

ZINC (II) METAL ION COMPLEXES OF CHITOSAN: TOWARD HETEROGENEOUS-ACTIVE CATALYSTS FOR THE POLYMERIZATION OF VINYL ACETATE

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ABSTRACT

A low cost biopolymeric ligand (Chitosan) was used as a stabilizer to synthesize Zinc(II)-chitosan biopolymer (Zn(II)-Chit). The Zn(II)-Chit was prepared by adding ZnSO₄ to chitosan in acetic acid solution under an inert atmosphere. The Zn(II)-Chit was further used to polymerize vinyl acetate (VAc) in an aqueous sodium sulphite (Na₂SO₃). Both the Chitosan and Zn(II)-Chit synthesized were characterized using FT-IR spectroscopy and UV-visible spectroscopy. The hydrated Polyvinyl acetate (PVAc) obtained was also characterized using FT-IR spectroscopy. The UV-visible spectrum of chitosan revealed no peak in the range 300 – 800 nm while Zn(II)-Chit showed an absorption band at 360 nm attributed to metal to ligand charge transfer. The FT-IR analyses revealed the presence of coordinating –NH₂ and –OH functional groups in chitosan, both –NH₂ and –OH stretching vibrations overlap at around 3441 cm⁻¹. The FT-IR spectrum of the Zn(II)-Chit indicates coordination of Zn²⁺ with the –NH, –OH and >C=O of the N-acetyl group in chitosan. The Application of Zn(II)-Chit for the polymerization of VAc yielded PVAc in good yield. The catalyst efficiency of Zn(II)-Chit for the polymerization of VAc was considerably high in terms of induction period and percentage yield of PVAc.

Keywords: Chitosan, Zn(II)-Chitosan Complex, Catalyst, Polymerization, Polyvinyl Acetate

INTRODUCTION

Most of the common heterogeneous catalytic systems that have been developed over the past decades have metallic species supported on inorganic materials (e.g SiO₂, Al₂O₃) or on charcoal (Corma and Garcia, 2003; Lipshutz *et al.*, 2008). The immobilization of transition metals on polymer supports derived from petrochemicals (e.g polystyrene) has also been the focus of many efforts (Ley *et al.*, 2000; Lead beater and Marco, 2002). Recent developments for cleaner and sustainable chemistry are driven by a shift from petrochemical-based feed-stocks to biological materials. There is considerable interest in exploiting natural polymer macrostructures, and in particular those of polysaccharides, to create high-performance and environmentally friendly catalysts (Chtchigrovsky *et al.*, 2009).

Finely divided metal particles have been described with capability to catalyse polymerization reactions (di Lena and Matyjaszewski, 2010). However, if the metal ions are not placed on a support the metal particles agglomerate after a while, the surface area decreases and become deactivated. Interestingly, among the readily

available biopolymeric supports, chitosan is a good biopolymer support that chelates/stabilizes the metals and prevents agglomeration (Adewuyi *et al.*, 2008; 2012).

Polyvinyl acetate (PVAc) emulsions are used as adhesives for porous materials, particularly for wood, paper and cloth. PVAc is also used in paper coatings, paint and other industrial coatings as binder in non-wovens glass fibers, sanitary napkins, filter paper and in textile finishing (Kim and Kim, 2005; Kim, 2009). Owing to the increase in the use of adhesives such as wood glue in carpentry, paper adhesive during paper packaging, book-binding and book arts, envelope adhesive, wallpaper adhesive etc. It is therefore desirable to utilize a high-performance and environmentally friendly catalysts for the polymerization of vinyl acetate.

In view of this, Zn(II)-Chitosan biopolymer was prepared by using a metallic precursor ZnSO₄ and a stabilizer (Chitosan). The Zn(II)-Chit was further used to heterogeneously polymerize vinyl acetate in an aqueous Na₂SO₃ and the results obtained are herein presented.

