Open Science Journal of Bioscience and Bioengineering
2020; 7(2): 20-25
http://www.openscienceonline.com/journal/bio
ISSN: 2381-3806 (Print); ISSN: 2381-3814 (Online)

Synthesis and Characterization of Vinyl Acetate Grafted onto Obeche Wood (*Triplochiton scleroxylon*) Cellulose Material

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To cite this article

Chiagozie Michael Ekwunife, Aghoghome Eruemrejovwo, Rosmary Uche Arinze, Theresa Uzoma Onuegbu. Synthesis and Characterization of Vinyl Acetate Grafted onto Obeche Wood (*Triplochiton scleroxylon*) Cellulose Material. *Open Science Journal of Bioscience and Bioengineering*. Vol. 7, No. 2, 2020, pp. 20-25.

Received: May 11, 2020; **Accepted**: June 3, 2020; **Published**: July 4, 2020

Abstract

This study was aimed at investigating the synthesis and characterization of vinyl acetate grafted on Obeche wood Cellulose. Vinyl acetate monomer was grafted onto the Obeche derived cellulose using benzoyl peroxide as initiator at varied temperatures. The Obeche cellulose-g-poly (vinyl acetate) was brown in colour. The effect of initiator concentration, monomer concentration and temperature on percentage grafting and grafting efficiency of the product was determined. Both percentage grafting and grafting efficiency increased with initiator concentration and monomer concentration for the Obeche cellulose-g-poly (vinyl acetate). The percentage grafting and grafting efficiency increased with temperature from 60°C – 70°C then dropped after 70°C for the Obeche cellulose-g-poly (vinyl acetate) sample. The graft copolymer was analyzed and characterized using various tests that included Fourier transformed infrared spectrophotometer, physico-mechanical tests that were, hardness test with durometer shore hardness tester, density with Monsanto Densitron 2000, softening point tester with HDT/Vicat Test Station and adsorption studies of bromothymol blue onto the sample was done with Ultraviolet-visible spectrophotometer. The result of the FTIR confirmed the presence of O-H of alcohol (3410 cm^{-1}), C=O of esters (1734 cm^{-1}), N-H of protein (2310 cm^{-1}), C-H of methyl, methylene (2935 cm^{-1}), and C-O of esters (1236 cm^{-1}) in the Obeche cellulose-g-poly (vinyl acetate), result of the hardness showed that the Obeche cellulose-g-poly (vinyl acetate) was 65D, the density was 0.85 mg/m^3, and the softening point was 125°C - 140°C. The percentage of bromothymol blue removed from aqueous solution by Obeche cellulose-g-poly (vinyl acetate) was 64.3%. The rate constants for the Obeche graft copolymer was determined using pseudo first order kinetics and it gave 3.36 x 10^{-2} min^{-1}. The research showed that Obeche cellulose-g-poly (vinyl acetate) could be used in the adsorption of bromothymol blue (dye) in aqueous solution.

Keywords

Obeche Cellulose-g-Poly (Vinyl Acetate), Obeche Wood Fiber, Graft Copolymer

1. Introduction

Cellulose is a naturally occurring polymer that consist of many repeated units of monomer molecules and due to its abundance, it is available at low cost. Cellulose is a long chain of linked sugar molecules that can provide strength for all kinds of plants [4].

Natural fibers, which also has cellulosic properties, are naturally occurring polymers in our environment that appears mostly in grasses, leaves, stalks of plants or even animals. In the composite industry, they are referred to as plant fibers and further categorized into wood or non-wood sources. They are also known as lignocellulose fibers since lignin and

cellulose are the main components in their structures. In spite of their advantages, the major challenge of natural fibers is the difficulty in molding them into the desired form or film because they cannot be melted or dissolved in a common solvent due to the strong intermolecular hydrogen bonding, high degree of polymerization, and high crystallinity degree [3].

Obeche (*Triplichiton scleroxylon*) is a tropical tree in Africa that is very rich in its cellulose property and cellulose can be obtained from it and used for making valuable product. Pre-treatment of the fiber modifies the surface, removes the lignin and disorders the intermolecular hydrogen bonds holding the structures before grafting [10].

