Effect of Iron Oxide Nanoparticles on the Thermal Characteristics of Supramolecular, Dendritic and Macromolecular Capping Agents

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Research Article

Keywords: Iron oxide nanoparticles, cyclodextrin, hyperbranched polyglycerol, starch, thermal

Posted Date: February 28th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1380478/v1>

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Abstract

The present study aimed at the enhancement of the thermal characteristics of different capping agents belonging to different macromolecular families, with the incorporation of iron oxide nanoparticles. Iron oxide nanocomposites were prepared following a simple reduction protocol using sodium borohydride (NaBH_4) succeeded by air oxidation. Three iron oxide composites were prepared using different biocompatible capping agents. The capping agents used in the present study were supramolecular β -cyclodextrin, dendritic hyperbranched polyglycerol and macromolecular starch. The chemical nature of the composites was successfully confirmed by spectroscopy. The well characterized composite systems were studied for their thermal characteristics using TG/DTG and DSC measurements. The primary focus of the study was to analyse any change in the thermal behaviour of the pure encapsulating systems on incorporation with the iron oxide species. The analysis was conducted by comparing the TG/DTG and DSC measurements of the pure capping agents- cyclodextrin, hyperbranched polyglycerol and starch with their respective nanoparticle incorporated composites.

1. Introduction

Macromolecular materials belonging to different classes have been in various applications that attracts the scientific community. For the past few decades, these giant molecules apart from their conventional characteristic applications, add more colour to the exciting world of materials science. They can be used as capping agents for the tiny nanoparticles to stabilize as well as enhance their characteristic properties. Both of them the nanoparticles and the macromolecular agents can be mutually benefitted from this encapsulation or incorporation. They are sometimes rather defined as nanocomposites because of this symbiotic effect on their properties. Research on one hand explores the property enhancement of nanoparticles by encapsulation with these stabilizing agents, while on the other hand it does emphasize on the improved characteristics of the macromolecular entities with the incorporation of the nanoparticles.

The property enhancement of a macromolecular matrix by incorporation of various organic/inorganic or micro/nano inclusion agents is being actively pursued in polymer research [1–3]. Nanocomposites in their reduced size dimensions, offer a wide range of superior properties when compared to their conventional microcomposites. These high-performance hybrid materials come from the need for significant improvements in the interfacial adhesion between the polymer matrix and the reinforcing material because the organic matrix is relatively incompatible with the inorganic phase. In recent years, polymers containing inorganic nanoparticles have become one of the prime concerns of frontline research in materials science [4–5].

The stabilization of nanoparticles using macromolecules can facilitate the surface properties and many size dependent properties of nanoparticles. On the other hand, these macromolecules which are either hydrophilic or lipophilic can be transformed into more solvent resistant with the introduction of inorganic nanoparticles especially of metallic origin. The nanoparticles can be loaded into the polymer matrix by

different methods which can be broadly categorized as: (1) precursor metal salts along with the polymer in a solvent is reduced to their respective metal nanoparticles during stirring, heating or solvent evaporation [6–8]; (2) a metallic precursor dissolved in a monomer can be reduced during polymerization [9–10]; (3) a colloidal precursor solution is mixed with either the monomer or polymer solution and reduced via route (1) or (2) [11]; and (4) a polymer matrix is impregnated with a precursor solution which then undergoes reduction or thermolysis [12–13]. Metal nanoparticles uniformly dispersed in a polymer matrix furnish these composite materials with strong functional possibilities in catalysis [14], sensing [15], optical [16], magnetic [17–18] or electrical [19–20] properties. There are also evidences for the thermal property enhancement of these macro stabilizing or capping agents on introduction of nanomaterials [3, 21]. Therefore, many researchers have devoted their work to the development of these novel hybrid materials with improved performance [22].

The selection of polymers to build the matrix for these composites depends on many factors like their hydrophilicity, solubility, extent of polymerization in presence of precursor, miscibility with the precursor, glass transition, melting temperature, method of preparation and so on. Rather simply, all polymers are not good candidates for the fabrication of nanocomposites. Our study used three macromolecular matrices for the preparation of iron oxide induced nanocomposites viz. supramolecular β -cyclodextrin (β -CD), dendritic hyperbranched polyglycerol (HPG) and macromolecular starch. All of them were randomly selected for their extensive hydrophilicity and intense biocompatibility.

