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Cure characteristics of alkali catalysed cashew nut shell liquid-formaldehyde resin

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Cashew nut shell liquid (CNSL) is a naturally occurring chemical monomer consisting four alkyl substituted phenols. Its phenolic nature makes it suitable for polymerisation into resins by formaldehyde using sodium hydroxide (NaOH) as a catalyst and hexamethylenetetramine (HMTA) employed as a hardener. There is intense interest in understanding the cure characteristics and properties of CNSL-based resins. In this work the DSC technique has been applied to study the change in the glass transition temperature of the oven-cured resin with and without HMTA in order to monitor the extent of cure. The glass transition temperature was found to rise when the alkaline catalysed resin was subjected to higher curing temperatures regardless of the concentration of formaldehyde used. The mode of cure of the NaOH-catalysed CNSL-formaldehyde resin has been found to be more regular with HMTA hardener. FT-IR spectroscopy has been used to study the neat CNSL and polymerised CNSL-formaldehyde resin with and without HMTA. The use of the DSC and FT-IR techniques to elucidate the extent of cure of CNSL resins is a valuable step towards the production of commercially successful CNSL-natural fibre composites.

1. Introduction

Cashew nut shell liquid (CNSL) is used to produce resins and is isolated from cashew nut shells as a by-product of cashew nut processing industry [1, 2]. *Anarcadium occidentale* is the cashew tree from which the cashew nuts are obtained and it is grown widely in coastal areas of tropical and subtropical countries. The major cashew tree growing countries are Brazil, Mozambique and Tanzania [3]. India also exports CNSL, sourced mainly from the Eastern, coastal countries of Africa. The use of plants as sources of resin and the development of CNSL from plants has some environmental advantages. The application of CNSL as a full replacement for synthetic resins may be of immense interest in these days of diminishing petroleum reserves. About 90% of CNSL put on the market is, used to make resins for clutches and disc brakes [3]. The chief components of CNSL have been found to be anacardic acid, cardanol and cardol (Fig. 1).

Minor components include methyl cardol and a small amount of polymeric materials [3]. The first four components have been found to comprise mixtures of four constituents differing in side chain unsaturation namely saturation, monoene, diene and triene. Anacardic acid can be decarboxylated to produce anacardol which when hydrogenated yields cardanol as shown in Fig. 2 [3]. All the constituents of CNSL are typically phenol compounds as seen in Fig. 1. Due to the presence of the hydroxyl (—OH) group, the carboxyl (—COOH) group and variable aliphatic unsaturation in the side chain, CNSL is able to take part in several chemical reactions. The long chains in CNSL impart flexibility due to internal plasticising, resulting in the formation of soft resins at elevated temperatures unlike phenol–formaldehyde resins which, are hard [1, 4].

Crude and distilled CNSL–formaldehyde have been polymerised by using sulphuric acid as well as sodium hydroxide as catalyst [3]. Addition of a curing agent such as hexamethylenetetramine (HMTA) and variations in the concentrations of catalyst [5] positively influence properties of the resin. However, *in situ* preparations of the resins for cellulose-based composites tend to favour alkaline media because of the adverse hydrolytic effect of the acid on the cellulose. Novolak and resole–type CNSL-based resins may be prepared by varying the CNSL: formaldehyde mole ratio whereby a ratio of 1:>1 and 1:<1 results in novolak and resole resins respectively. Gedam and Sampathkumaran [3] and Tyman [4] report on the production of laminates for electrical insulation and printed circuit boards using resins derived from CNSL or its derivatives.

However, the determination of the reaction mechanism of CNSL is complicated by the presence of its constituents, which have four different chemical structures including some polymeric materials [3, 4]. This implies

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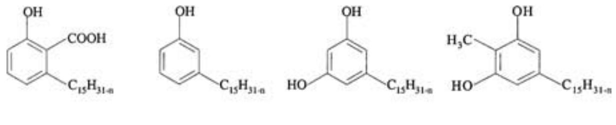
(a) Anacardic acid (b) Cardanol (c) Cardol (d) 2 – methyl cardol

Figure 1 The three main constituents of CNSL (a, b and c) and (d) 2-methyl cardol, which is a minor constituent.

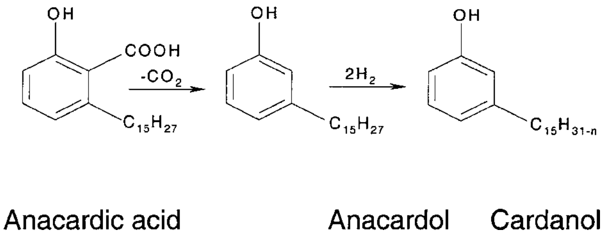

Figure 2 Conversion of anacardic acid into anacardol then cardanol.