MATERIALS AND METHOD

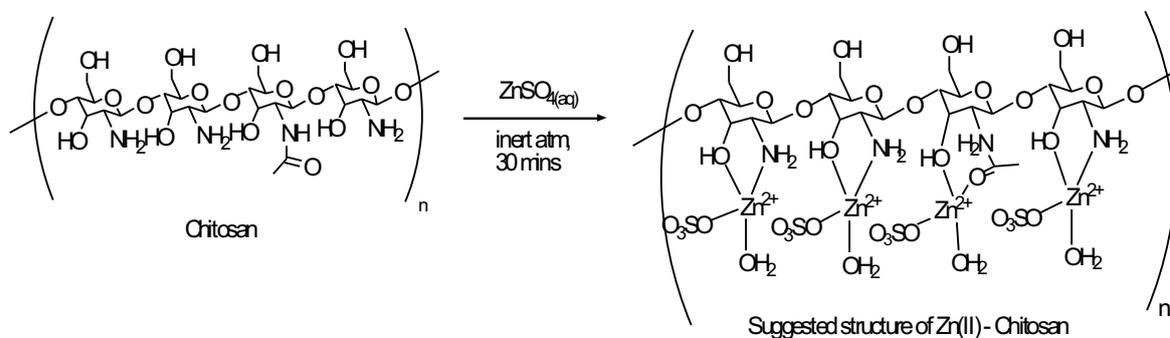
Materials

All chemicals were of analytical grade, purchased from Sigma–Aldrich (St. Louis, MO) and were used without further purification. All aqueous solutions were prepared from reagent-grade chemicals using distilled water. The electronic spectra of the Zn(II)-Chitosan biopolymer were recorded on Shimadzu, UV-1650PC, UV-Vis Spectrophotometer (Tokyo, Japan). IR spectra of KBr disc pellets of the biopolymer samples were recorded on a Perkin-Elmer Fourier Transformed Infra-red (FTIR) spectrophotometer version

10.03.07, while that of PVAc product was recorded on high resolution SCHIMADZU FTIR-8400S (Tokyo, Japan).

Synthesis of Zn(II)-Chitosan Biopolymeric Complex

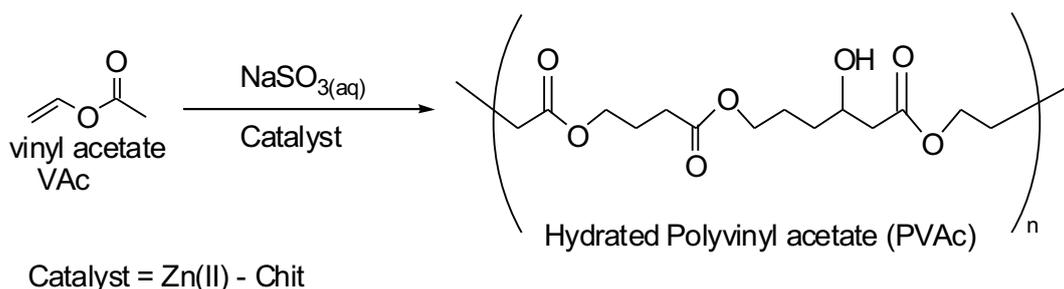
Zn(II)-Chit was synthesized following literature procedure (Adewuyi *et al.*, 2012) by reacting 25 mL, 10% ZnSO_{4(aq)} with 1 g of chitosan in acetic acid solution (Eq. 1). The resulting solution was spread in a Petri dish and allowed to dry at room temperature for 24 h.



Polymerization of Vinyl Acetate.

Catalytic amount (0.5 g) of the Zn(II)-Chit and 1 mL of vinyl acetate (VAc) were added in Na₂SO₃ aqueous solution (pH 7) in a beaker. The mixture was allowed to stand until a white precipitate appeared on the surface of the catalyst (Eq. 2) at

varied time intervals. The PVAc product obtained was filtered, washed, and finally dried in an oven at 80 °C (Hua-min and Xian 2004). The induction period (the time taken for the polymer to start forming) and percentage yield were calculated.