Cyclodextrins, composed of glucose units linked by α -(1,4)-glycosidic linkage contain a somewhat lipophilic central cavity and a hydrophilic outer surface [23–24]. β -cyclodextrin is the most accessible and cheap among the different classes of cyclodextrins [25]. The propensity of cyclodextrins to form inclusion complexes is enabling them to be used in various fields of medicine like drug delivery. They possess supramolecular cages that can entrap small sized particles like nanomaterials through host-guest type interactions, which make them practically available for a wide range of applications. Since they can easily link covalently or non-covalently with each other, cyclodextrins form supramolecular aggregates which are capable for host-guest interactions. It is in this cavity formed by these supramolecular aggregates that the nanoparticle-like small molecules are trapped.

Hyperbranched polyglycerols explore the salient features of encapsulation by means of their bizarre potentiality for host-guest interactions. These giant molecules are peculiar for their phenomenal biocompatibility, low viscosity, high solubility and their three dimensional dendritic architecture [26–28]. The third capping matrix starch belonging to the family of macromolecules, is a polysaccharide with many glucose units linked through glycosidic bonds and is one of the most common biocompatible polymers.

The study aimed at the thermal stability enhancement of these capping agents on incorporation of iron oxide nanoparticles (IONPs). Stabilized iron oxide nanoparticles often exhibit superparamagnetism [7, 29] which can be propagated to be applied in most modern, suave theranostic techniques including

hyperthermia, MRI contrasting and so on. Hence the thermal properties of iron oxide nanocomposites are to be studied in detail.

2. Experimental

2.1 Materials

Ferrous sulphate heptahydrate was purchased from Nice Chemicals Pvt. Ltd. India. β -Cyclodextrin (β -CD), starch (soluble) and sodium borohydride (NaBH_4) were all purchased from Merck Specialities Pvt. Ltd. Mumbai and used without any further purification. Hyperbranched polyglycerol (HPG, m.w-5000) was obtained from the research group of Prof. Holger Frey of Johannes-Gutenberg University, Mainz, Germany.

2.2 Instrumentation

FTIR spectra of the samples were recorded as KBr discs in the frequency range $4000 - 400 \text{ cm}^{-1}$ on Shimadzu-400 FTIR spectrophotometer. TG/DTG and DSC measurements were carried out on a Perkin Elmer thermal analyser.

2.3 Synthesis of cyclodextrin/hyperbranched polyglycerol/starch-iron oxide nanoparticle composites

500 mg of the capping agent (β -CD/HPG/starch) and 1000 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were separately dissolved in 100 ml Milli-Q water and the two solutions were sonicated by a probe sonicator at 25W for 5 minutes. After sonication, the Fe^{2+} precursor solution was added dropwise to the aqueous solution of the encapsulating agent. Now the capping agent and precursor mixture was stirred for 4 hours using a magnetic stirrer. 0.5 M freshly prepared solution of sodium borohydride (30 ml) was added with vigorous stirring till the completion of $\text{Fe}(0)$ formation, and the solution was stirred further for 1 hour. The filtered black $\text{Fe}(0)$ was air oxidized to reddish brown $\alpha\text{-Fe}_2\text{O}_3$, at room temperature. The sample was heated at 200°C to oxidize all hydroxides if present [7]. The composite corresponding to each capping agent and their representative notations used throughout this paper is denoted in Table 1.

Table 1
Newly developed nanocomposites and their notations

Capping agent	IONP incorporated nanocomposite
β -Cyclodextrin	IONP-CD
Hyperbranched Polyglycerol	IONP-HPG
Starch	IONP-STARCH

3. Results And Discussions

3.1 FTIR characterization

Fourier transform infrared spectroscopy was used to confirm the successful synthesis of the newly developed composites.

FTIR spectrum of the pure β -CD and IONP-CD nanocomposite were recorded as KBr discs in the wavenumber range of 4000-400 cm^{-1} (figure 1).

