



Evaluation of Grafting Parameters of Styrene onto Alkaline Modified Sugarcane Bagasse using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2\text{-N}_2\text{H}_4$ initiator systems and Characterization of the Hydrolyzed Grafted Polystyrene Chains

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ABSTRACT: Cellulose the most abundant natural fibre can be modified, via grafting with vinyl monomers, in homogenous or heterogeneous reaction medium. Therefore, the objective of this paper was to study the grafting parameters of styrene onto alkaline modified sugarcane bagasse using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2\text{-N}_2\text{H}_4$ initiator systems and characterized the hydrolyzed grafted polystyrene chains for their viscometry and average molecular weight distributions using standard appropriate methods. The grafting parameters increases within 0.10-0.25 M styrene concentration in both initiator systems and initiator concentration within the range 1.0×10^{-3} to 6.0×10^{-3} for $\text{Fe}^{2+}/\text{H}_2\text{O}_2\text{-N}_2\text{H}_4$ and 1.0×10^{-3} to 9.0×10^{-3} for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems, *albeit* with higher values in the former system. These parameters decrease at higher monomer and initiator concentrations in both systems. The viscometry of hydrolyzed polystyrene chain prepared at optimum initiator concentrations and 0.10-0.30 M styrene concentration in both initiator systems are in the range (1.6416-4.5327 cP), (0.6416-3.5327 cP) and (73.2277-202.1927 cP) for relative, specific and inherent viscosities respectively, consistent with increases in activation energy of flow ($1.24\text{-}5.30 \text{ KJmol}^{-1}$) and average viscosity molecular weights ($307.92\text{-}565.79 \text{ gmol}^{-1}$), these parameters decreases at higher monomer concentration in both initiator systems. The number and weight-average molecular weight distributions and polydispersity indices indicates that grafted polystyrene chains in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system are broader and more polydispersed than those for $\text{Fe}^{2+}/\text{H}_2\text{O}_2\text{-N}_2\text{H}_4$ initiator system. The results showed that the hydrazine enhanced initiator system was more effective for the copolymerization reaction with polystyrene polydispersity indices comparable to those of synthetic chain-growth polymers.

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Grafting of vinyl monomers onto cellulose is an important chemical technique for the modification of cellulosic fibre based materials to broaden its industrial applications Elena *et al.*, (2023), depending on the medium and monomer grafted on the cellulose backbone polymer, the macromolecule gains new

properties. Cellulose-graft-vinyl copolymers are unique in their own stead, as the modification gives room to maneuver and tailor the copolymer material with the requisite characteristics for specific application Yigit *et al.*, (2019). Grafting reactions can be initiated in heterogeneous medium using; free

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radical, redox system or photochemical process as initiator El-Hamshary, (2012); Deepak *et al.* (2017). Free radical initiators such as ceric ammonium nitrate (CAN) various persulphates, Azobisisobutyronitrile (AIBN) and redox systems; Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) have been reported Jideonwo and Adimula, (2006); Goyal *et al.*, (2008); Meng *et al.*, (2009). Following the discovery of ceric ammonium nitrate (CAN) as initiator in free radical polymerization reactions by Mimo and Kizerman Yigit *et al.*, (2019), a plethora of studies on graft copolymerization of hydrophobic and hydrophilic vinyl monomers onto natural or synthetic backbone polymers have been reported Deepak *et al.*, (2017). These graft copolymers, with characteristics, which are at variance with the monomer and pristine backbone polymer finds applications in fibre science, pulp and paper industry, mulch film in agriculture, drilling aid in petroleum industries, flocculants in water treatment, membrane in separation technology, adsorbent materials for metal ion remediation and drug delivery systems Wang *et al.*, (2011); Salisu *et al.*, (2016); Samuel *et al.*, (2019); Nasiru *et al.*, (2021); Elena *et al.*, (2023). However, in ceric ion initiated systems, the preponderant formation of the vinyl-type homopolymer constitutes a major drawback in the copolymerization reaction Gupta and Khandekar, (2002). Redox initiating systems with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ coupled with a reducing agent which shows enhanced graft efficiency have been established as the most effective redox systems. Mateva and Nikolov, (1991); Jideonwo and Adimula, (2006); Meng *et al.*, (2009). Sugarcane bagasse, a cellulosic pulp left after juice has been extracted from sugarcane or sugarbeets find uses as fuel, cattle feeds or starting material for paper making Samuel *et al.*, (2023). Cellulose is a linear polysaccharide with long chain consisting of β -D-glucopyranose units joined by β -1, 4 glycosidic linkages Qui *et al.*, (2008). This renewable polymer contains two types of hydroxyl groups, primary hydroxyl in methylol group at carbon number 6 and secondary hydroxyl groups at carbon number 3 and 4 both of which are hydrophilic in character Liu and Sun, (2008). Cellulose is a semicrystalline polymer; it exists in four polymorphic forms with varied crystalline and amorphous phases in their structural assemblage Wang *et al.*, (2011), susceptible to modification to derive a branched macromolecular material with immense industrial applications Inagaki *et al.*, (2010); Wang *et al.*, (2011). Though much work has been reported on the grafting of vinyl monomers, either as single monomer Abdulganiyu *et al.*, (2017), binary monomer mixture Samuel *et al.*, (2019) or mosaic grafting of two different kind of monomer side by side onto cellulose based backbone polymeric materials Mao *et al.*, (2004); Kang *et al.*, (2008);

