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Potential application of resin extracts of *Anogeissus leiocarpus* plant

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ABSTRACT

This work reports the application of tannin obtained from *Anogeissus leiocarpus* plant and its use in formulation of a thermosetting material for domestic and industrial use. The ploy condensation of tannin with formaldehyde produced a thermosetting resin with useful properties; formaldehyde (10.5 ml), tannin (2.5 g), glycerol (0.6 ml), hexamine (5.5 g), pH 7.5 and temperature 60 °C. Gel viscosity and effect of temperature on gel time were determined. Absorption behaviour of the films from the thermosetting material formulated under aqueous, acid and basic conditions were investigated. Water absorption up to 90% was obtained between 1 to 3 hrs. Perhaps due to differences in chain topology of the material formulated related to the molecular size holes in the polymer structure which depends on the morphology and crosslink density of the material. No acid absorption was observed after 12 hrs indicating that cross-linking reaction was still taking place in the solution. © 2013 International Formulae Group. All rights reserved.

Keywords: Thermosetting, Resin, Polycondensation, Tannin, polymerization, viscosity.

INTRODUCTION

Thermosetting resins are materials that require addition of curing agents or hardener and impregnation onto a reinforcing material, followed to produce a cured or finished part. Once hardened, this part cannot be changed or reformed, except for finishing (Billmeyer, 1984). These resins been heavily crosslinked become hardened by the use of heat and pressure due to the occurrence of three-dimensional network structure. They cannot be softened by heat for the purpose of reprocessing (re-cycle), but will rather decompose on prolonged heating. Some of the more common thermosetting resins include epoxies, polyurethanes, bakelite, tannin-formaldehyde and phenol-formaldehyde resins (Trezza, 2001).

As a group, the thermosetting resins form bonds; which are essentially infusible and insoluble through the action of heat, catalysts or combination of these. In contrast to thermoplastics, thermosetting resins display good creep resistances and provide the basis for many structural adhesives intended for high-loaded application and exposure to severe environmental condition such as heat, cold, radiation, humidity and chemical

atmosphere (Mirmohseni and Hassanzadeh, 2000).

Most thermosetting resins are synthesized via condensation or step- reaction polymerization. Condensation reaction takes place between two polyfunctional molecules to produce one large polyfunctional molecule with possible elimination of small molecules such as water, (Billmayer, 1984). Hence heat is used to convert the materials from fusible and soluble materials into one which is infusible and insoluble through the formation of a covalently crosslinked thermally stable network. Thermosetting resins used in advanced composite processes have or possess high molecular weight (Mw > 10,000), with low vapour pressure (Hollman, 2005). This study is aimed at developing of thermosetting material from *Anogeissus leiocarpus plant* for domestic and industrial application.

MATERIALS AND METHODS
Materials

Tannin was prepared from polyphonelic extract obtained from *Anogeissus leiocarpus* Stem bark which is a plant collected from Sangere a community in Yola metropolis, Adamawa State, Nigeria. And on longitude 12°, 20 min. East and latitude 9°, 16 min., 30 sec., north formaldehyde, glycerol, hexamine, sodium hydroxide, hydrochloric acid, were purchased from BDH laboratories, and used as supplied without further purification. Laboratory apparatus were likewise employed in the research including instrument, glass wares and distilled water.

Optimization of reaction conditions
Effect of gelation times

Prior to the formulation of the thermosetting resin, some tests were conducted using the raw material and the other reagents to determine the optimal reaction condition for the synthesis of the resin. The reaction between *Anogeissus leiocarpus* extract and formaldehyde under various reaction conditions was studied by observing the reaction time as the period elapsed until the resin could support a 22 g ball bearing of 0.247 mm in diameter. The effects of the following variables on reaction time and optimization of reaction condition were considered (Ebewele et al., 2000)

Effect of solvent and pH on resin

An aqueous solution (45% W/V) of *Anogeissus leiocarpus* (extracts) was adjusted pH value ranging between 1.5 to 10.5 by adding of 0.1 M NaOH and 0.1 M H_2SO_4. The beaker containing the solution was placed in a water bath maintained at 60 °C and formaldehyde (10.5 ml) was added after the solution had reached 60 °C .The gelation time was then measured at constant amount of hexamine. The gel formed was then exposed to air by casting on a glass plate for complete curing and cross-linking so as to obtain good thermosetting properties. The experiment was repeated using 50% aqueous ethanol instead of pure water as the solvent medium following same procedure.

Effect of formaldehyde concentration on the viscosity of resin

Tannin extracts (3 g) were dissolved in water (2 ml) and mixed with glycerol (0.6 ml) in a beaker (50 ml) and was placed on a water bath maintained at 60 °C and pH adjusted to 4.5 using 10% Sodium hydroxide solution. Different volume of formaldehyde (ranging from 2.5 ml to 10.5 ml) relative to the mass of the total solids, were added after the solutions had reached 60 °C. Also, the viscosities of the resins at constant amount of hexamine were measured and recorded. The gel formed was air-dried by casting it on a plastic Petri dish for complete curing and cross-linking to give good thermosetting properties.

Effect of reaction temperature on the resin

Four test tubes were each charged with the bark extract (5 g) of *Anogeissus leiocarpus* and water (5 ml) was added and mixed thoroughly. The tubes were placed on water bath maintained at the 20 °C, 40 °C, 60 °C, and 70 °C and the gelation times were measured. Also the time taken a ball bearing mass 22 g to reach the bottom of each test tube at various temperatures was observed and recorded. All the extract solutions were maintained at a pH of 4.5.