Pure β -CD IR(KBr): 3315.87 cm^{-1} : $\nu_{\text{O-H}}$ (str), 1330.32 cm^{-1} : $\nu_{\text{O-H}}$ (in-plane bend), 1148.07 cm^{-1} : $\nu_{\text{C-O}}$ (str), 1023.25 cm^{-1} : $\nu_{\text{C-O-C}}$ (sym.str) of glycosidic linkage. A tiny dip at 2329.31 cm^{-1} may be due to the presence of atmospheric CO_2 .

IONP-CD nanocomposite IR(KBr): 3201.23 cm^{-1} : $\nu_{\text{O-H}}$ (str), 1362.44 cm^{-1} : $\nu_{\text{O-H}}$ (in-plane bend), 1100.35 cm^{-1} : $\nu_{\text{C-O}}$ (str), 544.23 and 465.51 cm^{-1} : $\nu_{\text{Fe-O}}$ (str). Dip at 2343.66 cm^{-1} indicates the atmospheric CO_2 adsorption by the sample. The peaks below 600 cm^{-1} of IONP-CD corresponding to Fe-O stretching vibrations, which were absent in pure CD, ensures the encapsulation of IONPs into the supramolecular cavities of β -cyclodextrin.

FTIR spectrum of pure HPG (figure 2(a)) and IONP-HPG nanocomposite (figure 2(b)) were recorded as KBr discs in the wavenumber range 4000-400 cm^{-1} .

Pure HPG IR(KBr): 3348.70 cm^{-1} : $\nu_{\text{O-H}}$ (str), 1633.90 cm^{-1} : $\nu_{\text{O-H}}$ (bend) of glycols, 1018.77 cm^{-1} : $\nu_{\text{C-O-C}}$ (str). The weak dip at 2329.34 cm^{-1} may be due to the adsorption of atmospheric CO_2 as in the previous cases.

IONP-HPG nanocomposite IR(KBr): 3228.15 cm^{-1} : $\nu_{\text{O-H}}$ (str), 2851.59 cm^{-1} : $\nu_{\text{C-H}}$ of CH_2 , 1640.02 cm^{-1} : $\nu_{\text{O-H}}$ (bend) of glycols [23], 1061.55 cm^{-1} : $\nu_{\text{C-O-C}}$ (str), 531.12 and 470.16 cm^{-1} : $\nu_{\text{Fe-O}}$ (str).

The peaks below 600 cm^{-1} in figure 2(b) corresponding to Fe-O stretching vibrations, confirm the successful encapsulation of iron oxide nanoparticles into the dendritic scaffolds.

FTIR spectrum of pure starch and IONP-STARCH nanocomposite were recorded as KBr discs in the wavenumber range 4000-400 cm^{-1} (figure 3).

Pure starch IR(KBr): 3312.91 cm^{-1} : $\nu_{\text{O-H}}$ (str), 1645.08 cm^{-1} : $\nu_{\text{O-H}}$ (bend), 1362.02 cm^{-1} : $\nu_{\text{C-H}}$ (bend) of CH_2 , 1003.94 cm^{-1} : $\nu_{\text{glycosidic linkage}}$. Dip at 2333.33 cm^{-1} indicates CO_2 adsorption by the sample.

IONP-STARCH nanocomposite IR(KBr): 3231.50 cm^{-1} : $\nu_{\text{O-H}}$ (str), 1631.16 cm^{-1} : $\nu_{\text{O-H}}$ (bend), 1352.04 cm^{-1} : $\nu_{\text{C-H}}$ (bend) of CH_2 , 1003.94 cm^{-1} : $\nu_{\text{glycosidic linkage}}$, 536.12 and 479.42 cm^{-1} : $\nu_{\text{Fe-O}}$ (str). Weak band at 2397.54 cm^{-1} is an indication of atmospheric CO_2 adsorption.

Here also, the two dips below 600 cm^{-1} confirm the successful development of the nanocomposite.

