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Comparative Study of Grafting Kinetics of N-Vinyl Imidazole and 4-Vinyl Pyridine onto Cellulose

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ABSTRACT: Being cost effective Cellulose and cellulosic's have vast scope in industrial and various technological applications. The graft copolymers of N-Vinyl imidazole and 4-vinyl pyridines have extensively been used as Catalysts, Biocides, Poly-soaps and Ion exchange resins. However how the graft copolymer will respond to any practical application depends upon the percent grafting of the monomer onto cellulose. Kinetics study of the grafting parameters of Vinyl Imidazole and 4-Vinyl pyridine onto cellulose has been studied and it has been found that 4-Vinyl pyridine has more grafting potential than the other. Percent total conversion for a given monomer concentration are found to be higher for 4 vinyl pyridine than the vinyl Imidazole. The radicals produced during the grafting of Vinyl Imidazole seem to be more soluble in the monomer and solvent than penetrating the hetereo backbone of the cellulose. Grafting efficiency of the Vinyl Imidazole is found to be less than that of 4-Vinyl pyridine for all equal monomer concentrations. Even rate of polymerization, homo-polymerization and grafting are found to be less for vinyl Imidazole than 4-vinyl pyridine. Graft copolymers have been used in Immobilization of Protease and BSA. It has been found that Percent grafting has greater effect in the case BSA immobilization than Protease immobilization which is increased due to grafting but is almost independent of its amount. Also the synthesized graft copolymers have capacity to absorb metal ions from solution. Fe^{2+} is absorbed to maximum extent at lower P_g levels but cellulose grafted with poly Vinyl Imidazole has better capacity to absorb Cu^{2+} ions.

Keywords: Cellulose, 4 Vinyl Pyridine, N-Vinyl Imidazole, Bovine serum albumin, Protease.

I. INTRODUCTION

Polymers of 4-Vinyl pyridine have been known as efficient catalyst and reagents. Also quaternerized vinyl pyridine not only has potential to catalyze organic reaction but also known as effective biocides. Suitable adsorbent for noble metal ions have been prepared by Bojanic *et al* by grafting of 4 Vinyl Pyridine onto cellulose [1]. Various coworkers [2-5]. has utilized CO^{3+}, Fe^{2+} ion as initiators for grafting of vinyl pyridines onto cellulosics and many others has used gamma ray initiation [6-8]. Grafting of 4VP onto cellulose and its derivatives by the use of gamma ray is less investigated area and also in present study, pine needles has been utilized as a stock material for cellulose. Ghanshyam *et al* has also reported Radiation induced graft co-polymerisation of Sty- Maleic anhydride onto cellulose [9]. Kinetics of the grafting of various monomers on to cellulose has also been reported by Moloktov *et.al* [2]. Grafting of 1,2 di-methyl 5 Vinyl pyridine provides good weatherability, antifungal and antimicrobial properties to cellulosics [10].

On the other hand poly N-vinyl imidazole is a good complexing agent and its complexes with certain metal ion which act as catalysts [11]. The complexes of poly(Vim) and Cu^{2+} are found to be active as enzyme. The Polyvinyl imdazole-Cu^{2+} has also been reported to accelerate polymerisaion of phenols to poly ethers [12-17]. Rivas *et al* has reported metal ion sorption studies using poly(VIm) [16]. Poly(N-Vim) hydro gels has also the ability to remove metal ions from polluted water [17]. Tobacovic *et al* has reported grafting of cellulose with nitrogen containing monomers including poly (Vim) for the metal ion sorption support systems. It is also attributed that binding site of the most of the proteins is the imidazole groups of histidine unit.

Cellulose beads offer good immobilization properties than the cellulose itself [18], derivatised cellulose films with diammines and nitro acetic acid [19-20] has been utilized as matrices for enzyme immobilization. Ghanshyam *et al* has also reported such type of enzyme immobilization [21-22].

Since gamma ray initiation method is quite handy and is impurity proof so in the present study grafting of both the monomers separately has been done using γ ray source and optimum graft conditions has been derived by varying various parameters. Most of the kinetic parameters like percent total conversions, Percent grafting, rate of grafting, polymerization and homo polymerisation and grafting efficiency etc has been derived and plotted as a function of monomer concentration. Evidence of grafting has been done with Scanning electron micrographs, FTIR, thermal and elemental analysis.

II. EXPERIMENTAL

Pine needles have been used as a source of cellulose by ammonia extraction method discussed below. 4 Vinyl Pyridine (Merck), Vinyl Imidazole (Fluka Chemicka, Buchs, Switzerland) were vacuum distilled and other chemicals were used as such received.

A. Extraction of Cellulose

Oven dried pine needles (*Pinus roxburgii*) were crushed to powder and were digested with ammonia for eight hours. The solid mass filtered and was subjected to bleach with calcium hypochlorite as reported by Ghanshyam *et. al.* [23]. Obtained cellulose was subjected to repeat washing with distilled water to ensure complete removal of lignins. The obtained mass was oven dried at 40°C and crushed to powder for further reactions.

Grafting of N-Vinyl Imidazole on to Cellulose. In definite amount of water 1.0 gram cellulose and monomer were irradiated simultaneously by γ rays for specific time. The samples were then analyzed for homo polymer, graft copolymer, which were separated by repeated washing with distilled water. The complete removal of homo polymer was ensured with both water and methanol till constant weight of graft copolymer was obtained. Then different kinetic parameters like monomer concentration, amount of water, radiation time, were varied one by one keeping the others constant to get the optimum grafting conditions.