Grafting with vinyl acetate (monomer) in the presence of benzoyl peroxide as initiator is an effective method of modifying the properties of cellulosic materials [2]. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as water absorption, improved elasticity, hydrophilic or hydrophobic character, ion exchange [1], dye adsorption capabilities [7], heat resistance, thermos-sensitivity [9], pH sensitivity [8], and resistance to microbial attack etc.

2. Materials and Methods

The Obeche wood fiber obtained from the sawmill site was pretreated first to get rid of lignins as well as break down the intermolecular hydrogen bonding linkage between the cellulosic material.

2.1. Preparation of Cellulose from Obeche Wood Fiber

The wood dust (250g) was weighed into a 100mL beaker. 500mL of 2M solution of NaOH was added with constant stirring and was allowed to stand for 24h. After which it was mixed with 100mL of 10% sodium hypochlorite solution with continuous stirring. The mixture was heated up to 60°C with a laboratory hot plate. It was allowed to cool at room temperature and 200mL of ethanol and Iso-butanol mixed in the ratio of 1:1 was added to the mixture. The mixture was allowed to stand for 24h. The wood slurry was sieved out of the mixture using a fine plastic sieve. It was washed with distilled water four times to eliminate unreacted material. The slurry was allowed to dry at room temperature for 48h. It was grinded again using a manual hand machine and sieved with a sieve of 200micro mesh. The flour obtained was used without further modification.

2.2. Preparation of Graft Copolymer of Vinyl Acetate onto Obeche Wood Fiber

Cellulose (2.5g) was dispersed in 50mL of distilled water. The substrate was initiated with 2 ± 0.5g of benzoyl peroxide and stirred for 5minutes. After initiation, about 20 ± 10 mL of 40 moles of vinyl acetate was added to the reaction flask and monitored with continuous stirring. The reaction mixture was heated up using the laboratory hot plate at various temperatures ranging from 60°C – 80°C and stirred continuously for 30mins of reaction time. After the completion of the reaction, the rough products were first precipitated in an excess of acetone and then separated by filtration. To obtain the pure graft copolymer, carbon-tetrachloride was used to extract the homo-polymer that might be produced during the polymerization. Extracting for 6h was sufficient to remove the polyvinyl acetate homo-polymer.

2.2.1. Grafting Percentage

The grafting percentage (GP) indicates the increase in weight of original cellulose subjected to grafting with a monomer and it is calculated generally from the equation (1):

$$\mathrm{GP} = \frac{\text{Weight of polymer Grafted}}{\text{Initial Weight of Backbone}} \times 100 = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

Where W_1 and W_0 are the weights of the cellulose graft copolymer and the original cellulose, respectively.

2.2.2. Grafting Efficiency

Grafting efficiency (GE) shows the fraction of monomer grafted onto cellulose and the amount of monomer converted to graft polymer plus the homo-polymer, in other words, fraction of polymer that is grafted to cellulose in total polymer, and it is calculated from the equation (2).

$$(\mathrm{GE}) = \frac{\text{Weight of Polymer Grafted}}{\text{Weight of Polymer Grafted} + \text{Weight of Homopolymer}} \times 100 = \frac{W_1 - W_0}{(W_1 - W_0)/(W_1 - W_0 + W_2)} \times 100 \quad (2)$$

Where the (W_0) represents weight of original cellulose, (W_1) is the weight of cellulose graft copolymer and (W_2) depicts the weight of the homo-polymer.

2.3. Physico-mechanical Properties Test

In the physico-mechanical test, the hardness test was conducted using the Durometer shore hardness tester ASTM D1415/ISO 48. The model of density instrument used was Monsanto Densitron 2000. The softening point was tested using the Vicat station equipment HDT/ Vicat tester.

2.4. Sorption Behaviour of Obeche Cellulose-g-Poly (Vinyl Acetate)

The cellulose-g-Poly (vinyl acetate) of Obeche wood was immersed in various organic solvents at room temperature and monitored to detect the increase and reduction in weight

of the cellulose material. The solvent used where acetone, chloroform and methanol in order of polarity. Therefore, the void size and accessible amorphous regions are supposed to be responsible for the reaction.

2.5. Fourier Transformed Infrared Spectrophotometer

The model of Fourier transform infrared spectrophotometer used was FTIR-8400S produced from SHIMADZU Company Japan. The test was performed to get authenticated information about the vibrational regions present in the cellulose graft copolymer of the Obeche wood cellulose.