Deepak *et al.*, (2017), to obtain the requisite character of the copolymer desired for specific application. Literature search shows no report was documented on grafting styrene onto an alkaline treated sugarcane bagasse. In light of the foregoing and taking cognizance of environmental and disposal challenges pose by sugarcane bagasse and the merit of its high cellulosic fibre content Esen *et al.*, (2011). It's imperative to develop a value-added material from this low-cost, non-toxic and eco-friendly cellulosic biopolymer. Accordingly, the objective of this paper was to study the grafting parameters of styrene onto alkaline modified sugarcane bagasse using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2\text{-N}_2\text{H}_4$ initiator systems and characterized the hydrolyzed grafted polystyrene chains for their viscometry and average molecular weights distributions.

MATERIAL AND METHODS

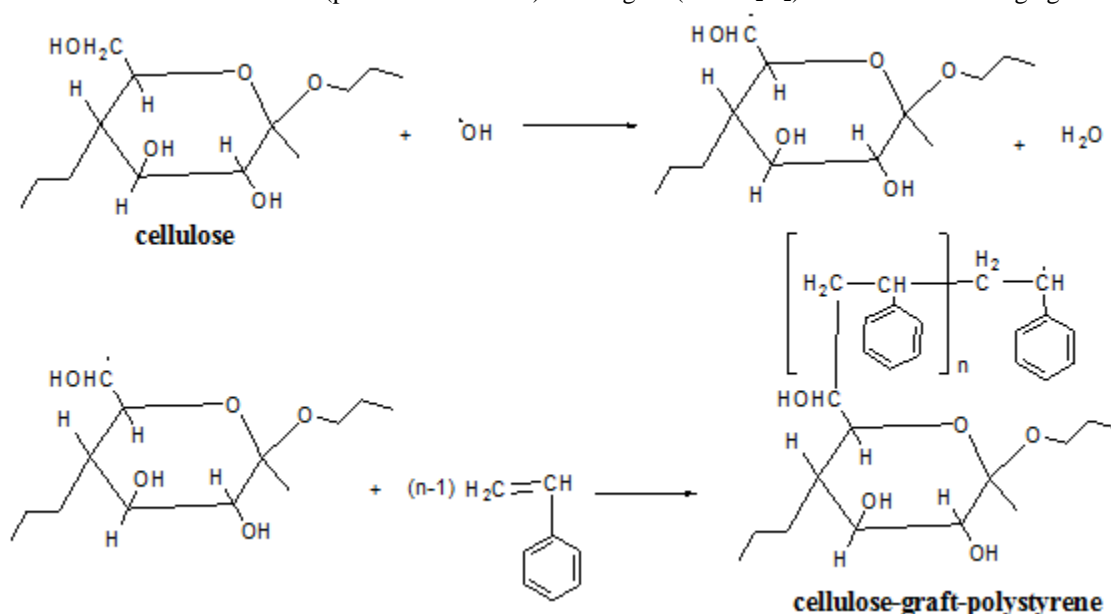
Preparation of sugarcane bagasse: Sugarcane bagasse was obtained from local sugarcane processors in Zuru market Kebbi State, and transported in plastic container to the laboratory, after removing foreign materials, it was soaked in distilled water for 24 h to remove sucrose and other water soluble fermented residues. The sugarcane bagasse was then strained in a muslin bag and dried (105°C) in a thermostatic oven for 12 h to remove sorbed water. The dried sugarcane bagasse was milled in an attrition mill and sieved (mesh: <50 micron), the powdered sugarcane bagasse was de-wax Jideonwo and Adimula, (2006) by soxhlet extraction for 24 h using 1:1 v/v mixture of benzene and ethanol, rinsed with water, dried (105°C) in a thermostat oven for 6 h, packed into polyethylene bag and stored in a cupboard.

Mercerization of Sugarcane Bagasse: Mercerization was done as described by Samuel *et al.*, (2023). Briefly, 100 g de-waxed sugarcane bagasse powder was weighed into a 500 ml beaker and 100 ml of 10% (w/v) NaOH solution was added. The mixture was equilibrated on a magnetic stirrer set at 150 rpm and 50°C for 1 h. The beaker was cooled to ambient temperature and then filtered. The residue was then washed repeatedly with deionised water until neutral to litmus. The mercerized sugarcane bagasse was then dried in an oven set at 105°C for 6h, cooled to ambient temperature and packed into a polyethylene bag.