Grafting of 4-Vinyl Pyridine on to Cellulose. Similar method of grafting has been adopted for the grafting of 4-Vinyl pyridine on to cellulose. In case of 4VP the removal of homo polymer was ascertained with 1:1 acetone water mixture. Variation of different kinetic parameters was carried out as it is as in the case of Vinyl Imidazole.

Kinetics has been studied for both of the monomers and different expressions used in the study are as follows:

$$Percent\ total\ conversion(\%Ct) = \frac{Wt\ of\ polymer\ grafted + Wt.of\ homopolymer\ formed}{Wt.of\ monomer\ charged}\ x\ 100$$

$$Percent\ grafting(Pg) = \frac{Wt\ of\ polymer\ grafted}{Wt.of\ cellulose}\ x\ 100$$

$$Percent\ grafting\ efficiency(\%GE) = \frac{Wt\ of\ polymer\ grafted}{Wt.of\ monomer\ grafted + Wt.of\ homopolymer\ formed}\ x\ 100$$

$$Rate\ of\ polymerisation(Rp) = \frac{Wt\ of\ polymer\ grafted + Wt.of\ homopolymer\ formed}{M.Wt.of\ monomer\ x\ time\ of\ reaction(s) x\ Vol.of\ reaction\ mixture}\ x\ 1000$$

$$Rate\ of\ grafting(Rg) = \frac{Wt\ of\ polymer\ grafted}{M.Wt.of\ monomer\ x\ time\ of\ reaction(s) x\ Vol.of\ reaction\ mixture}\ x\ 1000$$

$$Rate\ of\ homopolymerisation(Rp) = \frac{Wt.of\ homopolymer\ formed}{M.Wt.of\ monomer\ x\ time\ of\ reaction(s) x\ Vol.of\ reaction\ mixture}\ x\ 1000$$

B. Characerisation of Polymers

Evidence of grafting has been ensured by taking FTIR spectra and Scanning Electron micrographs. SEMs of graft copolymer were studied on Cambridge Stereo scan 150. Elemental analysis and FTIR spectra were recorded over Carlo Erba-1150 and Nicolet Magha IR 750 series II in KBr pellets.

C. Metal Ion Sorption Studies

The specific weighed graft samples individually immersed in 50 ml solutions of Cu^{2+} and Fe^{2+} ions for 24 Hrs.

Filtrate of these solutions were analysed for rejected ions with spectrophotometer(Hach Co.) Copper sulphate and ferrous sulphate were used as such as received from CDH .The following calculations were made to judge the metal ion absorption studies. Fig. 5 Displays the sorption capacity of these graft copolymers.

$$Percent\ Uptake(Pu) = \frac{Wamount\ of\ metal\ ions\ sorbed}{Total\ ions\ of\ metal\ in\ feed} x\ 100$$

D. Protease Immobilisation

Cellulose as well as its graft copolymers with 4VP and N-Vim were analysed for the support for protease immobilization. Protease assay was performed using Manachini method [24]. Casein (Hammerstein) solution was dissolved in 50 mM Tris HCl buffer at basic pH 8 and (0.5% w/v) tris chloroacetic acid using tyrosine 10-100µg/ml as standard. Known weight of cellulose and its graft copolymers were immersed in 1.0 mL of protease enzyme (50 µL) for 24 Hrs. At the interval of 24 HRs. washed polymer support with Tris HCl were dipped in 4 mL casein solution. It is followed by incubation for 10 minutes at 55°C. The reaction was terminated with trichloroacetic acid and vortexed. The contents are then filtered and absorbance of the supernant liquid was measured on Shimadju Spectrophotometer at 275 nm.

E. Bovine Serum Albumin Immobilisation

Lowry method has been taken as a base for the Bovine serum albumin immobilization [25]. 1% $CuSO_4$, 2% sodium carbonate, 2% sodium potassium tartarate Lowry alkaline reagent, Folin ciocalteau's phenol reagent 10-100µg/ml BSA were taken. Cellulose and graft-copolymers were dipped in 1 mL BSA for 24 Hrs. and after that were washed with water and mixed with 3mL of Lowry alkaline reagent. Resultant solution was vortexed and allowed to stand for 15 minutes. Then Folin ciocalteau's phenol reagent is added and maximum colour development is noticed. Optical density was measured at 670 nm against blank reagent and concentration of protein was calculated from standard curve. The material has been already published online (April 2006) in Wiley Interscience (www. Interscience.wiley.com)

III. RESULTS AND CONCLUSIONS

A. Comparison of Kinetic Parameters

Leaving one exceptional value, percent total conversions for both the monomers, proceeds smoothly with increase and decrease. It is cyclic change in case of 4 vinyl pyridine but it slightly increases with increase in monomer concentration for Vinyl Imidazole. The maximum percent conversion value oscillates between 80 to 98 percent in both the monomers.