2.6. Adsorption of Bromothymol Blue Dye using Obeche Cellulose-g-Poly (Vinyl Acetate)

Bromothymol blue (0.5g) was weighed out and made up with Analar grade ethanol to 50mL using a measuring cylinder and poured into a conical flask. 2.5±0.5mL each of the dye in solution was measured out and made up to 50mL, after which a fixed weight in grams of the cellulose beads was immersed in each flask with intermittent shaking at room temperature of 25±1°C. The bromothymol blue pH was maintained at buffer 4 by adjusting them with addition of sulfuric acid (H_2SO_4).

Thereafter, the amount of dye adsorbed was analyzed at Λ_{max} 570nm. The initial concentration and adsorbent dosage were varied and the variation in the amount of dye taken up by the adsorbent was analyzed. In each flask 1.0g of the adsorbent beads were added prior to a continuous shaking at temperature of 25±1°C. This solution was filtered after a particular time interval and spectrophotometric analysis was performed for the amount of the dye uptake.

The amount of dye adsorbed (q_e) onto the cellulose beads and the percentage of removal (R) were calculated using the equations 3 and 4.

$$q_e = (C_o - C_e)\frac{V}{W} \quad (3)$$

$$R = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (4)$$

Where C_o and C_e are the initial and equilibrium concentration (mg/l), respectively, V is the volume of the solution (L) and W is the amount of adsorbent (g).

2.6.1. Effect of Time

The study was done to know the amount of dye adsorbed at various time intervals by a fixed amount of the adsorbent.

2.6.2 Effect of Initial Dye Concentration

The study was done to know the concentration of dye that was adsorbed by the adsorbent at different concentrations.

2.7. Kinetic Studies

In the kinetic analysis of the reaction of the pseudo first order, the amount of dye adsorbed was calculated at various time (t) in q_t (mg/g) and at equilibrium in (mg/g) as follows:

$$q_t = \frac{(C_o - C_t)}{M} V \quad (5)$$

$$q_e = \frac{(C_o - C_e)}{M} V \quad (6)$$

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (7)$$

Where C_o and C_e are the initial and equilibrium concentration of the dye in solution (mg/L). C_t is the concentration of the dye in solution at time (t) (mg/L), V is the volume of the solution (L) and M is the mass of the adsorbent in (g). In addition, the removal percentage at equilibrium was calculated by the equation (7).

In this study, kinetic investigation was carried out to monitor various experimental conditions like dye concentration, time, pH, and temperature to measure the rate of reaction throughout the adsorption process with the goal of reaching equilibrium.

In order to determine the rate of adsorption of bromothymol blue on the graft copolymer, the well-known Lagergrens pseudo first order equation was employed, [6]. The values of log ($q_e - q_t$) was calculated for each time interval at 30°C in equation (8).

$$\text{Log}\ (q_e - q_t) = \log_{qe} - k\ \text{ads}\ t/2.303 \quad (8)$$

Where q_e and q_t signifies, the amount adsorbed at equilibrium and at any time (t). The graph of log ($q_e - q_t$) versus (t) time gave a straight line and confirmed the pseudo first order rate kinetics for the adsorption process.

3. Result and Discussions

Table 1. *Percentage Grafting and Grafting Efficiency of Obeche Cellulose-g-Poly (Vinyl Acetate) Versus Initiator Concentration.*