RESULTS AND DISCUSSION

Infra Red Analysis of Zn(II)-Chitosan Biopolymeric Complexes

The Infra red spectra of Chitosan and Zinc(II)-Chit complex are shown in Figures 1 and 2 respectively. FT–IR absorption spectrum of chitosan showed band around 3441 cm⁻¹ which is associated with –OH and –NH stretching

vibrations. These bands are evident in the spectra of the isolated polymers by Muzzarelli *et al.*, (1986). A metal – chitosan interaction is generally revealed by shift in O–H_{str} and N–H_{str} in the region of 3000–3600 cm⁻¹ as well as bending vibrations between 1600 – 1000 cm⁻¹ (Adewuyi *et al.*, 2012). The FT–IR spectrum of Zn(II)-chitosan

coordination complex in this work showed some of these changes. The broad band at 3441 cm^{-1} attributed to the O-H_{str} and overlapping N-H_{str} groups of the chitosan shifted to 3225 cm^{-1} in Zn(II)-Chit . Also, the band at 1597 cm^{-1} attributed

to C=O_{str} of the N-acetyl unit of chitosan was observed at 1620 cm^{-1} in the Zn(II)-chit . These observations suggest a possible chitosan-zinc interaction with N and O as donor atoms (Rehman *et al.*, 2011).