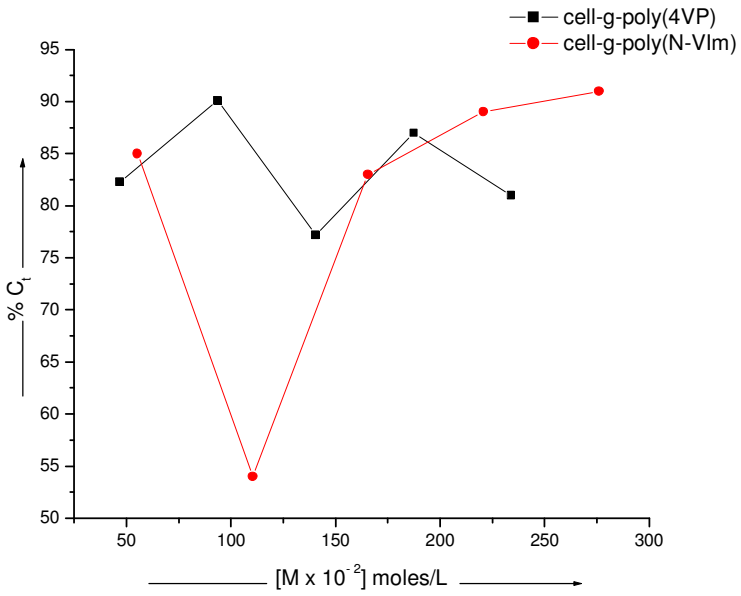


Fig. 1. Variation of % C_t with Monomer concentration.

For [4VP] = 93.70 × 10^{-2} m/L percent total conversion is found to be 98% while for [N-Vim] = 276 × 10^{-2} m/L the value is 91%. Thus indicating almost equal reactivity of both monomers in solution to get polymerizes. A perusal of the rates of polymerization for both the monomers, reflects their individual reactivity. Corresponding rates for 4 vinyl pyridine are found to be 10 times higher than the vinyl imidazole. Also flow of increase in the rates is much more abrupt for the vinyl pyridine than the vinyl imidazole. Reactivity of 4VP increases rapidly with increase in monomer concentration than the smoother in case of Vinyl Imidazole. Also the rate of homo-polymerization is increasing in parallel way for vinyl imidazole with almost equivalent rates; on the other hand there is a large gap between the corresponding values for 4 Vinyl pyridine.

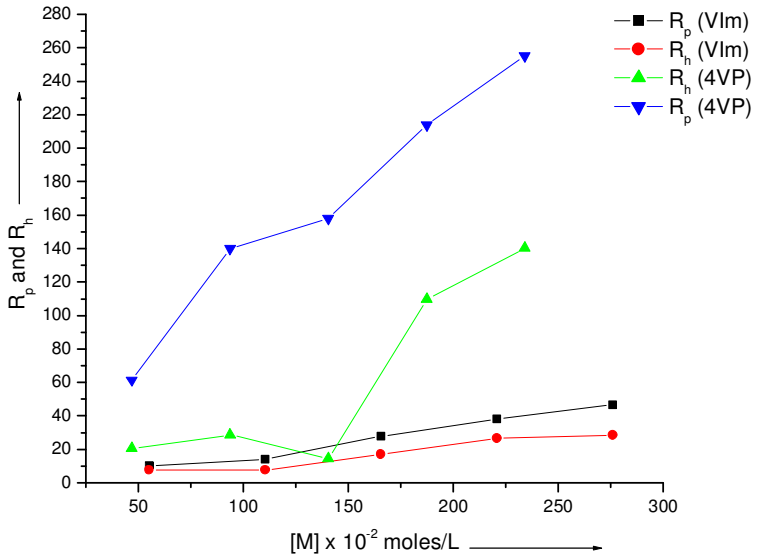


Fig. 2. Variation of Rate of polymerization and rate of homo polymerisation with monomer Concentration.

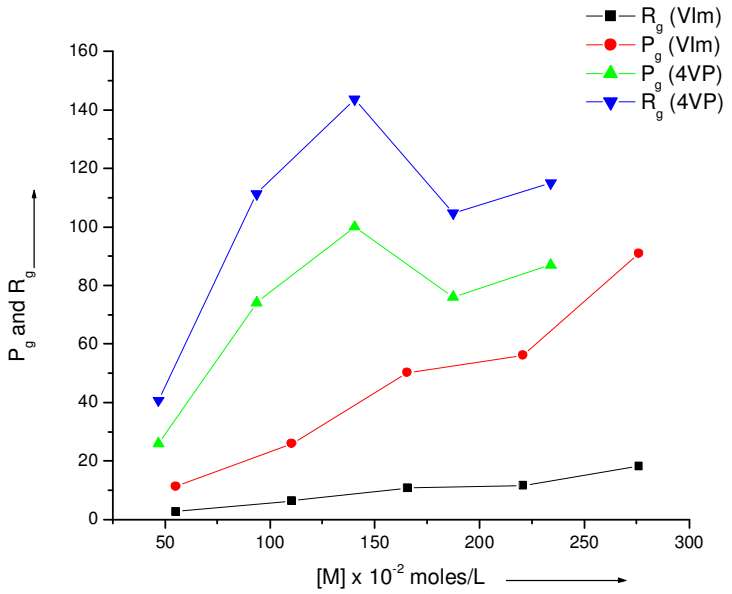


Fig. 3. Variation of P_g ad R_g with monomer concentration.

There is a sharp increase in the percent grafting in case of Vinyl imidazole but the corresponding values are less than for the case of 4VP. There is increase and decrease in the values of P_g for 4 vinyl pyridine as has been same is reflected in percent total conversion with varying monomer concentrations. For a given monomer concentration higher P_g values suggest that grafting of 4VP onto cellulose is cost effective but same is not the case of Vinyl imidazole where more lose of monomer is there at the cost of less grafting. Cluster formation in case of Vinyl imidazole means attached polymer chains are solubilised / hydrogen bonded, intra molecularly then reaching to the crystalline region of cellulose. But in 4VP case there is no cluster formation means it has opened the structure of the cellulose. Grafting efficiency values are again higher for 4 VP than the case of Vinyl imidazole. First the %GE increases with increase in the monomer concentration up to [100 × 10^{-2}] moles/L and than falls with further fall in monomer concentration. Fall in grafting efficiency may be attributed due to easy accessibility of monomer to the radical sites than penetrating the crystalline region of cellulose.