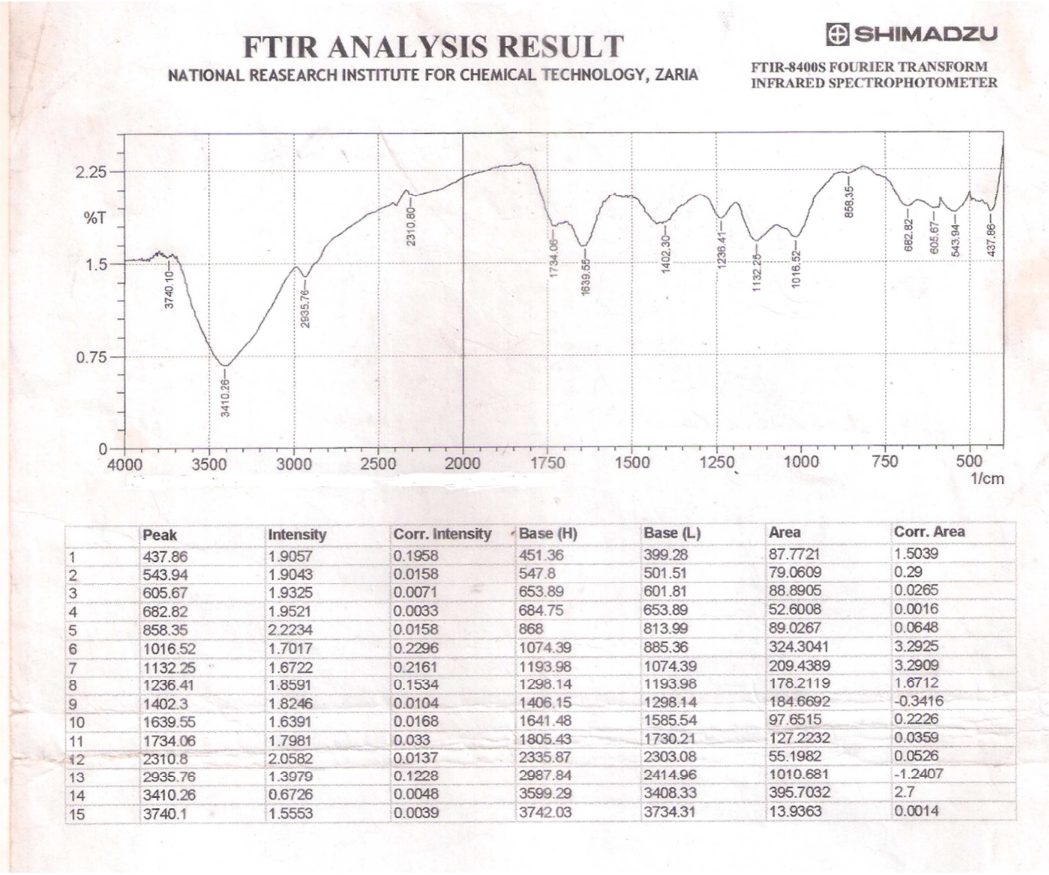
Preliminary test	Weight of initiator (g)	Weight of Obeche Wood Cellulose (g)	Final weight of Obeche Wood Cellulose (g)	Percentage grafting (%)	Grafting Efficiency (%)
1	0.5	2.5	6.9	176	77.0
2	1.0	2.5	7.2	188	78.0
3	1.5	2.5	7.5	200	79.0
4	2.0	2.5	7.6	204	79.5
5	2.5	2.5	7.8	212	80.0

Table 2. *Percentage Grafting and Grafting Efficiency of Obeche Cellulose-g-Poly (Vinyl Acetate) Versus Monomer Concentration.*

Preliminary test	Weight of monomer (g)	Initial weight of Obeche Wood Cellulose (g)	Final weight of Obeche Wood Cellulose (g)	Percentage grafting (%)	Grafting Efficiency (%)
1	10	2.5	6.9	176	77.0
2	15	2.5	11.4	356	81.0
3	20	2.5	13.5	440	89.0
4	25	2.5	14.6	484	90.0
5	30	2.5	16.3	552	91.0

Table 3. *Percentage Grafting and Grafting Efficiency of Obeche Cellulose-g-Poly (Vinyl Acetate) Versus Temperature.*

Preliminary test	Initial weight of Obeche cellulose (g)	Final weight of Obeche cellulose (g)	Temperature (°C)	Percentage grafting (%)	Grafting Efficiency (%)
1	2.5	6.9	60	176	77.0
2	2.5	7.2	65	188	78.0
3	2.5	7.4	70	196	79.0
4	2.5	7.1	75	192	77.0
5	2.5	7.1	80	184	78.0