Effect of tannin content on the resin

Portions of the freshly prepared extract of tannin ranging from 1.0 to 4.0 g were introduced, one after the other into 50 ml beakers containing 2 ml of the corresponding solvent used to dissolve the extracts in the beakers and then heated to 60 °C for 10 minutes using water bath and allowed to cool. The mixture was then adjusted to pH of 7.5 using 0.1 M NaOH. Formaldehyde (10.5 ml) was added followed by hexamine (5.5 g) as hardener and emission reducer and the mixture was thoroughly stirred to obtain a homogenous gelly resin. Glycerol (0.6 ml) was added to increase the plastic properties of the materials and to reduce the moisture and water intake by the film.

Effect of hexamine concentration on resin

Freshly prepared extract (2.5 g) was introduced into a beaker containing 1.5 ml of the corresponding solvents used to dissolve the extract in the beaker and heated to 60 °C for 15 minutes over water bath and was allowed to cooled at room temperature for a gelation. Glycerol (0.6 ml) was added to the mixture, and then heated again for an additional three minutes and then allowed to cool again at the same room temperature. The pH of mixture was then adjusted to 7.5 using 0.1 M H_2SO_4. Formaldehyde (10.5 ml) was then added followed by hexamine (1-5.5 g),

which act as a hardener and emission reducer to yield good thermosetting properties.

Formulation of the thermosetting resins

A portion of 3 g freshly prepared tannin extracts was introduced into 50 ml beaker containing 2 ml of the corresponding solvent used to dissolve the powder extract in the beaker and its content was heated for 20 min over water bath at 60 °C and then cooled to room temperature for the gel to be properly formed from the extract obtained with the binary solvent mixtures. Glycerol (0.6 ml) was added to the mixture and then heated for an additional two minutes and allowed to cool. The mixture was adjusted to pH 7.5 with 10% NaOH. Formaldehyde (10.5 ml) was then added and the contents were mixed thoroughly and finally hexamine (5.5 g) was added. The hexamine is used to lower the effect of formaldehyde emission yielding hardeners and consequently produced a completely cross linked thermosetting plastic through exposing it to air for one day.

Determination of viscosity and gel point of the thermosetting resin

Due to the relatively high viscosity of the resins, the capillary viscometers were not suitable for this type of measurement. To overcome this handicap, plastic macrosyringe and constructed rotational viscometers were used for the viscosity measurements.

Macrosyringe method

A 100 ml (phywe) graduated plastics macrosyringe was utilized for the measurement. The apparatus was standardized with 20% (W/V) sucrose solution whose viscosity is 2.0 x10^{-3} Nsm^{-2} at 30 °C (Barminas and Osemeahon, 2006). The viscosity of the resin was evaluated in relation to that of the standard sucrose solution at 30 °C. Six different readings were taken for each sample and average value was calculated. The gel points of the different resins obtained at the different synthetic temperatures were

determined through monitoring the viscosity of the resins with time until a constant viscosity profile was obtained. (Barminas and Osemeahon, 2007).

$$\frac{t_r}{t_s} = \frac{V_r}{V_s}$$

Where

t_r= Flow time of resin in seconds

t_s=Flow time of 20% sucrose in second

v_r=Viscosity of resin

v_s=Viscosity of the reference solution (20% sucrose at 30 °C)

$$\frac{t_{standard}}{t_{60\%}(w/v)_{Sucrose})} = \frac{viscosity\ of\ standard}{viscosity\ 60\%\ (w/v)\ Sucrose}$$

Rotational viscometer method

A rotational viscometer constructed in the department of Chemistry, Federal University of Technology, Yola was used for this measurement. It was made up of a retort stand to hold the 12 V DC motor dynamos, 12 V DC converters to step down and also to convert AC to DC supply, a scale counter to count the number of turns of the scale in the prepared resin in relation to the viscosity of the resin. The apparatus was standardized with 60% (W/V) sucrose solution of viscosity 2.94 x 10^{-3} NSM^{-2} at 30 °C relative to 20% sucrose solution.

A volume (10 ml) of the freshly prepared resin was introduced into 50 ml beaker mounted on a retort stand. The rotor of the viscometer was placed in the resin and was allowed to rotate gently at a voltage (8 V) DC supply. The scale counted, counts the number of oscillations per unit time. The experiment was repeated for different amount of hexamine introduced into the beaker and was determined for each concentration as

$$T = t_A /20$$

Where

T = Period of Oscillation ($t_A /20$)

t_A= Average oscillating time ($t_1 + t_2$)/ 2

Determination of water, acid and base absorption characteristic of the formulated resin

The interaction between water, base and acid of different film materials formulated were determined gravimetrically. Known weight (15 g) of each of the samples was introduced into a 50 ml beaker containing water (30 ml) and swirled for 0.5, 1, 2, 3, 4 and 24 h. The weight of each sample was then monitored until maximum weight was obtained. The difference between the wet weight and dry weight of each sample was then measured and recorded as the water absorbed by the material.

$$Water\ absorption = \frac{W\ W\ S - W\ D\ S}{W\ D\ S}\ X\ 100$$

Where

W. W. S : Weight of wet sample

W. D. S : Weight of dry sample

The procedure was repeated using solutions of acid and base i.e. 0.1 M HCl and 0.1 NaOH.

RESULTS AND DISCUSSION
Effect of solvent and pH of the resin

The effect of the interaction of *Anogeissus leicocarpus* bark extract at a given pH medium is illustrated in Figure 1. It would be observed that the highest reactivity occurred in highly alkaline and moderately acidic solution (pH of 6.5 to 7.5 and 50/50 of water /ethanol. On the other hand, the minimum reactivity, i.e, longest gelation time, occurred at pH 7.5. It was also observed that a change of medium from purely aqueous to aqueous ethanol resulted in a retardation of the reactivity of the bark extract with formaldehyde and hexamine concentrations (Table 1).