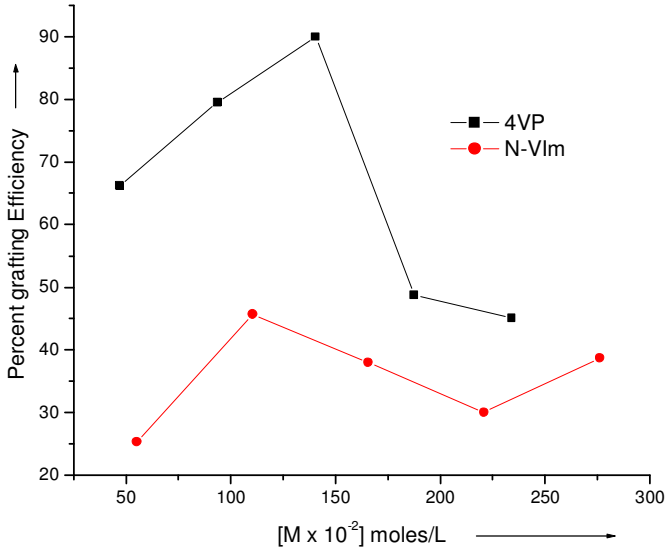


Fig. 4. Variation of % age with monomer concentration.

B. Metal Ion Sorption Studies

Cellulosed based ion exchangers are cost effective, having high thermal stability and chemical resistance than the conventional ion exchangers. Present graft copolymers are not the ion exchangers but absorb the ions in bulk or they complex with the nitrogen present in the anchored polymer chains. Percent uptake of the Cu^{2+} and Fe^{2+} ions by the cellulose is very less having value 4.4% and 6.25%, respectively which has been increased significantly to 90% for both ions indicating that grafting has improved the retention capacity of cellulose. Almost parallel lines for the absorption of Fe^{2+} ions by the both graft copolymers indicate that Fe^{2+} ion uptake is independent of the P_g value. Nearly 95-100% of the ions are being absorbed by the graft copolymer and even 20% grafting of the monomer is sufficient to absorb all of the ions feeded. It seems that only nitrogen presence is effective for the uptake of the Fe^{2+} ion but independent of the ring attached with nitrogen.

But for the absorption of Cu^{2+} ions both the graft copolymers behave differently. A minimum P_g value 20 to 60 % is sufficient to absorb the copper ions from the solution by the cellulose grafted with 4VP but increased amount of 4VP on cellulose chains is having reverse effect that most of Cu^{2+} ions are being rejected. On the other hand Vinyl Imidazole grafted on to cellulose is having good complexing properties than the cellulose grafted with 4Vinyl pyridine as has been reported in case of Vinyl Imidazole by Tsuchida and Nishide [26].

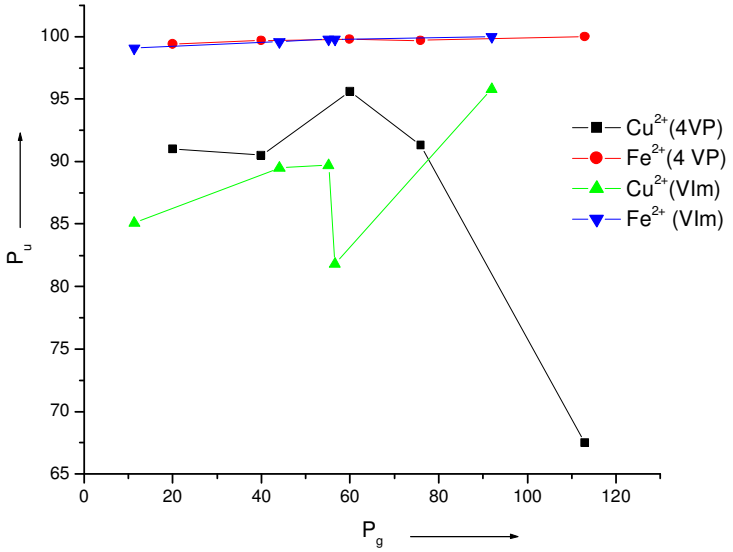


Fig. 5. Variation of %uptake of Cu^{2+} and Fe^{2+} ions with varying P_g.

C. Immobilisation of BSA And Protease

Cellulose alone is not a good a good support for the protease and BSA immobilization but grafting has increased its immobilization property effectively. Immobilisation of BSA with cell-g-poly(4VP) is straight forward linked with % graft as it is maximum(86%) with P_g values 20 but as the P_g increases there is a sharp fall in the Immobilisation of BSA. It indicates that 4 vinyl pyridine offers good support / biding site for the BSA Immobilisation.

Poly Vinyl imidazole chains of graft copolymers also provide anchoring effect to BSA however there is less effect of P_g onto the % immobilization and also BSA is immobilized to lesser extent (maximum 47.5 %) than the poly vinyl pyridine(maximum 86 %).

Protease is better immobilized by the both graft copolymers than the BSA. Increase in Percent graft of vinyl Imidazole onto cellulose increases the support system of the cellulose indicating that Imidazole unit provide good binding site for the protease.