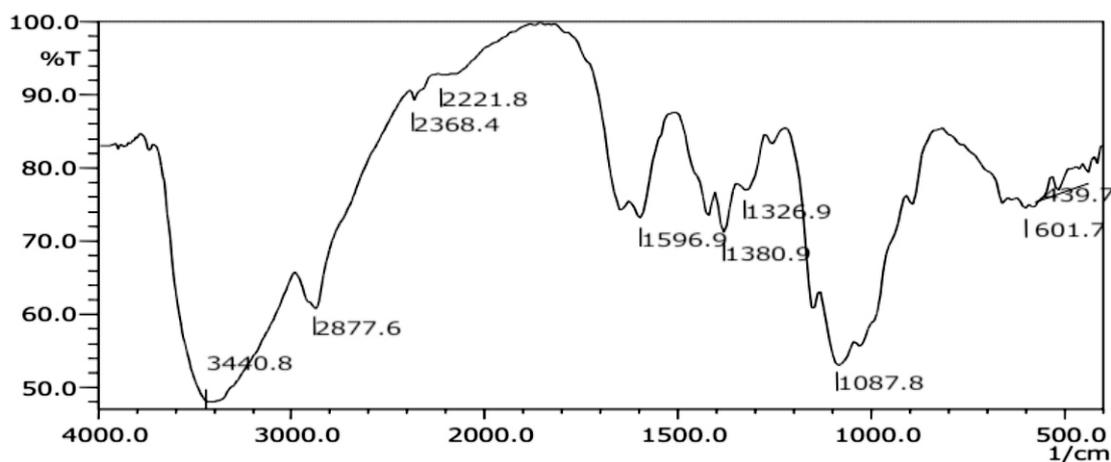


Figure 1: FT-IR Spectrum of Chitosan

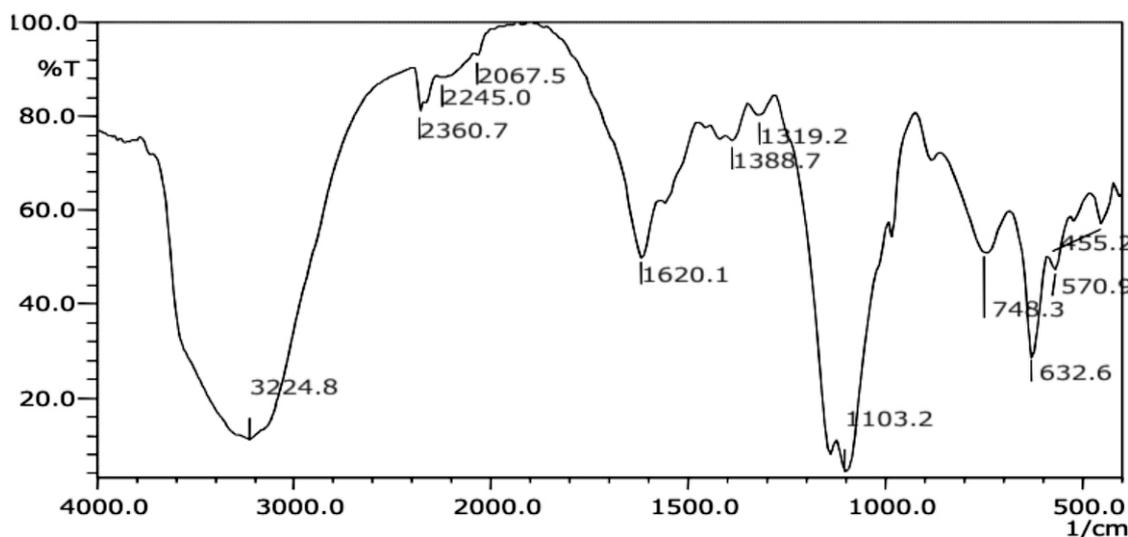


Figure 2: FT-IR Spectrum of Zn(II)-Chit Complex

UV-visible Analysis of Zn(II)-Chitosan Biopolymeric Complexes

The UV-visible spectra of chitosan and Zn(II)-Chit are shown in Figure 3. It is known from the literature that there is no peak observed in the UV-visible spectrum of chitosan at the range of 300 – 800 nm (Kumar *et al.*, 2010). However, the band around 280 nm can be attributed to the $n \rightarrow \pi^*$ intra ligand electronic transition due to the C=O of the N-acetyl group in chitosan (Fig. 3a). Conversely, in

the spectrum of Zn(II)-Chit , two absorption bands at 295 and 360 nm were observed (Fig. 3b). The band at 295 nm is a red shifted $n \rightarrow \pi^*$ due to the C=O of the N-acetyl group in chitosan further suggesting interaction between chitosan and zinc metal. The absorption band at 360 nm is assigned to metal to ligand charge transfer (Rehman *et al.*, 2011). This result further confirms the complexation of Zn^{2+} metal ion with chitosan to form the Zn(II)-chitosan biopolymeric complex.