3.2 Enhancement of thermal stability capping agents on incorporating iron oxide nanoparticles

The different thermal decomposition steps and thermal events of all the samples under study were monitored using TG/DTG and DSC measurements respectively. TG/DTG measurements were recorded to monitor the thermal degradation of each sample with increase in temperature from 35°C to 700°C at $10^{\circ}\text{C}/\text{min}$. TGA is a technique in which the weight of the sample was measured as a function of temperature, under controlled heating. The analysis gives an overall idea about the thermal stability of the samples.

Different thermal events for each sample were monitored using DSC measurements in the same temperature range. Thermal characteristics of IONP incorporated nanocomposites were compared with those of the respective capping agents in their pure state. TG/DTG and DSC to measure mass change and heat flow rate were recorded simultaneously from 35°C to 700°C under nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}/\text{minute}$.

TG/DTG curve of pure β -CD (figure 4 (a)) showed two mass loss steps. The minor one centered at 97.82°C contributing about 10.95 % weight loss of the initial weight can be accounted for the loss of water molecules associated externally or internally with the supramolecule. The major weight loss of 67.98 % at 324.61°C is of course due to decomposition of cyclodextrin molecules [30]. At 700°C , only 5.97 % weight remained.

While TG/DTG curve of IONP-CD aggregates (figure 4 (b)) exhibited three major mass losses. The initial one at 63.35°C with a weight loss of 2.21 % is obviously due to loss of external water molecules at the sample surface and the one at 258.78°C contributing a total weight loss of 2.55 % is due to the loss of chemically bonded or interstitially trapped water molecules in the sample.

The major loss of the aggregate appeared at 357.50°C with 11.246 % weight loss, which can be attributed to cyclodextrin decomposition on comparison with (figure 4 (a)). It is quite worth to mention the increased stability of the supramolecule on incorporation with IONPs. The chemical decomposition of pure β -CD (figure 4 (a)), started at 277.77°C and reached a maximum at 324.61°C . Whereas on incorporation of IONPs, the decomposition of cyclodextrin started only at 296.86°C with a maximum at 357.50°C (figure 4 (b)). This clearly indicates the increased thermal stability of β -CD on encapsulation of IONPs.

Differential scanning calorimetry was performed on all the samples synthesized to monitor the various thermal events. The samples were heated from 35°C to 700°C at the rate of $10^{\circ}\text{C}/\text{minute}$.

Figure 5 shows the DSC curves of pure cyclodextrin and IONP-CD nanocomposite. Pure CD showed (Figure 5 (a)) two endothermic peaks at 100.82°C and 315.84°C , which respectively corresponds to evaporation of water molecules and melting of CD, which can be correlated to the TG/DTG analysis

(figure 4(a)). On incorporation of IONPs, melting of CD occurs at a lower temperature of 270.18⁰C with an increase in ΔH (Figure 5 (b)).

The TG/DTG curve of pure HPG noted two mass losses- a minor one at 117.02⁰C comprising of 8.96 % mass loss and a major one at 402.47⁰C which witnessed 67.71 % mass loss (figure 6(a)). The initial weight loss can be attributable to loss of free water and water linked through hydrogen bonds and the second one to thermal degradation of the dendritic macromolecule [31].

IONP-HPG aggregates displayed three major decompositions (figure 6(b)). The first one below 100⁰C with a maximum at 52.19⁰C is of no doubt due to loss of superficial water molecules present at the sample surface. The second decomposition starting at 176.89⁰C and ending at 482.60⁰C included two major dips that may involve a combination of loss of chemically bonded water molecules in the interstitial sites of IONP solid network and HPG degradation. From the nature of the second dip, we can understand that the decomposition of HPG shifted to a higher temperature range on encapsulation of IONPs on comparison with pure HPG.

In contrast to IONP-CD aggregates, IONP-HPG aggregates marked a third mass decomposition in the range 613.53⁰C – 695.74⁰C with a maximum at 662.64⁰C. Decomposition of HPG in the second weight loss step may result in evolution of oxygen and other gases which may result in crystal defects [32] or formation of any other oxides or compounds of iron [33]. The decomposition of these newly formed compounds result in the third mass loss centered at 662.64⁰C.