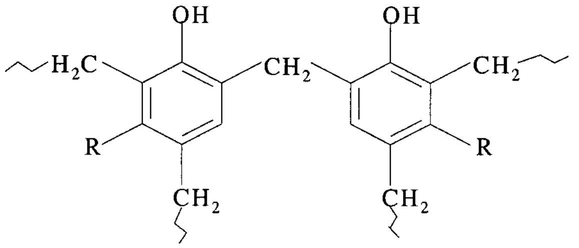

Figure 3 Possible CNSL-formaldehyde structure.

that an understanding of the polymerisation reactions and therefore the structure of CNSL are best explained by analysing its constituents. CNSL is distilled under atmospheric and reduced pressure between 180–230 °C, to obtain cardanol. The application of cardanol in resin production is of great value in the production of thermoset resin [6]. Fig. 3 shows a possible structure of cross-linked CNSL-formaldehyde resin where R stands for the side chain.

HMTA is some times added to a CNSL-formaldehyde resin to facilitate the curing process. In this case HMTA is said to degrade into dimethylenimine ($-CH_2-NH-CH_2$) and other groups which cause a deeper spatial cross-linking. The understanding of the cure characteristics of thermoset resins are based on the principle that the heat flow in an isothermal reaction is proportional to the reaction rate. This relationship is valid only in a single curing reaction where no other enthalpy reaction occurs. This implies that there is no evaporation of solvents, no enthalpy relaxation and there is no significant change in heat capacity with conversion [7]. In this work, therefore, CNSL has been polymerised using formaldehyde and catalysed by sodium hydroxide. Polymerisation was repeated with the addition of HMTA as a hardener. The change in T_g of the oven cured resin as a measure of the extent of cure was determined by the DSC technique. FT-IR was applied to determine the chemical groups present in the uncured and cured resin. The application of the DSC and FT-IR techniques is a new development in the cure characterisation of CNSL-based resins.

2. Experimental techniques

2.1. Materials

TANITA Company Ltd of Tanzania supplied the cashew nut shell liquid. Sodium hydroxide pellets of 98% strength, sulphuric acid with 99% strength and glacial acetic acid were supplied as general laboratory reagents. Merck Ltd of England supplied acetic anhydride with density of 1.08 g/cm^3 and boiling temperature of 140 °C, formaldehyde solution of about 40% weight of solid per unit volume of liquid and HMTA. Chemicals were diluted to various concentrations.

2.2. The effect of HMTA on cure characteristics of CNSL by oven and DSC method

The polymerisation of CNSL–formaldehyde resin was carried out whereby 1 ml of sodium hydroxide solution was added to the resin mixture. In the second stage of experimentation 1 ml of 15% HMTA was also added (Table I).

2.3. The effect of time on cure characteristics

The CNSL–formaldehyde resin at a mole ratio of 1:2 respectively was cured in the oven at 140 °C for 5, 10, 15, 60, 120, 180, and 240 minutes without HMTA. The experiment was repeated with the same CNLS–formaldehyde formulations with HMTA and cured at the same oven temperature for 2.5, 5, 10, 15, 60, 120, 180, and 240 minutes.

2.4. The effect of CNSL-formaldehyde ratio on cure characteristics

Another set of experiment was carried out using CNSL–formaldehyde mixture at a mole ratio of 1:1.33 respectively and cured in the oven at 110 °C for 15, 60, 180, 240 and 300 minutes without HMTA. This was repeated using CNSL–formaldehyde ratio of 1:2 and oven temperature of 140 °C. In each experiment the resin was rapidly quenched and then heated in the DSC using a single run from 0 to 500 °C at 10 °C/min. in a nitrogen environment.

2.5. Extent of cure analysis

The natural log of the ratio of the initial formaldehyde to reacted formaldehyde is defined as the extent of cure of the resin, α.

$$\text{Extent of cure,}\quad \alpha = \ln\left(\frac{C_\mathrm{f}}{C_\mathrm{f} - X_\mathrm{rf}}\right), \tag{1}$$

TABLE I Polymerisation of CNSL–formaldehyde with and without HMTA

NaOH (moles)	CNSL:H_2CO (mole ratio)		HMTA (%)
0.02	1:1.33	1:2	—
0.02	1:1.33	1:2	15

where C_f = concentration of formaldehyde and X_{rf} = amount of reacted formaldehyde. Misra and Pandey [6] applied a similar relationship to determine the kinetics of alkaline-catalysed cardanol-formaldehyde reaction. In this work the extent of cure of the resin is followed as a function of In time.

