration at a much lower temperature of 205°C. A comparison of degradation temperature and various thermal parameters of various nanocomposites revealed that MCH has the maximum thermal stability till the highest representative temperature of study and has the least enthalpy in both endothermic as well as exothermic events.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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