Effect of formaldehyde concentration on the resin

It has been observed that the viscosity of resin increased with an increase in the concentration of formaldehyde Figure 2. This may suggest that at this increasing profile, the polymerization reaction was still ongoing. The increase in the viscosity after a particular point became constant at 2.5 ml of formaldehyde concentration (gel point.) and the viscosity profile tends to drop (Table 2). This may be due to the establishment of a branched chain or the reactive molecules getting interconnected to form a three-dimensional network structure (Jeffrey, 2000). Therefore, at this point, the repeat unit of the polymer may be equivalent or nearly equivalent to the monomer or starting material from which the polymer resin is formed.

Effect of tannin concentration on the resin

The dependence of the reactivity of *Anogeissus leiocarpus* powder extract (tannin) with formaldehyde on the type of solvent and pH of medium is a typical polycondensation reaction. The quantity of extractable material due to each of the solvent is attributable to the pattern or behaviour shown by the monomers (tannin –formaldehyde).

Figure 3 shows the results of the viscosity profile of traditional capillary and those of constructed rotational viscometer. The two viscosity profiles indicated the effect of powder tannin extract to formaldehyde hexamine and glycerol. The viscosity measured by traditional capillary viscometer increases rapidly with increase in the concentration of tannin extracts, i.e. from 1.0 g to 3.0 g but steeply decrease from 3.5 g to 4.0 g (Table 3). The rise in the viscosity may be due to the increase in polycondensation reaction which gave rise to higher molecular weight polymer molecules, hence increase resistance to flow (viscosity). The steep

decrease in viscosity profile may be due to the molecules becoming saturated causing depolymerization (Chain, 2001). The polymer formed at this point gets decomposed by stepwise reaction resulting in the loss of monomer unit in the reaction which is essentially the reverse of polymerization.

Effect of temperature on the resin

Generally, gelation of a polymer solution is observed precisely with time when the polymerizing mixture suddenly becomes viscous or loses fluidity for example, when bubbles or emission of gases or particles are no longer observed in the solution molecules (Hemingway, 2000). However, if the extent of reaction has been followed as a function of time, say by removing aliquots of the solution and polymerized with another functional groups present, the gel point can even be determined.

Figure 4 shows that the curing behaviour and gel viscosity increase with increase in temperature and becomes constant between 60 and 70 °C, beyond which the viscosity begins to decreases. Up till this point (i.e 60 - 70 °C) gel time increased with increase in temperature since heat fastens some polymerization reaction. This may be as result of an increase in viscosity due to the closing of fluidity of the molecules in the solution as the temperature is increased, resulting in the formation of branched chain or reactive molecules get interconnected to form a three dimension network structure and the required solution ability to flow becomes very high (resist-flow) (Ahamad et al., 2000).

It was observed that at 60 °C, gel time became constant, that is, point the resin started exhibiting some chemical thermosetting properties or behaviour, heat-resistant and chemically stability (Table 4).

Hexamine concentration on the resin

To produce water resistant thermosetting material, there is the need to take note of the level of polycondensation between the tannin extract and formaldehyde yielding hardeners at appropriate temperature. However, other technique that can replace the temperature as hardening agent is the addition of hexamine (hexamethyletetramine). A peculiar behaviour was found in tannin – formaldehyde in the presence of hexamine. A clear theoretical justification to the applied finding is that under many application conditions, hexamine is not just formaldehyde yielding compound, but providing extremely low formaldehyde emission formaldehyde reducer (Hemingway et al., 2000).

Figure 5 shows the behavioural pattern through addition of hexamine to formaldehyde tannin resin with respect to viscosity measured by traditional capillary and locally made rotational visconmeter. Amounts ranging from 1.0 g to 3.5 g of hexamine show a gradual increase in the viscosity (Table 5). At this point, the cross-linking effect was not yet much effective rather polycondensation was in progress. At the point of rapid increase in the viscosity, the methylene bridge is completely replaced by the hexamine which affect the cross-linking, leading to the formation of branch chain polymer molecules, hence show great resistant to flow. Similar result was reported by Ebewele et al. (1984).

Water absorption behaviour of the formulated thermosetting polymer films at different tannin concentrations

Many resins and other polymer related materials absorb water by instantaneous surface absorption and diffusion. The rate of water absorption depends on several factors including resin type, be it thermosetting or thermoplastic, concentration of the monomers used, and temperature among others.

Figure 6 shows the effect of tannin extract at different concentrations on water absorption of the formulated thermosetting materials. For 1.0 g and 1.5 g tannin concentration, the water absorption initially increase gradually to 80% after 30 minutes and further increased steeply to higher value of 90% between 1 to 3 h after which a sudden decrease in value was observed after 24 h. This behaviour may be due to the difference in the chain topology which is related to the molecular size holes in the polymer structure, which also depends on morphology and crosslink density (Hancox, 1998). The increase in the absorption noticed after 0.5 h, 1 h and 24 h was perhaps due to the molecular size holes in the polymer structure increased at very low concentration of tannin extract. However, the increase was optimal due to the relatively low crosslink density in the polymer material. While the decrease in the absorption seen after 24 h may be attributed to the complete cross linking dissociation, however, at a point of losing out some polymer particles through the solution. No water absorption was observed at concentrations of 2.0 g; 2.5 g and 3.0 g of tannin extract after 0.5 h, but slightly increased between 1-4 h. This was probably due to the stability of the polymer materials over this period and the chain topology may be equal to the molecular size holes of the polymer structure. There was a steep increase in water absorption of these polymer materials between 42 to 92% with increase in tannin concentration when tannin concentrations. This may be due to the dissociation of the highly cross linked polymer materials between 1-4 hr, thereby giving rise to the increase in molecular size holes in the polymer material (Brune et al., 1992).