The glass transition temperature, T_g, measured by DSC should be approximately proportional to the extent of cure (α). In this work the glass transition temperature T_g of the resin has also been followed as a function of In (time) to determine the relationship between T_g and the extent of cure of the resin.

In the DSC measurements, the dynamic mode was used because it was difficult to control the reaction in isothermal mode and the T_g was determined from the first DSC endotherm. A plot of T_g versus ln t gives the extent of cure of CNSL resin which reaches a constant value at full resin cure. Also the determination of the consumption of formaldehyde gives a useful indication of the conversion and hence the cure characteristics of the resin.

2.6. FT-IR analysis

The infrared spectra were obtained using a Perkin Elmer FT-IR spectrometer model Paragon 1000. A small droplet of the liquid CNSL and a small amount of the polymerised CNSL resin powder with and without HMTA were separately mixed with KBr and pressed into a small disc about 1 mm thick. In both cases, the FT-IR spectra were analysed by studying the intensity of the transmittance peaks and comparing with the control spectra. A sample of CNSL liquid was also prepared as a control.

3. Results and discussion

3.1. Cure characteristics by oven and DSC method

Tests were carried out to determine the cure characteristics of sodium hydroxide catalysed CNSL–formaldehyde resin at two different molar ratio and cure temperatures. Adding hexamethylenetetramine (HMTA) provided another set of tests. The glass transition temperature of the oven-cured CNSL-formaldehyde resin at the respective mole ratios of 1:1.33 and 1:2 was determined at two temperatures of 140 °C and 110 °C (Tables II and III). The natural logs of the cure time and the extent of cure based on the concentration of formaldehyde (Equation 1) were determined. The graphs of the glass transition temperature versus the natural log of time and that of the extent of cure based on formaldehyde concentration versus the natural log of time were plotted and analysed at various concentrations of CNSL-formaldehyde ratios and temperatures. Results at 140 °C are tabulated in Table II and plotted in Figs 4 and 5. Tables I–III have been included to allow easy comparison between data values to be made.

Fig. 4 shows a rapid initial change in the glass transition temperature, T_g, which appears to stabilise as the reaction approaches completion. The same observation is noted when the extent of cure based on the determination of the reacted formaldehyde is plotted against the natural log of time (Fig. 5). This implies that the speed at which the resin cure and therefore, cross-linking proceeds depends on the amount of residual formaldehyde present in the reaction. A higher T_g is achieved without the hardener than with the hardener (Fig. 4) and (Table II). Also the extent of cure proceeds at higher values without HMTA than with HMTA through the

TABLE II Cure characteristics of sodium hydroxide catalysed CNSL-formaldehyde at a ratio of 1:2 and 140 °C with and without HMTA

With HMTA				Without HMTA			
Time (min)	ln t	T_g (°C)	$\ln\left(\frac{C_f}{(C_f - X_{rf})}\right)$	Time (min)	ln t	T_g (°C)	$\ln\left(\frac{C_f}{(C_f - X_{rf})}\right)$
2.5	0.92	34.67	3.545	5	1.61	54.92	4.006
5	1.61	49.96	3.909	10	2.30	64.56	4.167
15	2.71	52.63	3.963	15	2.71	64.38	4.164
60	4.09	53.06	3.971	60	4.09	54.97	4.006
120	4.79	53.16	3.974	120	4.79	59.00	4.780
180	5.19	50.45	3.919	180	5.19	55.90	4.023
240	5.48	54.34	3.995	240	5.48	62.09	4.129

TABLE III Cure characteristics of CNSL-formaldehyde without HMTA

110°C (1:2)*				140°C (1:1.33)*		
Time (min)	ln t	T_g (°C)	$\ln\left(\frac{C_f}{(C_f - X_{rf})}\right)$	ln t	T_g (°C)	$\ln\left(\frac{C_f}{(C_f - X_{rf})}\right)$
15	2.71	30.2	3.408	2.71	59.61	4.088
60	4.09	47.6	3.863	4.09	61.8	4.125
180	5.19	50.0	3.912	5.19	56.11	3.742
240	5.48	52.0	3.500	5.48	56.13	3.742
300	5.70	52.6	3.963	5.70	53.14	3.974

*The figures in brackets represent CNSL–formaldehyde ratio respectively.