Graft copolymerization of styrene onto mercerized sugarcane bagasse: Graft copolymerization of styrene onto mercerized sugarcane bagasse was as described by Jideonwo and Adimula, (2006); Guifang *et al.*, (2021), with slight modifications. 5 g of mercerized sugarcane bagasse was dispersed in 50 ml 1% w/v aqueous ferrous ammonium sulphate solution in a 250

ml volumetric flask, the flask was mounted on a magnetic stirrer and stirred (100rpm) for 30 minutes at 30°C. The content of the flask was filtered and the residue rinsed repeatedly with distilled water to obtain the Fe²⁺ treated mercerized sugarcane bagasse. The Fe²⁺ absorbed cellulosic material was aggregated with 0.1 M of styrene monomer after purification by extracting twice with 10% NaOH to remove the Monomethyl hydroquinone inhibitor Samuel, (2019) and 20 ml of methanol in a 250 ml three-neck reaction flask, which was allow to stand for 10 minutes (for swelling of the cellulosic biomass and styrene monomer). 10 ml 1.0x10⁻³ M H₂O₂ and 1.0 g of N₂H₄ (Hydrazine) were aggregated into the flask and allowed to stand for 30 minutes (pre-oxidation time)

Samuel *et al.*, (2023). The flask was then fitted with a stirrer, nitrogen inlet tube and thermometer. The grafting reaction was allowed to proceed at 30°C with continuous stirring (100 rpm) for 90 minutes under nitrogen atmosphere. Polystyrene homopolymer was extracted in a soxhlet extractor with ethyl benzene until constant weight was obtained. The purified copolymer was filtered (sintered funnel), rinsed repeatedly with methanol, before drying (under vacuum at 40°C) to constant weight. The experiment was repeated for 3.0x10⁻³, 6.0x10⁻³, 9.0x10⁻³ and 1.2x10⁻² M H₂O₂ and 0.15, 0.20, 0.25 and 0.3 M initiator and styrene concentrations respectively. Similar experimental protocol was repeated for Fenton reagent (Fe²⁺/H₂O₂) without the reducing agent.



Scheme 1: Mechanism for the grafting of Styrene onto mercerized Sugarcane bagasse Guilkaume *et al.*, (2015); Deepak *et al.*, (2017).

Evaluation of graft parameters of styrene onto alkaline modified sugarcane bagasse

The Grafting parameters namely; Grafting percentage GP (%) and Grafting efficiency GE (%) were determined by weight measurements using equations 1 and 2 respectively.

$$GP(\%) = \frac{W_1 - W_2}{W_2} \times 100 \quad (1)$$

$$GE(\%) = \frac{W_1 - W_2}{W_3 - W_2} \times 100 \quad (2)$$

Where GP = Grafting percentage; GE = Grafting efficiency, W_2 is the weight of copolymer after extraction of styrene homopolymer, W_2 is the weight of mercerized sugarcane bagasse and W_3 is the weight of crude copolymer before extraction of styrene homopolymer.

Hydrolysis of Grafted Polystyrene chain: The hydrophobic polystyrene chain was hydrolyzed by the method as described by Abdulganiyu *et al.*, (2017) with slight modification. Briefly, 2g of the purified copolymer was weight into a 250 ml conical flask, 50 ml 3M HCl was added, the flask and its content was mounted on a magnetic stirrer set (100 rpm at 90°C) for 12h. The content was then allowed to stand in a separatory funnel for 6h and filtered. 50 ml of chloroform was added to the residue and poured into 200 ml of methanol in a 1litre Erlenmeyer flask to precipitate polystyrene. Hydrolyzed polystyrene was dried under vacuum at 40°C, prior to viscosities and molecular weight studies.

Determination of Viscosity of Hydrolyzed Graft Polystyrene Chain: The viscometry of the optimized sample (samples prepared at 9.0x10⁻³M and 6.0x10⁻³ M initiator concentrations for Fe²⁺/H₂O₂ and

Fe²⁺/H₂O₂-N₂H₄ initiator systems respectively) was determined as outlined by Martin, (2014). 2.0 g of hydrolyzed polystyrene was dissolved in 50ml toluene in a 250 ml Erlenmeyer flask to prepare the polymer solution, stopped with aluminum foil and homogenized (200 rpm) in an orbital mechanical flask shaker (Innova 2000) at ambient temperature for 20 minutes. Viscosity of the solution was measured using an Ostwald viscometer. The viscometer was rinsed with acetone and dried in an aspirator; it was then placed in a thermostat oil bath and allow to equilibrate (30^o C). A pipet bulb was used to draw the polymer solution into the upper bulb of the viscometer. The efflux time for the polymer solution to flow from the upper to the lower bulb by capillary action was recorded with a stop watch. Similarly, the flow time for solvent (toluene) was measured. The relative, specific and inherent viscosities were evaluated using equations 3, 4 and 5 respectively.

$$\eta_r = \frac{t}{t_o} \quad (3)$$

$$\eta_{sp} = \eta_r - 1 \quad (4)$$

$$\eta_{inh} = \left[\ln \frac{t}{Ct_o} \right] \quad (5)$$

Where t_o is the efflux time for solvent, t is the efflux time for polymer solution and c is the concentration (g/ml) of polystyrene solution.