At concentration 3.5 g and 4.0 g of the tannin extract, high water absorption of up to a value of 80 and 95% after 30 min and 1 hr respectively were observed (Table 6). This

was maintained between 92 to 102% after 24 hrs. The rapid increase may be attributed to either the dissociation of the mainly low crosslink polymer structure or due to poor proportion of the active monomers in the solution or both. The tannin extract as a monomer tends to be concentrated, hence saturate the whole solution, and thereby inhibits the polymerization reaction.

Many polymer materials react in acid solution by instantaneous surface absorption and diffusion. The absorption of acid depends on several factors as stated in Figures 4 and 6.

Figure 7 show the behaviour of the film in acid solution. The acid absorption was initially about 5% after 0.5 h, however and a rapid increase was observed between 1 - 3 h at

1.0 and 1.5 g tannin content attaining a value of 49% and no further was observed after 24 h (Table 7). This behaviour may be due to partially cross linking reactions taking place and with small increase in the molecular size holes in the polymer structure at tannin concentration of 2.0, 2.5 and 3.0 g concentrations, no absorption was observed after 30min, and 1-4 h. This showed that at these concentrations, crosslinking reaction was completed after its initiation to a value of 10%. The molecular size holes in the polymer structure decreases with increase in cross-linking reaction (Ginear, 1996).
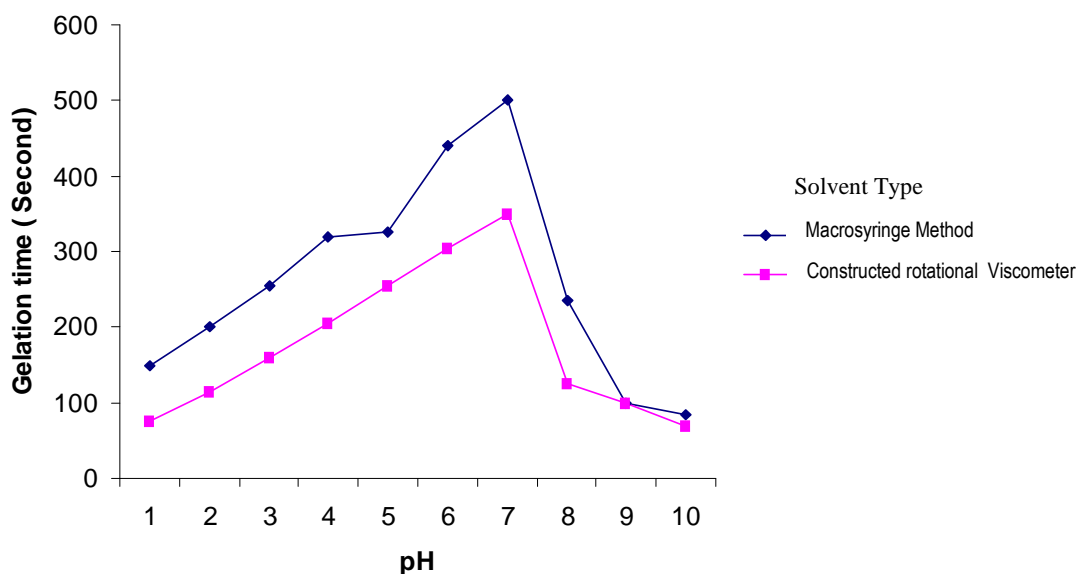

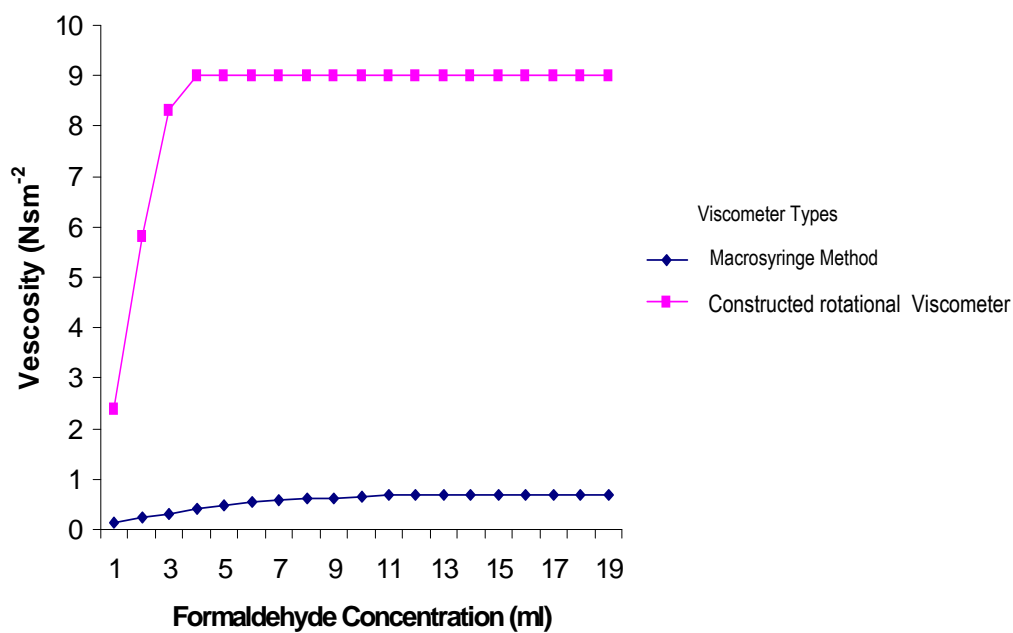**Figure 1**: Effect of solvent time and pH.