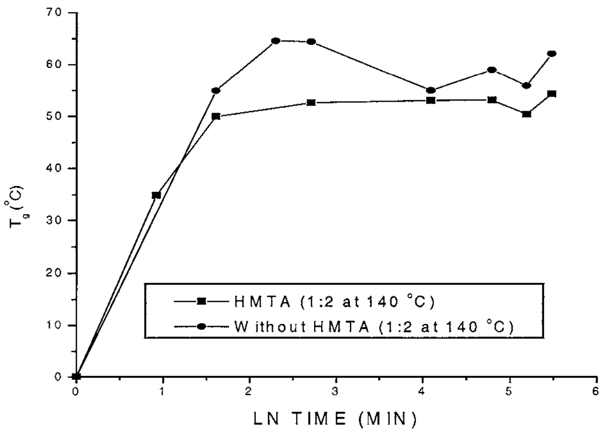

Figure 4 Glass transition temperature versus ln of time for CNSL–formaldehyde (1:2 ratio).

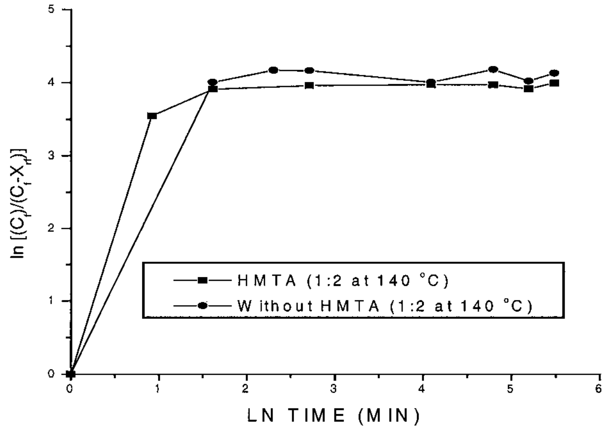

Figure 5 Extent of cure of CNSL–formaldehyde (1:2 ratio) with and without HMTA at 140 °C.

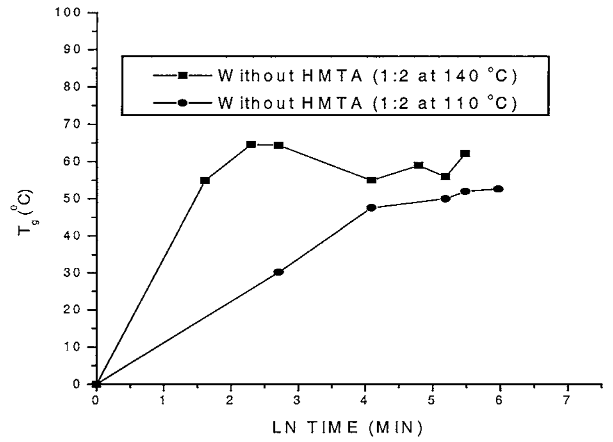

Figure 6 Glass transition temperature versus the natural log of time for CNSL–formaldehyde (1:2 ratio) without HMTA at 110 °C and 140 °C.

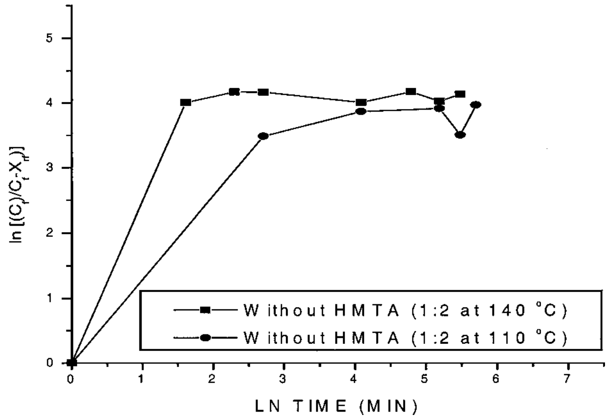

Figure 7 Extent of cure of CNSL–formaldehyde (1:2 ratio) without HMTA at 110 °C and 140 °C.