Figure 7 describes the DSC curves of (a) pure HPG and (b) IONP-HPG nanocomposite. Pure HPG showed 3 endothermic processes. The first one at 121.95⁰C is undoubtedly due to the loss of water molecules and the third one at 422.65⁰C due to melting of HPG. But the endothermic peak at 379.07⁰C, where no weight loss was observed is probably the glass transition temperature (T_g) of this dendrimer.

IONP-HPG composite showed only one endothermic peak at 257.30⁰C, which may be due to evaporation of trapped water molecules as described by the second weight loss of 21.46% in TG/DTG (figure 6 (b)). On incorporation of IONPs, melting of HPG is found to disappear which justifies the perfect encapsulation.

Figure 8 (a) represents the TG/DTG curve of pure starch in which two mass loss steps were observed. The first sudden loss of 10.98 % at 76⁰C undoubtedly confirms the escape of surface water molecules. The second decomposition at 303.42⁰C constitutes the major mass loss which is accountable for the carbohydrate degradation.

In case of IONP-STARCH composite (figure 8 (b)), the first weight loss of 11.63 % below 200⁰C can be attributed to evaporation of surface water molecules or escape of chemically bonded or interstitial water molecules trapped in the crystal lattice of IONP. The second decomposition of 14.12 % weight loss indicates the macromolecular disintegration. But the broadening of the decomposition peak from

220.71⁰C to 214.83⁰C with a maximum decomposition at 304.23⁰C, on comparison with that of pure starch where the decomposition peak was more sharp and steep, confirms a slow decomposition of starch on encapsulation of IONP into the macromolecular scaffolds. IONP-STARCH aggregates as in the case of IONP-HPG aggregates showed a third decomposition step at 679.27⁰C which constitutes a weight loss of 2.22 %. This as in the previous case of HPG composite can be explained on the basis of decomposition of newly formed compounds due to interaction of iron or existing iron oxide with the evolved gases resulted from decomposition of starch [33]. Or the increased oxygen evolution from decomposition of starch may result in some crystal defects due to hexagonal distortion that can cause increased compressive stress on the hematite surface [32].

Pure starch showed three endothermic thermal events (figure 9 (a)). The one at 83.49⁰C can be accounted for the water loss. The second one 279.59⁰C is due to melting of starch and a weak peak with a very small ΔH (4.28 J/g) at 325.81⁰C may be related to the oxidation reaction of the solid carbonaceous residue and is termed as a region of 'glowing combustion' [34]. IONP-STARCH aggregates showed two endothermic curves at 102.59 and 138.66⁰C, which can be associated with the evaporation of external and internal water molecules as explained by the first thermal weight loss in TG/DTG analysis.

The different thermal decomposition steps observed in TG/DTG analysis for all the IONP incorporated composite samples are enlisted in table 2 and compared with those of the respective capping systems (marked in red).

Table 2. Thermal decomposition steps recorded in TG/DTG measurements

Sample	Decomposition temperature (°C)			Weight loss (%)	Thermal event
	Onset	Endset	Peak (T _{max})		
IONP	36.84	154.30	68.74	5.783	Superficial water loss
	251.57	373.31	296.77	0.50	Loss of chemisorbed or interstitial water molecules
IONP- CD CD	37.44	166.54	63.35	2.21	Evaporation of superficial water molecules
	46.68	127.19	97.82	10.95	
	176.28	290.16	258.78	2.55	Evaporation of chemically bonded or interstitially trapped water molecules
	NIL	NIL	NIL	NIL	
	296.86	394.90	357.50	11.25	Degradation of cyclodextrin
	277.77	420.36	324.61	67.96	
IONP- HPG HPG	38.04	80.67	52.19	0.61	Evaporation of superficial water molecules
	104.09	164.39	117.02	8.96	
	176.89	482.60	258.88	21.46	Evaporation of interstitial water molecules and degradation of HPG
	272.42	448.91	402.47	67.712	
	613.53	695.74	662.64	0.60	Decomposition of newly formed compounds or crystal defects due to increased oxygen content
	NIL	NIL	NIL	NIL	
IONP- STARCH STARCH	37.67	205.61	138.18	11.63	Evaporation of superficial and interstitial water molecules
	36.21	155.25	76.00	10.98	
	220.71	514.83	304.23	14.12	Decomposition of starch
	223.26	436.25	303.42	59.80	
	545.05	741.42	679.27	2.22	Decomposition of newly formed compounds or crystal defects due to increased oxygen content
	NIL	NIL	NIL	NIL	

The major thermal events (from DSC measurements) of all the synthesized IONP incorporated composite samples compared with the corresponding stabilizing systems (marked in red) are summarised in table 3.