Determination Activation Energy of Polystyrene Flow: The activation energy of the hydrolyzed polystyrene flow for the optimized copolymerization reactions (samples prepared at 9.0x10⁻³M and 6.0x10⁻³ M initiator concentrations for Fe²⁺/H₂O₂ and Fe²⁺/H₂O₂- N₂H₄ initiator systems respectively), was determined via viscosity measurement. 2.0 g of hydrolyzed polystyrene sample was dissolved in 50 ml toluene to obtain the polymer solution with concentration expressed in (g/ml). The specific viscosity of the polymer solutions at temperatures; 30, 40, 50, 60 and 70^oC were determined and the intrinsic viscosities derived therefrom (equation 6). The Arrhenius-type equation (equation 7) Martin, (2014); Yigit *et al.*, (2019), was used to determine the activation energy of hydrolyzed polystyrene flow (E_η).

$$\eta_{int} = \frac{\eta_{sp}}{C} \quad (6)$$

$$\ln \eta_{int} = \ln A - \frac{E_{\eta}}{RT} \quad (7)$$

η_{int} is the intrinsic viscosity, η_{sp} is the specific viscosity and c is the concentration of polymer

solution. A plot of ln η_{int} against 1/T gave a straight line with intercept ln A on the vertical axis, the value of E_η was evaluated from the slope (-E_η/R) where R is the molar gas constant.

Determination of Viscosity Average Molecular Weight of Hydrolyzed Polystyrene: The viscosity average molecular weights of the hydrolyzed polystyrene chain prepared at optimum condition for Fe²⁺/H₂O₂ and Fe²⁺/H₂O₂- N₂H₄ initiator systems were determined from the measured values of their intrinsic viscosities and Mark-Houwink-Sakaruda (equations 8), and equation constants K' and α at 25^oC for Polystyrene-Toluene was taking as 1.10 x 10⁻⁴ mL/g and 7.25 x 10⁻¹ respectively Martin, (2014).

$$[\eta] = K' (M_v)^{\alpha} \quad (8)$$

Where M_v is the viscosity average molecular weight, K' and α are the Mark-Houwink-Sakaruda constants.

Determination of Number and Weight-Average Molecular Weights of Hydrolyzed Polystyrene : The number average molecular and weight average molecular weights were investigated by Gel Permeation Chromatography (Shimadzu Shim-Pack GPC- 805) with a refractive index indicator (RID-20A), a column (CTO-40C), force air circulation column temperature and Sus piping (ID. 0.3 mm x 600 mm). Determinations were done at 36^oC with Tetrahydrofuran (THF) at a flow rate of 10.0000 mL/min, a parallel double plunger mobile phase delivery and a degassing line flow rate of 400μL. Polystyrene standard with molecular weight range 3.10x10³ to 4.35x10⁶ was used to calibrate the system for analysis.

RESULTS AND DISCUSSION

The results of copolymerization of styrene onto mercerized sugarcane bagasse without and with the reducing agent within initiator concentration range of 1.0x10⁻³ – 1.2x10⁻² M are presented in tables 1 and 2 respectively. The values for percentage graft (GP) and graft efficiency (GE) shows an increment which is in direct proportion for GP and GE depict an inverse relation with respect to increase in monomer concentration in both initiator systems. However, the values for GE decrease for both systems as styrene concentration increases, which may suggest the preference of both systems to homopolymerization reactions at higher monomer concentrations. At 0.25 M monomer concentration in both systems, the graft yield in Fe²⁺/H₂O₂ is lower relative to those for Fe²⁺/H₂O₂- N₂H₄ initiator system, even though the latter system was mediated at lower initiator

concentration. The higher values of graft parameters recorded in the latter initiator system compared to those for the former system could be added to the following; the addition of hydrazine predominate Fe^{2+} by reducing Fe^{3+} previously produced in the presence of atmospheric oxygen during the treatment of mercerized sugarcane bagasse with ferrous salt. In addition, the amine based reducing agent could also potentiate the dissociation of H_2O_2 Misra *et al.*, (1979); Mateva and Nikolov, (1991).