Figure 2: Effect of Formaldehyde Concentration on the by resin macrosyringe and constructed rotational viscometer.
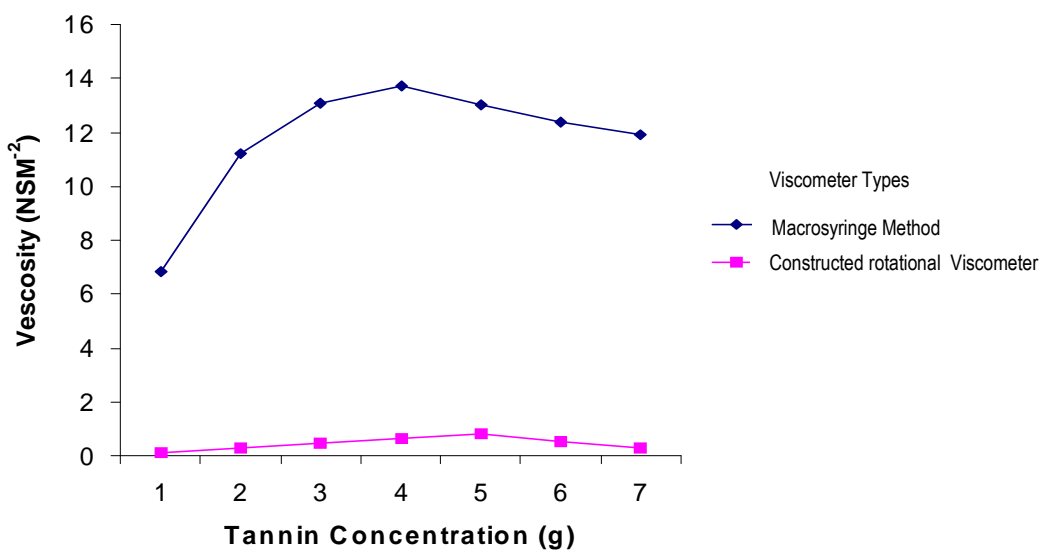

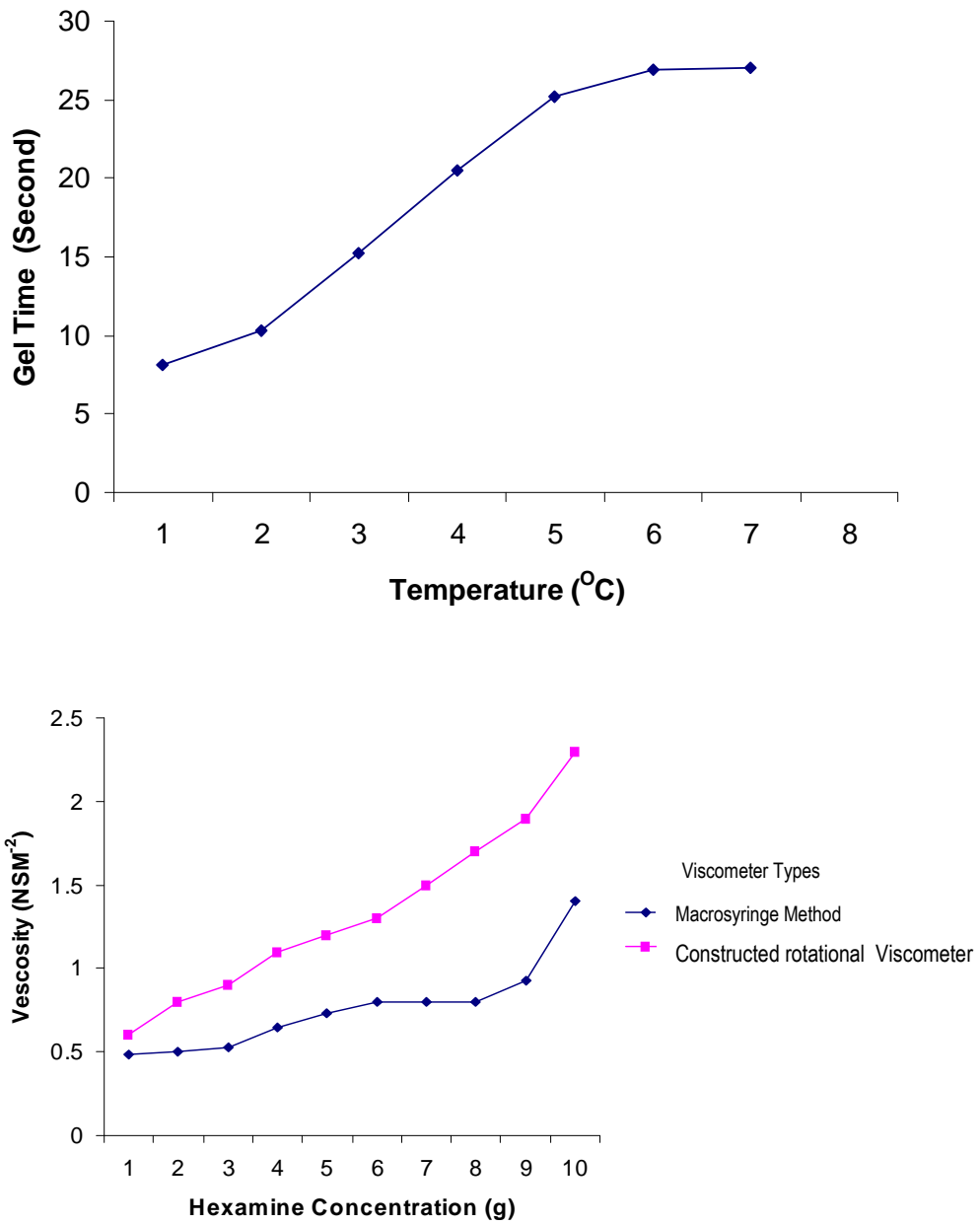**Figure 3**: Effect of tannin concentration on viscosity of resin by macrosyringe and rotational viscometer.