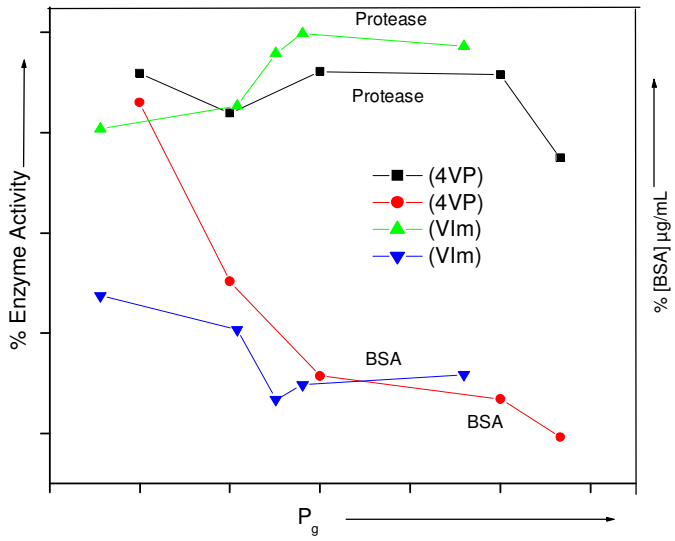
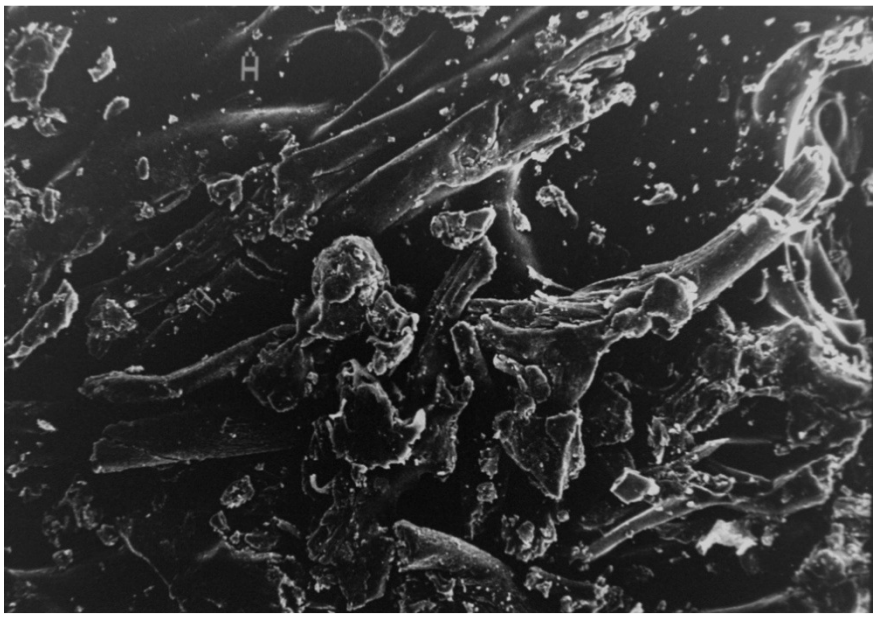


Fig. 6. Immobilisation of BSA and protease by the graft copolymer.

Nearly 97% enzyme activity is noticed in case of vinyl Imidazole than the 4 VP case, where first immobilization increases with increase in Pg and then it falls. Thus protease immobilsation is more, selectively for the poly vinyl Imidazole graft copolymers than the 4 Vinyl pyridine grafted onto cellulose.

D. Characterisation of Graft Copolymers

Comparison of Surface Morphology. Evidence of grafting has been done by taking the electron micrographs of Cellulose and its graft copolymers .These micrographs clearly shows that surface morphology has been changed due to grafting onto cellulose. In case of grafting with 4 vinyl pyridine planer structure is indicating that it has opened the structure of cellulose as it is able to approach the inner core of cellulose. Cluster formation is noticed in cellulose grafted with Vinyl imidazole means that chains of graft copolymers are coiled up due to hydrogen bonding.



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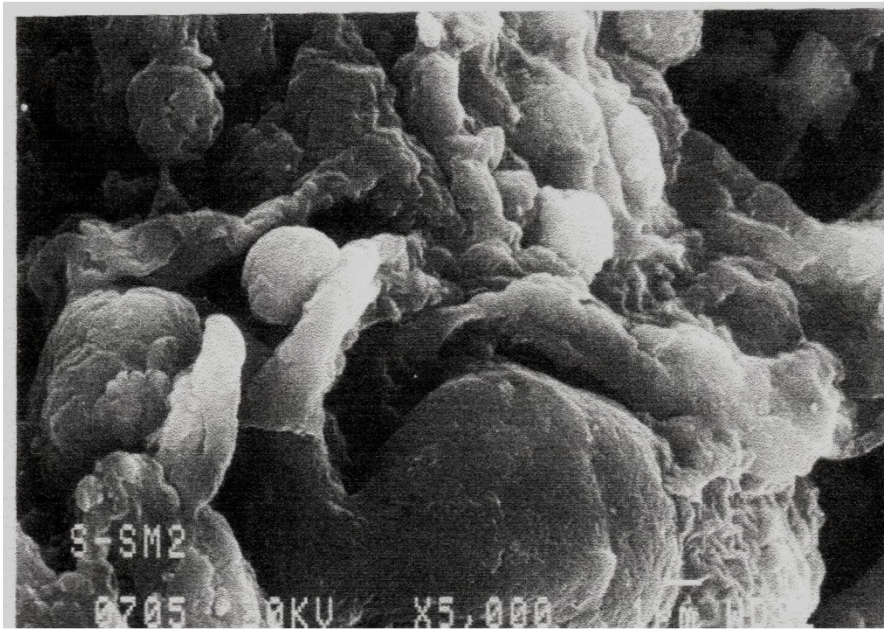