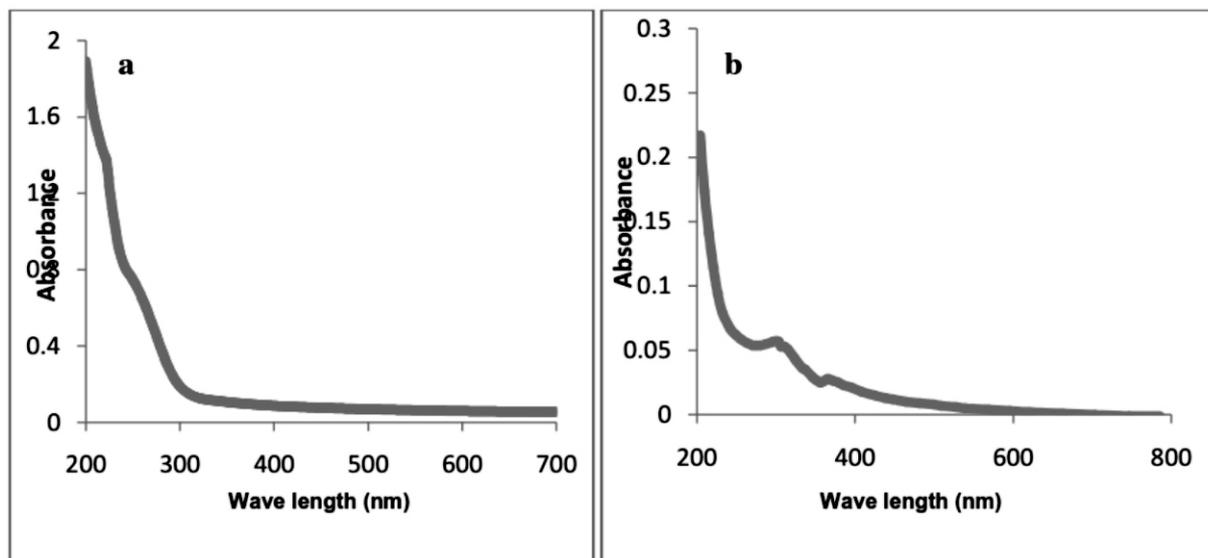


Figure 3: UV-visible spectra of (a) Chitosan and (b) Zn(II)-Chit Complex

Polymerization of Vinyl Acetate

The polymerization of VAc at a neutral pH using Zn(II)-Chit as catalyst afforded a rubbery polymeric material at moderately high yield. In order to confirm the product, the FT-IR of the dried product sample was carried out and compared with industrially based PVAc polymer of a glass transition temperature (T_g) of 30°C (Figs. 4 and 5). The assignment of the spectrum was made in analogy with available literature values. The strong band at around 1740 cm^{-1} is assigned to $\text{C}=\text{O}_{\text{str}}$ of the acetate units of PVAc, which is a major identifying peak in PVAc spectrum (Srinivasan *et al.*, 2005). Similarly, a band at 1124

cm^{-1} is assigned to $\text{C}-\text{O}_{\text{str}}$ in accord with Renukadevi and Madivanane, (2012). According to Zhang *et al.* (1991), The C-H in-plane bending vibrational modes are assigned to the frequency around 1240 cm^{-1} , hence, the strong band at 1242 cm^{-1} can be attributed to the C-H in-plane bending of the sample product. What is more, the asymmetric stretching vibration of PVAc methyl and methylene groups usually appear at around 2973 and 2940 cm^{-1} respectively (Renukadevi and Madivanane, 2012). In line with this, the bands at 2976 and 2938 cm^{-1} are attributed to C-H asymmetric stretching in CH_3 and CH_2 groups respectively.

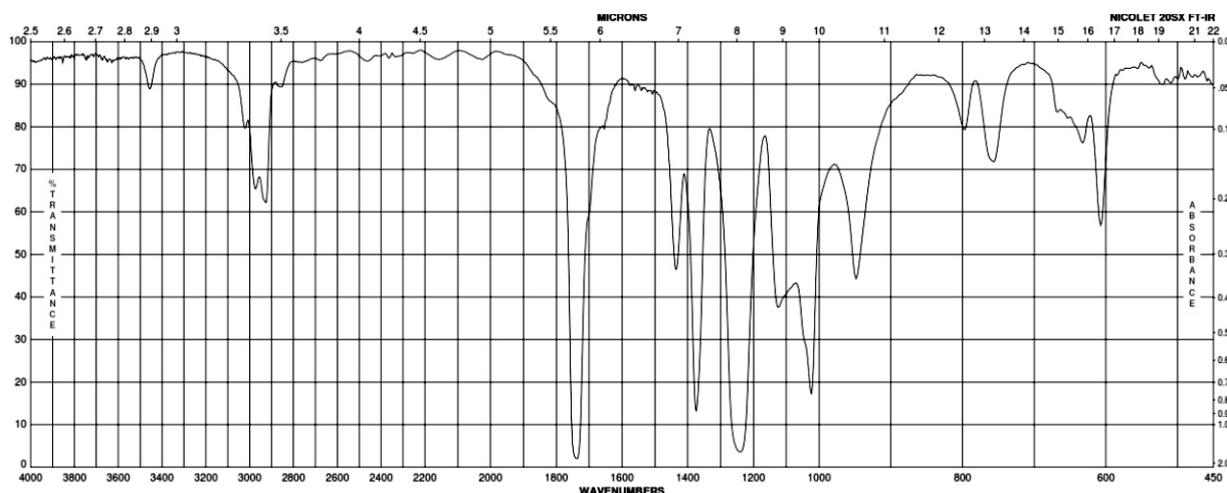


Figure 4: FT-IR Spectrum of Industrially based PVAc Polymer

(Source: <http://www.sigmaldrich.com/spectra/ftir/FTIR002085.PDF>)