Figure 5: Effect of hexamine concentration on viscosity of resin by macrosyringe and constructed rotational viscometer.
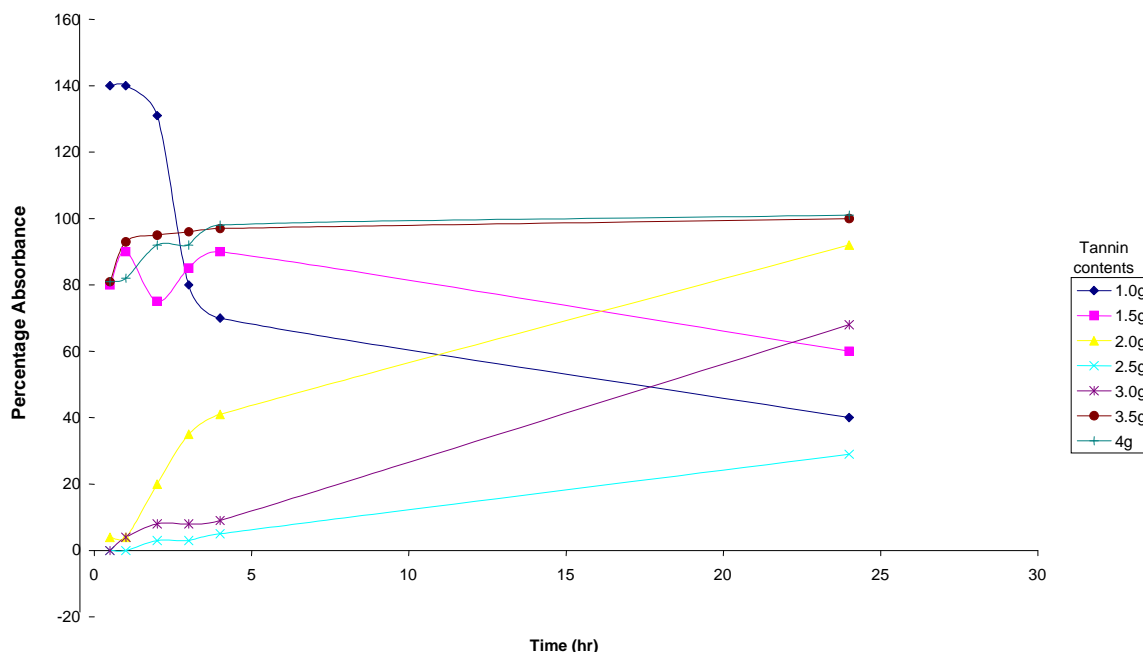
Figure 6: Water absorption behaviour on the thermosetting material.
Formaldehyde = 10.5 cm^3, Glycerol = 0.6 cm^3, Hexamine = 5.5 g, pH 7.5.

Tannin formaldehyde polymer materials show very low level of resin fortification with tannin or formaldehyde due to hydrolysis behaviour with alkalis resulting to poor cleave interflavonoid bond and closing of the heterocyclic rings of the flavononid unit in hydrolysable tannin. However, tannin formaldehyde polymer showed a great closslink dissociation and polymer degradation in solution which is essentially, the reverse of chain formation.

Base absorption behaviour of the formulated thermosetting polymer films at different

Tannin concentration

Figure 8 shows the effect of tannin extract at different concentration. The behaviour shows a reverse effect compared to water and acid absorption perhaps due to the hydrolysis of tannin- formaldehyde polymer with alkalis contributing to this great crosslink dissociation and polymer degradation in solution (Table 8).
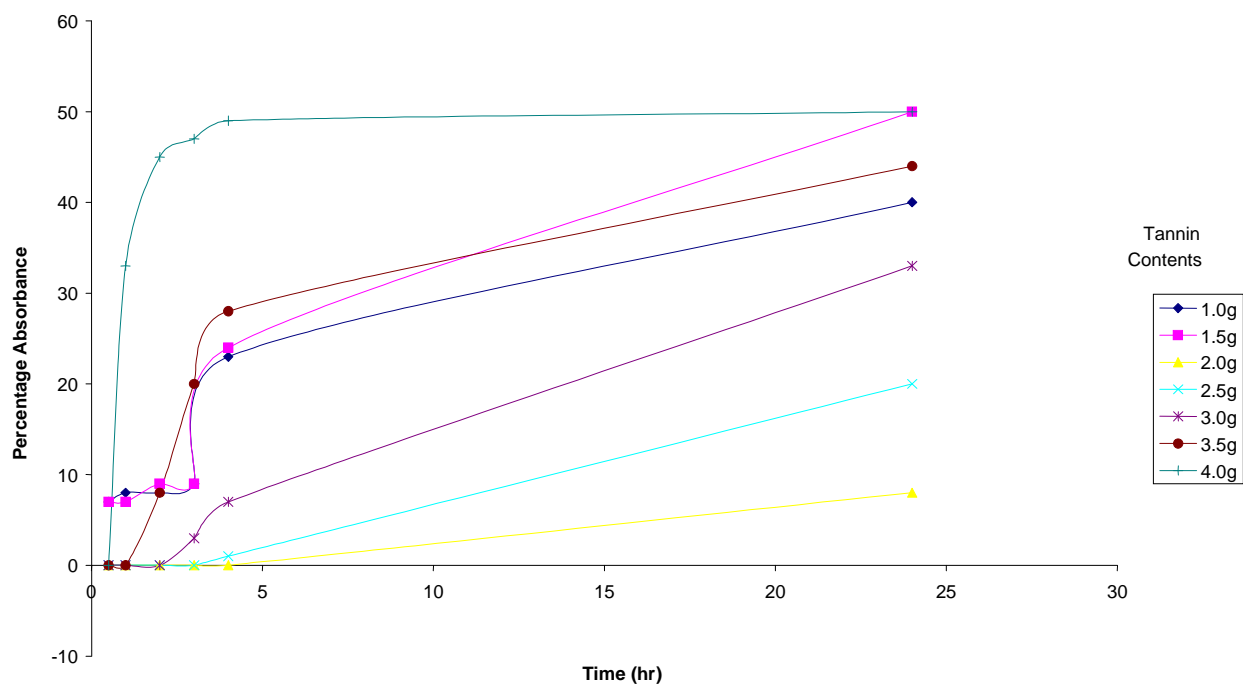
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Figure 7: Acid Absorption behaviour on the Thermosetting material.
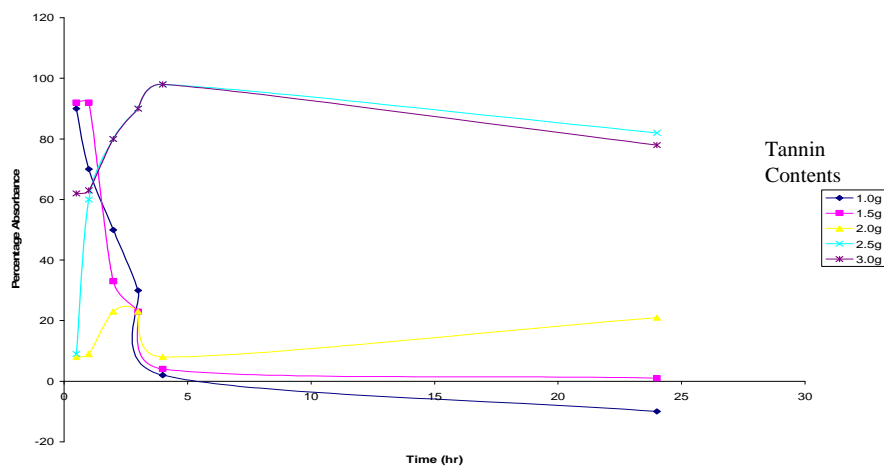Formaldehyde = 10.5 cm^3, Glycerol = 0.6 cm^3, Hexamine = 5.5 g, pH 7.5.