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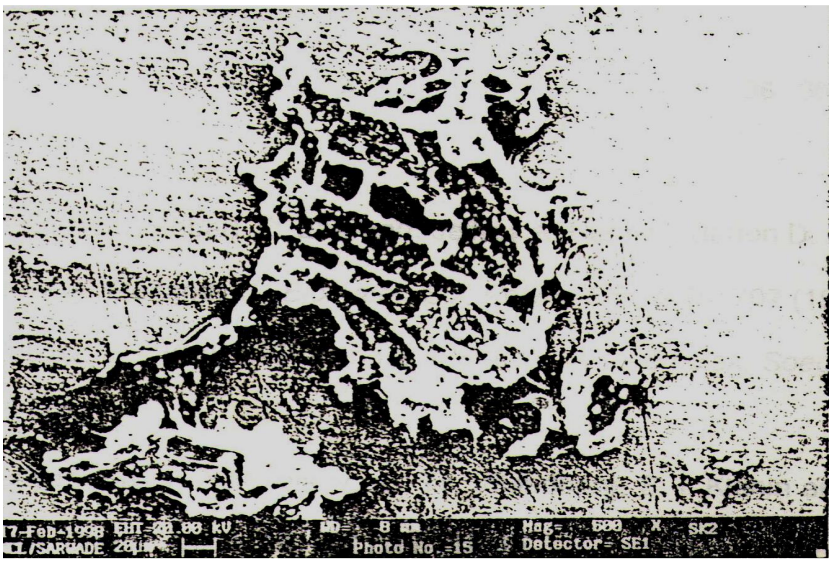
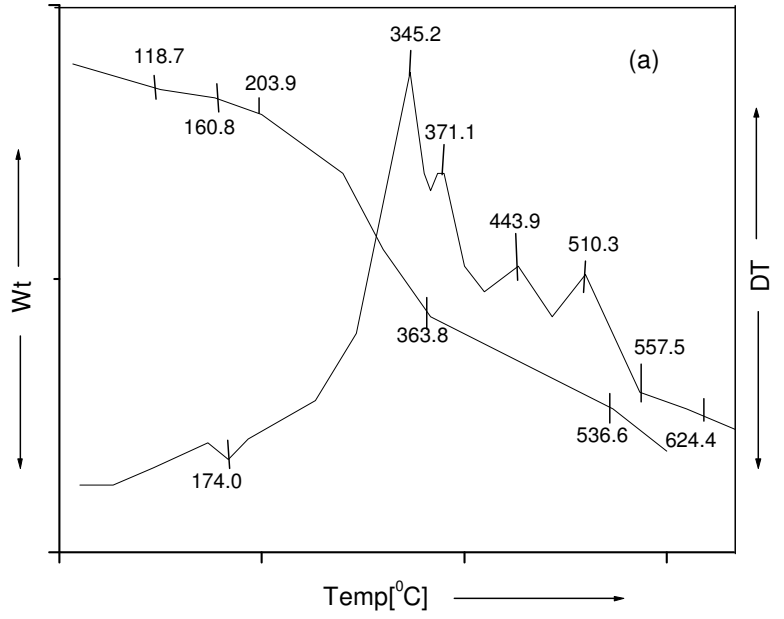


(c)

Fig. 7. Scanning Electron Micrographs of (a) Cellulose, (b) Cell-g-poly(N- Vinyl Imidazole), (c) Cell-g-poly(4 Vinyl Pyridine).

E. Thermogravimetric Analysis

TGA and DTA of cellulose and its graft copolymers were investigated. Cellulose shows two stage decomposition while its graft copolymers show single stage decomposition. Primary loss of weight of 5-6% is due to moisture and trapped ammonia. First stage of decomposition is up to 367°C and second is after that which is due to loss of crystalline region of Cellulose. Shift in the endothermic and exothermic peaks in case of graft copolymer than native cellulose provides the evidence of grafting. The exothermic peak at 345.2°C for native cellulose has been shifted to high value for graft copolymers; indicate that thermal stability of the cellulose has been increased due to grafting.



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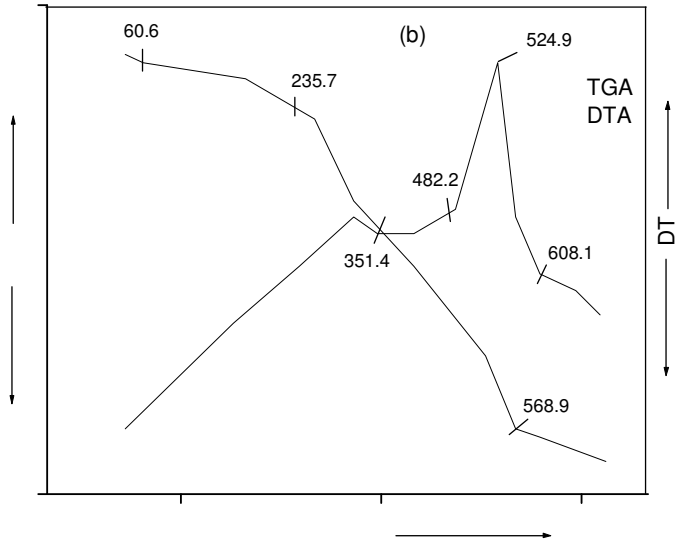