The molecular proliferation of graft initiating moiety ($\cdot OH$) in equation 9 and stabilization of Fe^{2+} occasioned by nitrogen atmosphere, resulted in the preponderance of secondary and tertiary cellulose macroradicals and imply a corresponding higher graft polystyrene chains onto the modified sugarcane bagasse in the $Fe^{2+}/H_2O_2-N_2H_4$ initiator system. The

initial increase recorded for graft percentage with increase in monomer concentration in both systems could be attributed to preponderance of activated grafting sites and styrene monomer available for copolymerization reaction. However, beyond the respective thresholds for monomer and initiator concentrations in both initiator systems, the excess styrene monomer resulted in decreased yield of mercerized sugarcane bagasse-graft polystyrene copolymer. At higher initiator concentration, excess radical moiety (OH^*), facilitates the ring opening of polysaccharide by hemolytic cleavage of the glycosidic bond between carbon 2 and 3 owing to their chemical similarities Guifang *et al.*, (2021), and styrene monomer could stereoselectively chain polymerized from the radicalized carbon-2 of the open ring cellulosic trunk.



Table 1: Grafting Parameters for Fe^{2+}/H_2O_2 initiator system

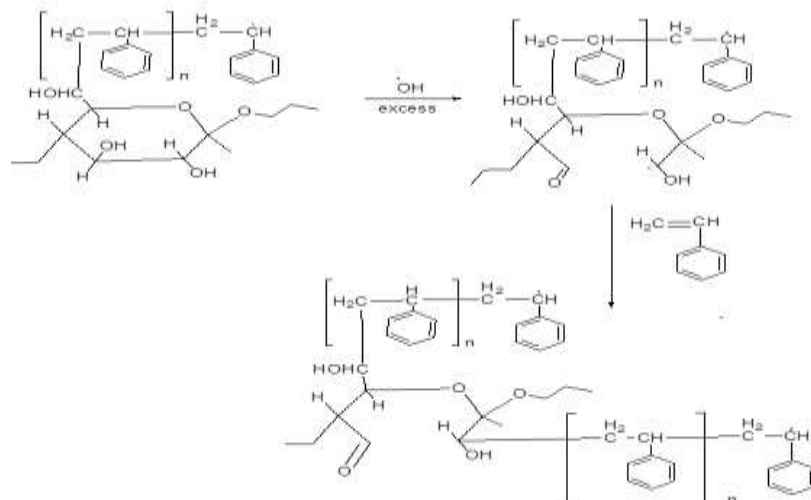
Initiator concentration (M)	Grafting parameter (%)	Monomer concentration (M)				
		0.10	0.15	0.20	0.25	0.30
1.0×10^{-3}	GP	22.34	31.06	33.23	35.42	32.75
	GE	20.07	19.04	18.21	17.11	15.22
3.0×10^{-3}	GP	24.20	33.21	36.61	40.22	34.08
	GE	23.01	22.03	21.13	19.23	17.32
6.0×10^{-3}	GP	29.41	37.72	41.62	43.70	37.04
	GE	26.71	24.90	22.23	21.15	19.52
9.0×10^{-3}	GP	33.23	40.06	43.04	46.11	41.01
	GE	31.40	30.22	28.12	26.51	24.33
1.2×10^{-2}	GP	18.30	16.54	14.64	12.39	10.72
	GE	15.01	13.03	11.02	9.21	7.05

Table 2: Grafting Parameters for $Fe^{2+}/H_2O_2-N_2H_4$ initiator system

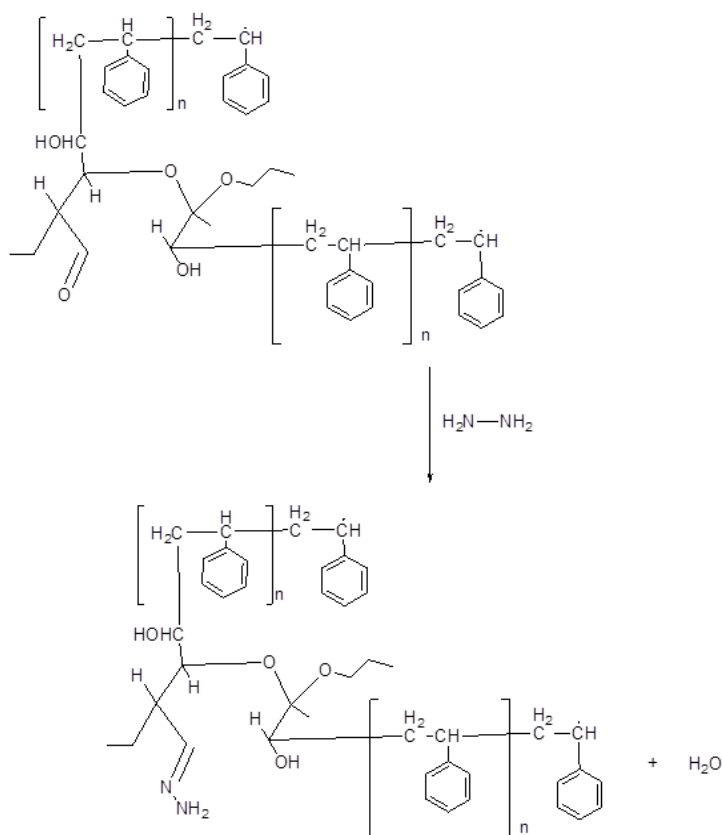
Initiator concentration (M)	Grafting parameter (%)	Monomer concentration (M)				
		0.10	0.15	0.20	0.25	0.30
1.0×10^{-3}	GP	37.74	39.44	41.35	44.17	42.56
	GE	34.33	32.64	30.08	29.61	27.09
3.0×10^{-3}	GP	45.35	48.25	52.16	55.51	50.66
	GE	43.06	41.54	39.44	35.14	31.05
6.0×10^{-3}	GP	48.74	52.44	56.35	63.41	60.20
	GE	44.08	43.22	42.45	39.88	36.54
9.0×10^{-3}	GP	34.89	26.75	23.55	20.74	17.30
	GE	19.68	17.97	15.77	13.65	12.42
1.2×10^{-2}	GP	24.42	20.81	18.64	15.32	13.61
	GE	17.35	16.71	14.50	12.58	10.08