Figure 8: Base Absorbance behaviour on the thermosetting material.
Formaldehyde=10.5 cm^3, Glycerol = 0.6 cm^3, Hexamine = 5.5 g pH 7.5.

Table 1: Effect of solvent and pH on the resin: 50%v/v (water/ethanol)® and 100% water$.

pH	Formaldehyde Conc. (vol/vol)	Hexamine conc. (wt/wt)	Gelation time® (seconds)	Gelation time$ (seconds)
1.5			150	75
2.5	10.5	3.0	200	115
3.5	10.5	3.0	255	160
4.5	10.5	3.0	320	205
5.5	10.5	3.0	325	255
6.5	10.5	3.0	440	305
7.5	10.5	3.0	500	350
8.5	10.5	3.0	235	125
9.5	10.5	3.0	100	100
10.5	10.5	3.0	85	70

Table 2: Shows the variation in formaldehyde by macrosyringe* and constructed rotational viscometer© method on resin (Formaldehyde, Tannin, glycerol, Hexamine viscosity).

Formaldehyde (Con (vol/vol)	Tannin extract (g)	Glycerol Conc. (vol/vol)	Hexamine Conc. (wt/wt)	Viscosit* (NSM^{-2})	Viscosit© (NSM^{-2})
1.0	3.0	0.6	5.5	2.40	0.15
1.5	3.0	0.6	5.5	5.81	0.23
2.0	3.0	0.6	5.5	8.32	0.32
2.5	3.0	0.6	5.5	8.99	0.40
3.0	3.0	0.6	5.5	9.00	0.48
3.5	3.0	0.6	5.5	9.00	0.55
4.0	3.0	0.6	5.5	9.01	0.58
4.5	3.0	0.6	5.5	9.00	0.61
5.0	3.0	0.6	5.3	9.00	0.63
5.5	3.0	0.6	5.5	9.00	0.65
6.5	3.0	0.6	5.5	9.00	0.68
7.0	3.0	0.6	5.5	9.00	0.68
7.5	3.0	0.6	5.5	9.00	0.68
8.0	3.0	0.6	5.5	9.00	0.68
8.5	3.0	0.6	5.5	9.00	0.68
9.0	3.0	0.6	5.5	9.00	0.68
9.5	3.0	0.6	5.5	9.00	0.68
10.0	3.0	0.6	5.5	9.01	0.68
10.5	3.0	0.6	5.5	9.01	0.68

Table 3: Effect of tannin concentration on resin by macrosyringe* and constructed rotational viscometer© method.

Tannin extract (g)	Glycerol Conc. (Vol/vol)	Formaldehyde Conc. (vol/vol)	Hexamine Conc. (wt/wt)	Viscosity* (NSM^{-2})	Viscosity© (NSM^{-2})
1.0	0.6	10.5	5.5	6.81	1.23×10^{-1}
1.5	0.6	10.5	5.5	11.20	3.1×10^{-1}
2.0	0.6	10.5	5.5	13.10	4.9×10^{-1}
2.5	0.6	10.5	5.5	13.70	6.7×10^{-1}
3.0	0.6	10.5	5.5	13.00	7.9×10^{-1}
3.5	0.6	10.5	5.5	12.40	5.5×10^{-1}
4.0	0.6	10.5	5.5	11.90	2.9×10^{-1}

Table 4: Shows the effect of temperature on gel time of the resin.