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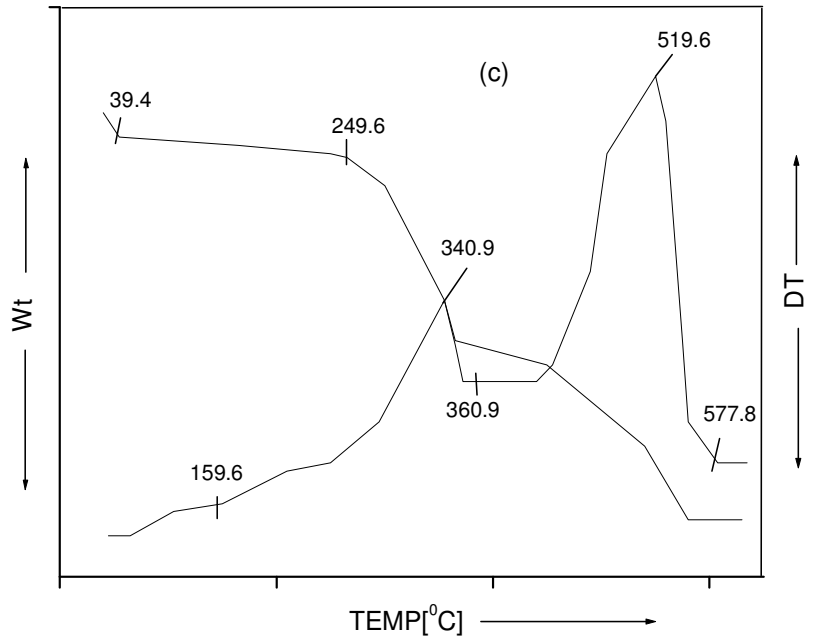


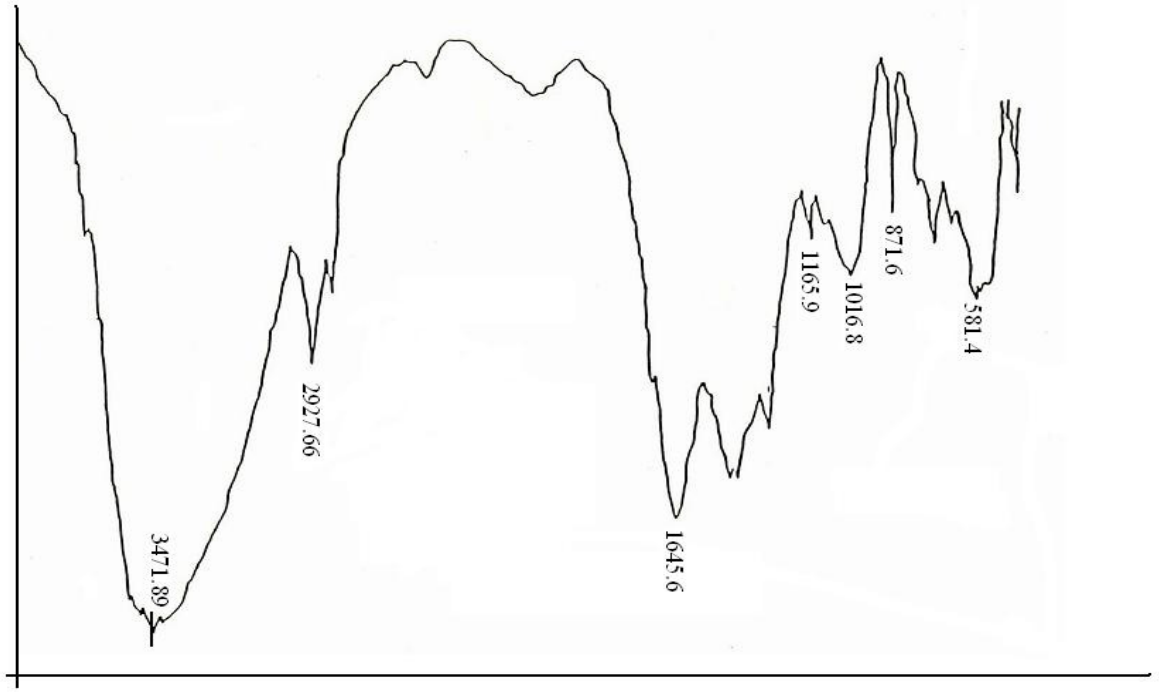
(c)

Fig. 8. TGA and DTA of (a) Cellulose, (b) Cell-g-poly(N- Vinyl Imidazole), (c) Cell-g-poly(4 Vinyl Pyridine).

F. FTIR Analysis of Graft Copolymers

Cellulose and its graft copolymers were analysed by FTIR spectroscopy. Graft copolymers shows well defined sharper peaks at 1623-1597cm^{-1} and doublets at 1416 and 1552cm^{-1} due to stretching vibration of C-N and C=C. In graft copolymers of 4 vinyl pyridine the O-H peak has become sharper and shifted down to 3185 cm^{-1}, means opening of crystalline region of cellulose.

It is also leading to lose of H bonding but with further formation of weak association. On the other hand same peak in graft copolymers with N-Vinyl imidazole is not sharper but has broadened. This clearly means that vinyl imidazole grafting does not leads to opening of crystalline structure but is further adding to association leading to polymeric association.