Hence, the preponderance of these macromolecules with propagated polystyrene chains at the methylol carbon and carbon-2 groups on the backbone polymer as elucidated in schemes 2 presumably, occludes potential active sites on the polymer backbone for chain-growth, making the hydroxyl radical and styrene more prone to participate in polystyrene homopolymer formation. Besides, the decrease in graft percentage for the $Fe^{2+}/H_2O_2-N_2H_4$ initiator system at higher initiator concentration may not be unconnected with

the following; oxidative degradation of the mercerized cellulosic chains by excess H_2O_2 Deepak *et al.*, (2017), increase in termination reaction of macroradicals by bimolecular collision due to its increased populace El-Hamshary, (2012) and regiospecific nucleophilic addition reaction to the aldehyde group by the amine based reducing agent Ibrahim *et al.*, (2008); Roy *et al.*, (2019) on carbon-3 in the open ring structure (reaction scheme 3).



Scheme 2: Mechanism for styrene grafting and ring opening on Carbon-2



Scheme 3: Mechanism for Nucleophilic addition of hydrazine to Aldehyde carbon centre



The water molecules produced dilutes the methanol in the heterogeneous reaction medium, decreases the solubility of the hydrophobic styrene monomer in the polymerization reaction medium Roy *et al.*, (2019) and hydrazine a weak base dissociates to produce its conjugate base as shown in equation 10 (Ibrahim *et*

al., 2008; Roy *et al.*, 2019). Thus, these entire negative effects which, resulted in viscosity build-up in the reaction medium due to steric factor pose by the hetero-macromolecule produced in scheme 3 and consequential Trommdorf-Norish effect El-Hamshary, (2012), suggest homopolymer formation

occasioned by preferential vicinal styrene chain-growth polymerization over and above graft copolymerization reaction. These observations affirms previous reports of grafting acrylamide onto cocoa wood holocellulose Jideonwo and Adimula (2006), synthesis of polystyrene-graft-cellulose acetate copolymers via Nitroxide-Mediated polymerization Guilkaume *et al.*, (2015), styrene onto chitosan a cellulose-type material Abdulganiyu *et al.*, (2017) and acrylamide-co-acrylic acid onto recycled cellulose Elena *et al.*, (2023). Moreover, the values 63.41 and 44.08% for GP and GE respectively recorded for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4 initiator system are higher than those reported for hydroquinone enhanced $\text{Fe}^{2+}/\text{H}_2\text{O}_2$

Jideonwo and Adimula (2006), at the same initiator concentration and temperature of reaction. This imply the greater stabilities of adsorbed Fe^{2+} on the sugarcane biomass and cellulose macroradicals by N_2H_4 under a nitrogen atmosphere and increased surface area of the sugarcane bagasse, due to increase in amorphous region occasioned by alkaline hydrolysis of glycosidic linkages Meng *et al.*, (2009), resulted in lower degree of chain transfer reactions in the hydrazine enhanced initiator system. The results of viscometry for the optimized graft polystyrene samples in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4 initiator systems are represented in tables 3.