Table 3. Thermal events recorded in DSC measurements

Sample	Peak temperature (°C)	ΔH (J/g)	Thermal event
IONP	74.61	65.12	Evaporation of superficial water molecules
IONP-CD	270.18	306.05	Evaporation of water molecules
CD	100.82	244.28	
	NIL	NIL	
	315.84	114.68	Melting of CD
IONP-HPG	257.30	141.63	Evaporation of superficial and trapped water molecules
HPG	121.95	123.05	
	NIL	NIL	
	379.07	102.33	Glass transition of HPG
	NIL	NIL	
	422.65	86.67	Melting of HPG
IONP-STARCH	102.59 & 138.66	37.87 & 77.83	Evaporation of superficial and interstitial water molecules
STARCH	83.49	171.38	
	NIL	NIL	
	279.59	180.65	Melting of starch
	NIL	NIL	
	325.81	4.28	Glowing combustion

4. Conclusions

The thermal studies performed on the newly developed iron oxide nanocomposites with β -cyclodextrin, hyperbranched polyglycerol and starch revealed that IONPs are suitable candidates for the thermal characteristic enhancement of macromolecular capping agents of different families and origin. All the pure stabilizing systems in the present study have poor thermal stabilities and decompose in the temperature range 250-450°C. On encapsulation of IONPs, these systems have gained more thermal stability, especially CD where the decomposition shifted to a higher temperature. All the dips corresponding to decomposition of the encapsulating medium broadened on encapsulation of IONPs, which suggests a slower degradation. DSC studies revealed that encapsulation of IONPs have prevented melting of CD, HPG and STARCH which evidently confirms the effective encapsulation of nanoparticles into these systems. These systems can be explored for different functional utilities where the thermal properties of either the iron oxide or the macromolecular entities are to be scientifically exploited.

Declarations

Acknowledgements

The authors acknowledge Prof. Holger Frey and his group, Johannes-Gutenberg University, Mainz, Germany. The first author thanks University Grants Commission for Junior Research Fellowship (Sr.No-2061410045 Ref.No-22/06/2014 (i) EU-V).

Funding: Current research was funded by University Grants Commission (India) under the Senior Research Fellowship scheme (Sr.No-2061410045 Ref.No-22/06/2014 (i) EU-V).

Conflicts of Interests/Competing Interests: The authors declare that they have no conflict of interest.

Availability of Data and Material: Not applicable

Code Availability: Not applicable

Authors' Contributions:

Both the authors contributed to the study conception and design. Synthesis and analyses were performed by the first author Sherin Philip. The first draft of the manuscript was prepared by the first author and commented and modified by the corresponding author Sunny Kuriakose. Both the authors read and approved the final manuscript.

Ethics Approval: The authors declare that the study conducted meet all the ethical standards as specified by the journal and did not involve any animal/human research. The data and materials as well as software applications used in the study comply with field standards.

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Figures

Figure 1

FTIR spectra of pure β -CD and IONP-CD nanocomposite

Figure 2

FTIR spectra of (a) pure HPG and (b) IONP-HPG nanocomposite

Figure 3

FTIR spectrum of pure STARCH and IONP-STARCH nanocomposites

(a)

(b)

Figure 4

TG/DTG curve of (a) pure β -CD and (b) IONP-CD nanocomposite

Figure 5

DSC curves of (a) pure β -CD and (b) IONP-CD nanocomposite

Figure 6

TG/DTG curve of (a) pure HPG and (b) IONP-HPG nanocomposite

Figure 7

DSC curves of (a) pure HPG and (b) IONP-HPG nanocomposite

Figure 8

TG/DTG curve of (a) pure STARCH and (b) IONP-STARCH nanocomposite

Figure 9

DSC curves of (a) pure STARCH and (b) IONP-STARCH nanocomposite