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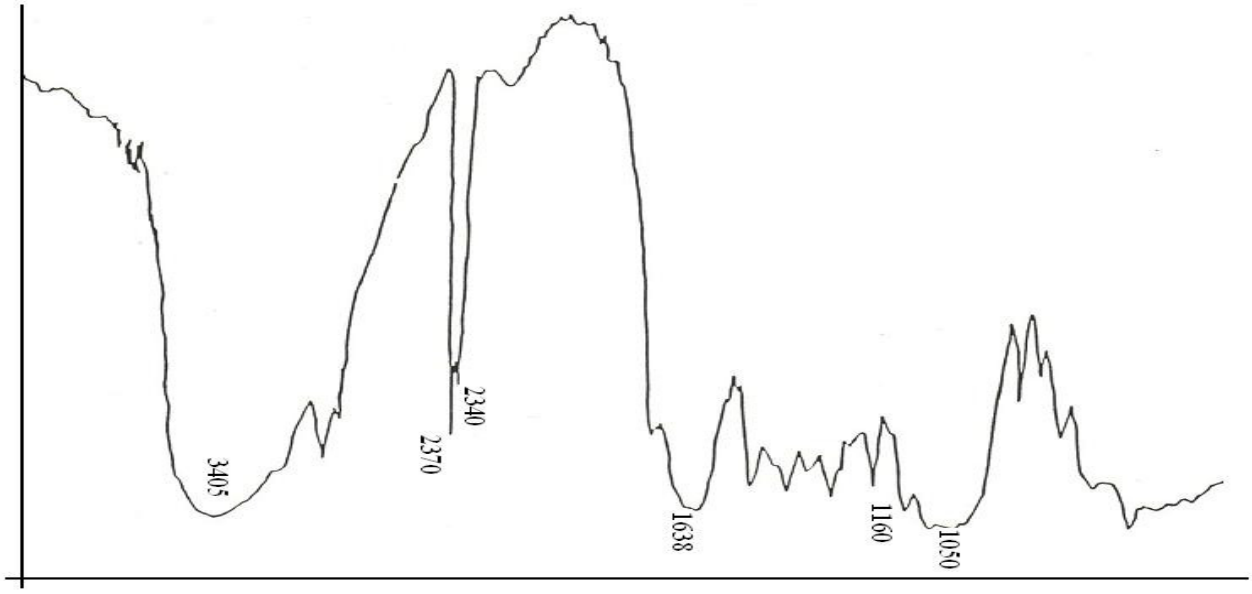

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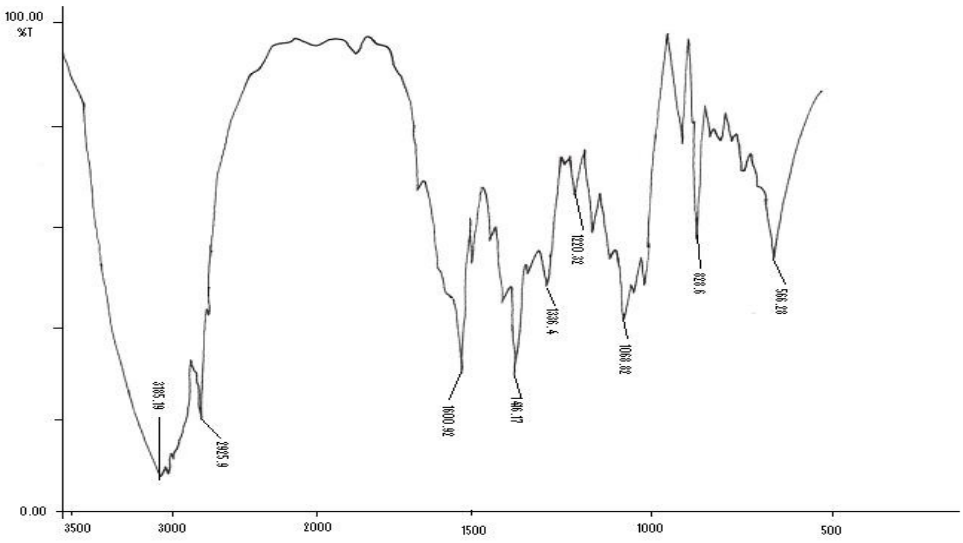

(C)

Fig. 9. FTIR of (a) Cellulose, (b) Cell-g-poly(N- Vinyl Imidazole), (c) Cell-g-poly(4 Vinyl Pyridine).

VI. CONCLUSIONS

No doubt grafting has enhanced the ability of cellulose to act support system for enzyme and has also improved its metal ion uptake properties. 4 Vinyl pyridine being hydrophobic monomer than the N-Vinyl Imidazole hence able to penetrate in the crystalline region of the cellulose leading to maximum grafting. Thus it is cost effective to use 4 vinyl Pyridine than the N-Vinyl Imidazole. On the other hand N-Vinyl Imidazole is more solubilised in solvent than grafting or approaching to binding sites onto cellulose. Both the monomers offer good binding ability to metal ion as well as offers support system to Enzyme and BSA. With minimum Pg 4 Vinyl Pyridine grafting offers a cost effective way for metal ion uptake or enzyme immobilization than the Vinyl Imidazole. However especially for the Cu^{2+} ions Its Imidazole graft copolymers are better than the 4 Vinyl pyridine graft copolymers.

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