Table 3: Viscosities of Hydrolyzed Graft Polystyrene Chain

Polystyrene graft prepared at varied styrene concentration (M)	Initiator system	Viscosity		
		η_r (cP)	η_{sp} (cP)	η_{inh} (cP)
0.10	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	1.6416	0.6416	73.2277
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	2.3816	1.3816	106.2374
0.15	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.0483	1.0483	91.3696
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	2.7432	1.7432	122.3675
0.20	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.2217	1.2217	99.1046
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	4.0104	3.0104	179.0548
0.25	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.8119	1.8119	125.4320
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	4.5327	3.5327	202.1927
0.30	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.5502	1.5502	113.7582
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	3.6165	2.6165	161.3233

Table 4: Activation energy of flow and Viscosity average molecular weight of polystyrene

Polystyrene graft prepared at varied styrene concentration (M)	Initiator system	Activation energy of copolymer flow (E_f) KJmol^{-1}	Viscosity average molecular weight (M_v) gmol^{-1}
0.10	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	1.24	307.92
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	1.76	364.47
0.15	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	1.53	312.59
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	2.08	386.40
0.20	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	1.88	324.57
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	2.45	447.68
0.25	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	3.17	352.66
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	5.30	565.79
0.30	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	2.62	370.95
	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4	4.96	477.83

The result shows that the viscosities of the hydrolyzed polystyrene chain increase as the monomer concentration increases, coherent with the increase in graft percentage and efficiency. However, at 0.30 M styrene concentration, the viscosities of the hydrolyzed chain-growth polymer decrease for both initiator systems relative to those for 0.25 M concentration. At higher monomer concentration styrene is more susceptible to homopolymerization and resulted in decreased graft yield with a corresponding reduced polystyrene molecular chain entanglement and hydrodynamic volume occupied by the polymer mass in solution Abdul-Rezik (1993). The viscosities of hydrolyzed polystyrene chain prepared at 0.25 M styrene concentration in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4

initiator system is 2-folds compared to values for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, this could be attributed to the oxygen scavenging character of N_2H_4 Deepak *et al.*, (2017), which prevented the oxidative degradation of the cellulose macroradical thereby making the reaction system more susceptible to formation of polystyrene graft rather than homopolymerization. Therefore, the higher graft yield in the amine-based enhanced initiator system endowed its polymer solution with lengthy hydrolyzed polystyrene chains and more intramolecular interactions in solution occasioned by molecular entanglement and overlap. The activation energy of flow and viscosity average molecular weight of the hydrolyzed chain-growth polymer is shown in table 4. Intrinsic viscosity which is the precursory

parameter to the derivation of the aforementioned is a measure of a solute's contribution to the viscosity of a polymer solution. Activation energy of flow and viscosity average molecular weight of polymer provides vital information about bulk properties inherent in a polymer mass Martin, (2014). The result shows that E_{η} and M_v values increase with a corresponding increase in the concentration of styrene content in the copolymerization reaction. Notably; 68.61% and 116.33% increase in E_{η} from 0.20 to 0.25 M monomer concentration was recorded for the Fe^{2+}/H_2O_2 and $Fe^{2+}/H_2O_2-N_2H_4$ initiator system respectively, consistent with a remarkable increase of 8.51% and 26.44% in their viscosity average molecular weights respectively. The higher values recorded for the hydrazine enhanced initiator system implies the stability of the secondary and tertiary-opening macroradicals of the cellulose backbone Guilkaume *et al.*, (2015), higher mobility of styrene monomer due to concentration gradient Meng *et al.*, (2009), low chain transfer reaction to solvent Mojtaba *et al.*, (2018) and better reducing potential of the amine-rich initiator system Misra *et al.*, (1979). All these enabled more coordinated chain-growth polymerization of styrene onto the alkaline treated cellulosic trunk backbone polymer. The viscosity average molecular weight of the hydrolyzed polystyrene prepared at 0.25 M styrene reference to the molar weight of styrene monomer (104.15 gmol^{-1}) Guifang *et al.*, (2021), connote 3.38 and 5.42 average degree of polymerization for the Fe^{2+}/H_2O_2 and $Fe^{2+}/H_2O_2-N_2H_4$ initiator systems respectively. This suggest the amine enhanced initiator system produced graft oligomeric hydrophobic polystyrene chains, with more uniform chain length, characteristic of a heterogeneous reaction medium Deepak *et al.*, (2017),

that tends to reorganize into a better polymer-solvent interactions with polymer coil volume Ndagana *et al.*, (2015), which promote intrinsic molecular drag, ascribed to internal friction as polystyrene molecular chain slip pass one-another. The higher polymer flow energy for polystyrene chain in $Fe^{2+}/H_2O_2-N_2H_4$ initiator system, substantiate the internal energy demand for molecular chain mobility. However, the decrease in viscosity average molecular weight for both systems at higher monomer concentration could be attributed to the equations 11 and 12 respectively. Equations 11 and 12 depicts the transfer reaction to styrene monomer El-Hamshary, (2012) and degradation of cellulose macroradicals, occasioned by transfer reaction to methanol owing to its high dielectric constant Deepak *et al.*, (2017); Roy *et al.*, (2019) respectively. Consequently, these drawback favours homopolymerization of styrene and corroborate the reduced values of viscosity average molecular weights of grafted polystyrene in both initiator systems *albeit* more in Fe^{2+}/H_2O_2 , as the amine based reducing agent in the enhanced initiator system could mitigate these chemical degradations thereby rendering the effects of these molecular transformations less pronounced. The highest viscosity average molecular weight 565.79 gmol^{-1} obtained for the enhanced initiator system compares well with 587 gmol^{-1} reported for grafting of styrene onto ethyl cellulose using UV Irradiation in an homogenous medium Abdul-Rezik (1999).