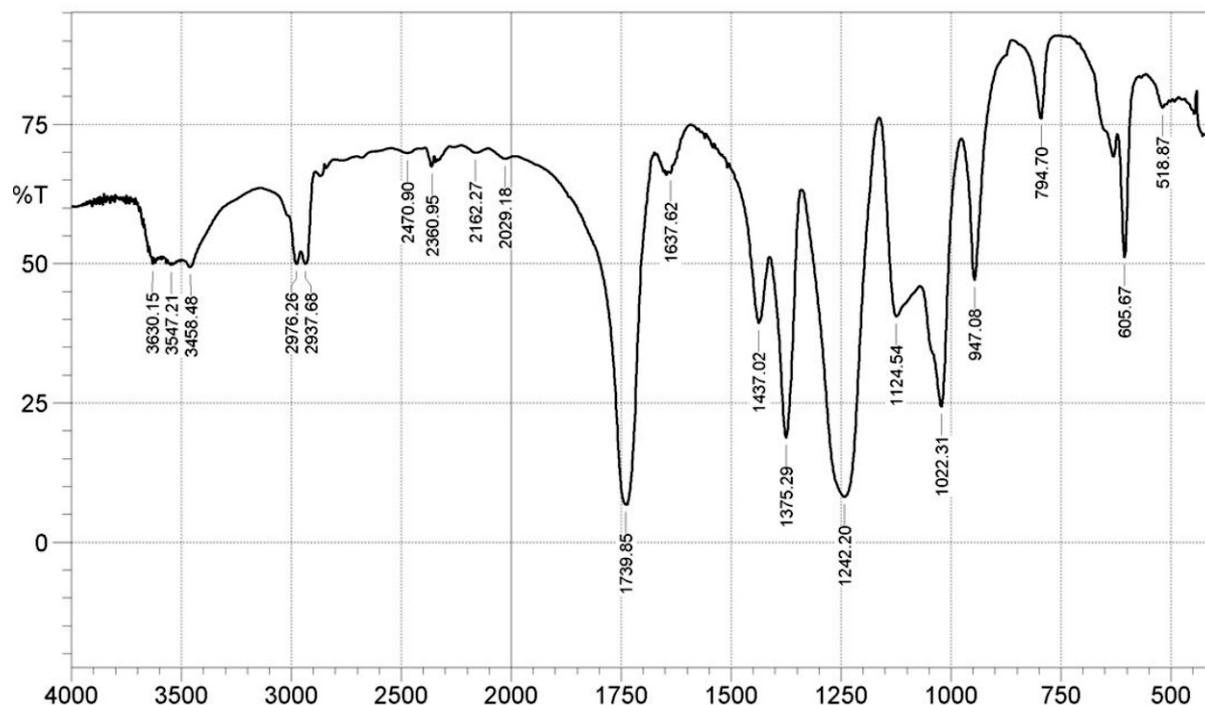


Figure 5: FT-IR Spectrum of PVAc product using Zn(II)-Chit Complex as a catalyst

Table 1 shows the induction period and percentage yield of PVAc in the presence of Zn(II)-Chit catalyst. The VAc and catalyst contact period was varied and lasted for 24 h. For all the entries, the induction period was relatively low showing that the Zn(II)-Chit has a large surface area and pore size for easy and quick diffusion of

the VAc reactant and PVAc product to and from the catalyst surface (Hua-min and Xian 2004). This suggests Zn(II)-Chit as an effective catalyst in terms of induction period. In the same vein, Zn(II)-Chit gave highest percentage yield of PVAc after 24 h of contact (Entry 5).

Table 1: Induction Period and Percentage yield of Polyvinyl Acetate (PVAc) using Zn(II)-Chit as Catalyst.

Entries	Contact Time (h)	Induction Period (s)	Percentage Yield (%)
1	0	0	0
2	6	50	10
3	12	30	35
4	18	25	45
5	24	20	50
6	30	20	50

CONCLUSION

The catalytic property of Zn(II)-Chit on vinyl acetate polymerization in $\text{Na}_2\text{SO}_{3(\text{aq})}$ was successfully carried out. The applied Zn(II)-Chit initiates vinyl acetate polymerization in $\text{Na}_2\text{SO}_{3(\text{aq})}$ with possible diffusion of vinyl acetate to the surface and pores of Zn(II)-Chit with formation of PVAc on Zn(II)-Chit. The result showed that the induction period for vinyl acetate

polymerization was relatively low yielding a considerable amount of PVAc after 24 h of contacts at room temperature. This result undoubtedly shows that Zn(II)-Chit can serve as effective heterogeneous catalyst for vinyl acetate polymerization under ambient conditions.

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