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	437.86	1.9057	0.1958	451.36	399.28	87.7721	1.5039
2	543.94	1.9043	0.0158	547.8	501.51	79.0609	0.29
3	605.67	1.9325	0.0071	653.89	601.81	88.8905	0.0265
4	682.82	1.9521	0.0033	684.75	653.89	52.6008	0.0016
5	858.35	2.2234	0.0158	868	813.99	89.0267	0.0648
6	1016.52	1.7017	0.2296	1074.39	885.36	324.3041	3.2925
7	1132.25	1.6722	0.2161	1193.98	1074.39	209.4389	3.2909
8	1236.41	1.8591	0.1534	1298.14	1193.98	178.2119	1.6712
9	1402.3	1.8246	0.0104	1406.15	1298.14	184.6692	-0.3416
10	1639.55	1.6391	0.0168	1641.48	1585.54	97.6515	0.2226
11	1734.06	1.7981	0.033	1805.43	1730.21	127.2232	0.0359
12	2310.8	2.0582	0.0137	2335.87	2303.08	55.1982	0.0526
13	2935.76	1.3979	0.1228	2987.84	2414.96	1010.681	-1.2407
14	3410.26	0.6726	0.0048	3599.29	3408.33	395.7032	2.7
15	3740.1	1.5553	0.0039	3742.03	3734.31	13.9363	0.0014

Figure 1. *FTIR result of Obeche Cellulose-g-Poly (Vinyl Acetate).*

It was observed in Table 1 and 2 that the percentage grafting and grafting efficiency increased with increase in initiator and monomer concentrations for the Obeche graft copolymer. The increase in initiator concentration may have occurred due to increment in the yield of initiator at the active site on the cellulose backbone.

The percentage grafting and grafting efficiency increased with temperature from 60°C – 70°C then decreased after 70°C in Table 3. This was because of decrease in the yield of the product and the molecular weight of the graft chains. As the monomer and initiator concentrations remains constant.

Table 4. *Physico-mechanical test on Obeche Cellulose-g-Poly (Vinyl Acetate).*

S/N	Parameters	Units	Obeche Cellulose-g- poly (Vinyl Acetate)
1	Hardness	Shore D	65D
2	Density	mg/m^3	0.85
3	Softening point	°C	125°C – 140°C

It was observed that the Obeche graft copolymer have

thermoplastic properties. The physico-mechanical test showed that the Obeche cellulose-g-poly (vinyl acetate) had a density of 0.85 mg/m^3, hardness of shore 65D, which showed that the material may have the properties to be resistant to chemicals except chlorine based compounds. They also may exhibit good abrasion resistance to many oxidative chemical compounds [5, 13]. The softening point also recorded 125°C – 140°C from the temperature when the dentation weight starts to penetrate into the material and stops at the temperature when the dentation weight reached the base of the material. Obeche cellulose needed more heat to accept dentation. These basic properties have proven the sample vitality and applications in some valuable areas like making of bottles for storing chemicals, car gaskets, highly vulcanized water tanks, industrial pipes and tanks etc.

Table 5. *Sorption results of Obeche Cellulose-g-Poly (Vinyl Acetate).*

Solvents	Amount (ml)	Obeche cellulose -g-poly (vinyl acetate) initial weight (g)	Final weight (g) After immersion every 6h	Mean weight (g) after immersion
Acetone	2ml	0.42	0.44 0.46 0.48 Adsorbed	0.46
Chloroform	2ml	0.30	0.27 0.25 0.23 Dissolved	0.25
Methanol	2ml	0.17	0.18 0.19 0.21 Dissolved	0.19

After immersion for 24h three different solvents. The Obeche cellulose-g-poly (vinyl acetate) adsorbed acetone and dissolved in chloroform and methanol [12].

The infrared analysis displayed the functional groups associated with O-H, N-H, C=O, C-O, CH_2 of methyl and methylene which are consistent with cellulose-g-poly (vinyl acetates).

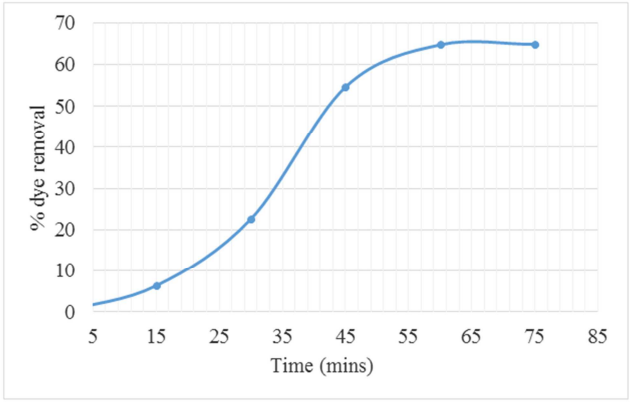


Figure 2. *Plot of percentage of dye removed by the graft copolymer versus time (t).*

The graph in figure 2 showed the effect of time on percentage dye removal on the graft copolymer. As the time increased more dye were removed by the Obeche cellulose-g-poly (vinyl acetate). As the colour of the graft copolymer changed to green with dye removal, a chemical modification must have taken place leading to colour change in the dye [7, 11, 14, 15]. This is collaborated by the fact that the graft copolymer got more closely packed molecules indicating that the dye had some chemical effect on the graft copolymer.