The Molecular weight distributions and polydispersity indices of hydrolyzed polystyrene chain prepared at optimum initiator concentrations for both initiator systems are shown in table 5.

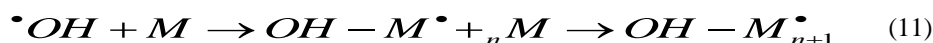


Table 5: Number and Weight-Average Molecular Weights of Hydrolyzed Polystyrene

Polystyrene graft prepared at varied styrene concentration (M)	Initiator system	Average molecular weight		Polydispersity index (M_w/M_n)
		Weight average molecular weight (M_w) g/mol	Number average molecular weight (M_n) g/mol	
0.10	Fe^{2+}/H_2O_2	61997	21015	2.95
	$Fe^{2+}/H_2O_2-N_2H_4$	84239	41523	2.03
0.15	Fe^{2+}/H_2O_2	65882	23035	2.86
	$Fe^{2+}/H_2O_2-N_2H_4$	87332	45485	1.92
0.20	Fe^{2+}/H_2O_2	69815	25573	2.73
	$Fe^{2+}/H_2O_2-N_2H_4$	89221	48227	1.85
0.25	Fe^{2+}/H_2O_2	76199	31101	2.45
	$Fe^{2+}/H_2O_2-N_2H_4$	94880	58931	1.61
0.30	Fe^{2+}/H_2O_2	60959	22745	2.68
	$Fe^{2+}/H_2O_2-N_2H_4$	92664	45201	2.05

The results present with increase in number and weight average molecular weights within 0.10-0.25 M styrene concentration, beyond which these weight distributions decreases. Correspondingly, their polydispersity indices, which decrease in the initial stages, also present higher values at 0.30 M monomer concentration in both initiator systems. Hydrolyzed polystyrene prepared in the absence of the reducing agent are more polydispersed, this broad molecular weight distribution suggest the preponderance of shorter polystyrene chain with lower degree of polymerization compared to longer chains in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4 initiator system. The greater stability of macroradicals and more coordinated propagation of polystyrene onto cellulose backbone in the hydrazine enhanced system could suffice for the narrow molecular weight distributions and polydispersity indices in the latter system. The polydispersity index of 1.61 for hydrolyzed graft polystyrene prepared at 0.25 M styrene concentration in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ - N_2H_4 initiator system, which falls within the range (1.50 to 20) for chain-growth polymers El-Hamshary, (2012); Yigit *et al.*, (2019), indicates a more homogenous polystyrene chain bonded covalently to the cellulose trunk of the mercerized sugarcane bagasse and the polystyrene chain size distribution is multimodal and consistent in physico-chemical properties. Furthermore, the broader molecular weight distributions for the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ initiator system imply the reaction proliferated graft initiating radical moieties on the backbone polymer, which resulted in uncontrolled polymer growth with preponderant polystyrene oligomers lower in degree of polymerization. These molecular weight distributions and polydispersity indices corroborate the viscosity average molecular weights of the hydrolyzed polystyrene judging that a broader weight distribution will produce low internal intramolecular drag Roy *et al.*, (2019), owing to reduce fluid resistance offered by decreased internal friction of polymer chains. The lowest polydispersity index for hydrolyzed graft polystyrene recorded for the enhanced initiator system at 0.25 M styrene concentration present with a narrow molecular weight distributions compare to 3.10 reported for grafting styrene onto chitosan a cellulose-type trunk biopolymer at optimum reaction conditions Abdulganiyu *et al.*, (2017).

Conclusion: Styrene has been grafted onto an alkaline modified cellulosic trunk material using fenton's reagent and hydrazine enhanced fenton's reagent initiator systems. The mercerized sugarcane bagasse – graft-polystyrene copolymer showed grafting parameters which were dependent on monomer and initiator concentrations. Viscosities, activation energy of polystyrene solution flow and average molecular

weights distributions of the hydrolyzed graft polystyrene chains, were largely influenced by monomer concentration and initiator type. The copolymers produced from the enhanced initiator system with lower polydispersity indices for the hydrolyzed graft polystyrene chain present these hetero-macromolecules with auspicious material properties and structural integrity.

Declaration of Conflict of Interest: The authors declare no conflict of interest

Data Availability Statement: Data are available upon request from the corresponding author or fourth author.

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