Temperature (°C)	Formaldehyde Conc. (vol/vol)	Glycerol Conc. (vol/vol)	Hexamine Conc. (wt/wt)	Viscosity (NSM^{-2})
10	10.5	0.6	2.0	8.1
20	10.5	0.6	2.0	10.3
30	10.5	0.6	2.0	15.2
40	10.5	0.6	2.0	20.5
50	10.5	0.6	2.0	25.2
60	10.5	0..6	2..0	26.9
70	10.5	0.6	2.0	27.0

Table 5: Shows the effect of hexamine concentration on the Resin by macrosyringe* and constructed rotational viscometer© method.

Hexamine Conc (wt/wt)	Glycorel Conc. (vol/vol)	Formaldehyde Conc (vol/vol)	Tannin Extract(g) (g)	Viscosity* (NSM^{-2})	$T = t_A / 20$ Viscosity© (NSM^{-2})
1.0	0.6	10.5	2.5	4.85×10^{-1}	0.6
1.5	0.6	10.5	2.5	5.0×10^{-1}	0.8
2.0	0.6	10.5	2.5	5.3×10^{-1}	0.9
2.5	0.6	10.5	2.5	6.5×10^{-1}	1.1
3.0	0.6	10.5	2.5	7.3×10^{-1}	1.2
3.5	0.6	10.5	2.5	8.0×10^{-1}	1.3
4.0	0.6	10.5	2.5	8.0×10^{-1}	1.5
4.5	0.6	10.5	2.5	8.0×10^{-1}	1.7
5.0	0.6	10.5	2.5	9.3×10^{-1}	1.9
5.5	0.6	10.5	2.5	1.4	2.3

Table 6: Water absorption behaviour of formulated thermosetting polymer films (1.0gβ, 1.5g¥, 2.0g# and 2.5g€ of tannin contents).

Time Min/h	W.D.S (g)	W.W.Sβ (g)	W.Aβ (%)	W.W.S¥ (g)	W.A¥ (%)	W.W.S# (g)	W.A# (%)	W.W.S€ (g)	W.A€ (%)
30 Min	0.100	0.240	140	0.180	080	0.104	04	0.100	00
1h	0.100	0.240	140	0.190	090	0.104	04	0.100	00
2h	0.100	0.231	131	0.195	095	0.120	20	0.103	03
3h	0.100	0.180	080	0.185	085	0.135	35	0.103	03
4h	0.100	0.170	070	0.190	090	0.141	41	0.105	05
24h	0.100	0.140	040	0.160	060	0.192	92	0.129	29

W.D.S: Weight of dry sample;   W.W.S: Weight of wet sample

Table 7: Acid absorption behaviour of formulated thermosetting polymer films (1.0gβ, 1.5g¥, 2.0g# and 2.5g€ of tannin contents).

Time Min/h	W.D.S (g)	W.W.Sβ (g)	W.Aβ (%)	W.W.S¥ (g)	W.A¥ (%)	W.W.S# (g)	W.A# (%)	W.W.S€ (g)	W.A€ (%)
30 Min	0.100	0.107	07	0.107	07	0.100	0	0.100	0
1h	0.100	0.108	08	0.107	07	0.100	0	0.100	0
2h	0.100	0.108	08	0.109	09	0.100	0	0.100	0
3h	0.100	0.109	09	0.109	09	0.100	0	0.100	0
4h	0.100	0.123	23	0.124	24	0.100	0	0.101	1
24h	0.100	0.140	40	0.150	50	0.108	8	0.120	20

W.D.S: Weight of dry sample; W.W.S: Weight of wet sample

Table 8: Shows Base absorption behaviour of formulated thermosetting polymer films (1.0gβ, 1.5g¥, 2.0g# and 2.5g€ of Tannin Contents).

Time Min/h	W.D.S (g)	W.W.Sβ (g)	W.Aβ (%)	W.W.S¥ (g)	W.A¥ (%)	W.W.S# (g)	W.A# (%)	W.W.S€ (g)	W.A€ (%)
30 Min	0.100	0.190	90	0.192	92	0.108	08	0.109	09
1h	0.100	0.170	70	0.192	92	0.109	09	0.160	60
2h	0.100	0.150	50	0.133	33	0.123	23	0.180	80
3h	0.100	0.130	30	0.123	23	0.123	23	0.190	90
4h	0.100	0.102	02	0.104	04	0.108	08	0.198	98
24h	0.100	0.090	-10	0.101	01	0.121	21	0.182	82

W.D.S: Weight of dry sample; W.W.S: Weight of wet sample

Conclusion

This research work reveals that *Anogeissus leiocarpus* plant would yield effective tannin- phenolic formaldehyde resin. The research work also provided a platform for small scale thermosetting industry which will serve as a basis for exploitation of other resin potentials of Nigeria's rich forest. The result shows that tannin formaldehyde polymer can be formulated at the following optimum conditions. Tannin extract powder (2.5 g), formaldehyde concentration (10.5 ml),

glycerol (0.6 ml) reaction temperature (60 °C), pH 7.5 and hexamine content (5.5 g). The viscosity was visualized as a result of physical interaction of polymer molecules when subjected to flow, hence revealed the properties of the thermosetting material formulated which have long chain hydrocarbon structure and the viscosity was found to increase with increase in chain length.

The absorption of water, acid and base was investigated and the result shows that water, acid or base uptake by the polymer materials changed its properties, hence improperly formulated tannin- formaldehyde polymer with open structure may allow ingress of water, acid or base which may cause crosslink dissociation and polymer degradation in solution. The water absorption behaviour shows that the maximum duration this material can resist water is 12 h. Above this, the material will begin to swell while with acid solution, the effect is noticeable only between 20 to 24 h. Therefore, the result shows that acid has little or no effect on the resin unlike water and base.

The result of this research work therefore, will contribute towards the optimization of the new synthetic route for formulation of thermosetting tannin- formaldehyde polymer with good creep resistance, low water, acid and base absorption for fabrication of durable heat resistance material.

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