The percentage of the dye removed by the graft copolymer increased with increase in the concentration of the dye. The concentration of the adsorbing species is linearly related to the adsorbance. The concentration of the dye were obtained from the adsorbance.

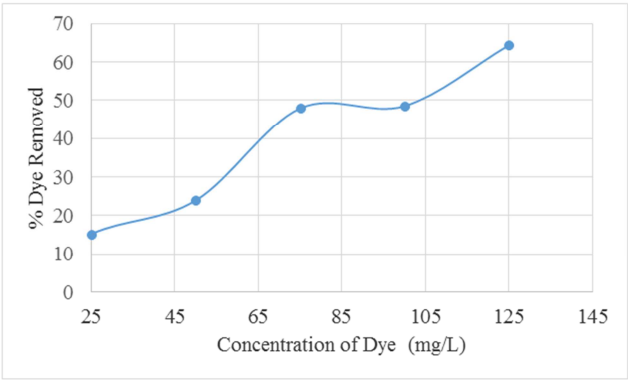


Figure 3. *Plot of percentage dye removed by the graft copolymer versus Concentration of dye.*

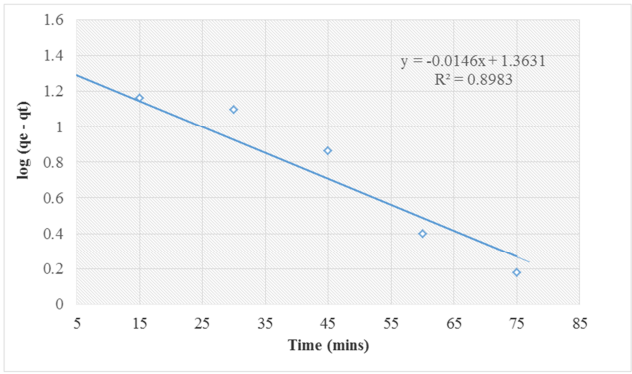


Figure 4. *Plot of log ($q_e - q_t$) versus time (t) for Obeche cellulose.*

The graph plotted between log ($q_t - q_e$) against time shows

the change of the value of the graph rate constant (k_1). The pseudo first order equation was applied to the adsorption of bromothymol blue by the graft copolymer. The rate constant was determined from the slope of the graph and was found to be 3.36 x 10^{-2} min^{-1} at 30°C. The (R^2) values was 0.898 which indicated the adsorption was reasonably good.

4. Conclusion

In this research, the grafting of Obeche wood cellulose was carried out, but first the Obeche wood cellulose was pre-treated with sodium hypochlorite, then it was grafted with different quantities of vinyl acetate and benzoyl peroxide at different temperatures and the outcome was a graft copolymer of Obeche cellulose-g-poly (vinyl acetate).

The physico-mechanical test results of the graft copolymer from this study showed that the Obeche cellulose-g-poly (vinyl acetate) gave (65D i.e. 65 shore D) for hardness, 0.85mg/m^3 for density and 125°C – 140°C for softening point.

In the adsorption of dye, it revealed that the removal of dye by the graft copolymer increased with increase in the concentration of the dye. The adsorption capacities of the graft copolymer had a removal efficiency of 64.3%.

It was also observed that the percentage grafting and graft efficiency increased with increasing initiator concentration due to the formation of great number of grafting site on the cellulose which in the presence of monomer induced grafting. Increase in temperature had a very strong effect on percentage grafting. The percentage grafting improved from 60°C to 70°C and then decreased after 70°C.

The infrared analysis showed that the groups in the Obeche cellulose-g-poly (vinyl acetate) functional groups are associated with O-H, N-H, C=O, C-O, CH_2 of methyl and methylene which are consistent with graft copolymer.

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