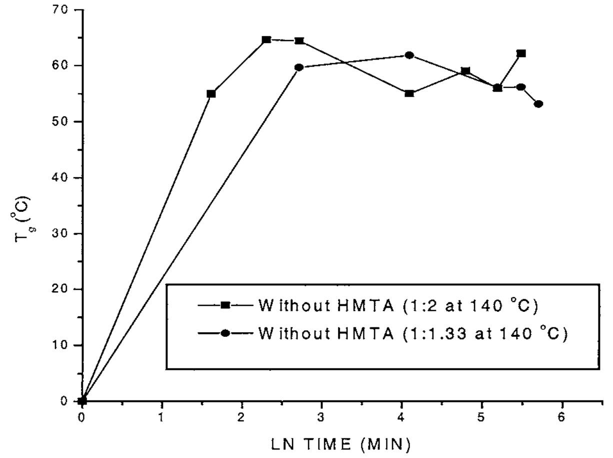

Figure 8 Glass transition temperature versus the natural log of time for CNSL–formaldehyde (1:2 and 1:1.33 ratio) without HMTA at 140 °C.

difference is not very significant (Fig. 5). This shows that there exists a relationship between the change in the glass transition temperature during the curing process of the CNSL–formaldehyde resin and the extent of cure.

This relationship is independent of the presence of the HMTA as hardener and/or curing agent. The effect of (a) keeping the ratio at 1:2 and decreasing the temperature to 110 °C and (b) keeping the temperature at 140 °C and changing the ratio to 1:1.33 is investigated in Table III. The initial rate of change in the T_g of CNSL–formaldehyde without HMTA at a mole ratio of 1:2 cured at a temperature of 110 °C is lower than the rate of change in the T_g of the resin at a mole ratio of 1:1.33 cured at a temperature of 140 °C shown in Table III. The final T_g, however, is almost the same (Table III). Figs 6 and 7 compare the change in the T_g and the extent of cure of the CNSL–formaldehyde resin without HMTA at a mole ratio of 1:2 respectively, at 140 °C and 110 °C curing temperatures (Table II) with the change in properties given in Table III. Figs 8 and 9 compare changes in T_g and extent of cure of the resin without HMTA at a temperature of 140 °C and mole ratio of 1:2 and 1:1.33.

The glass transition temperature and the extent of cure of the CNSL-formaldehyde resin without HMTA increases at higher rates when the resin is cured at higher temperature at the same formaldehyde concentration (Figs 6 and 7). However, when the temperature is kept the same and the concentration of formaldehyde lowered (Figs 8 and 9), the rate of change in the glass transition temperature of the resin at low formaldehyde concentration is initially less than that of the CNSL-formaldehyde resin with higher formaldehyde concentration. At longer times the T_g reaches an equilibrium value of about 60 °C in both cases. This trend is similar when the extent of cure is compared. This implies that the amount of formaldehyde has little influence on the

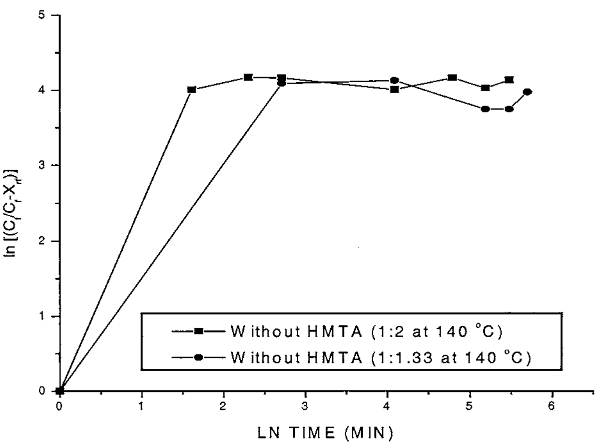

Figure 9 Extent of cure of CNSL–formaldehyde (1:2 and 1:1.33 ratio) without HMTA at 140 °C.

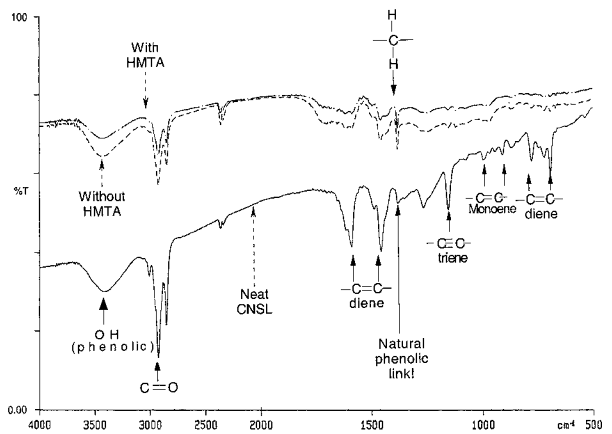

Figure 10 Infrared spectra of neat CNSL (—), alkali catalysed polymerised with (— · —) and without (— — —) HMTA CNSL–formaldehyde resin.

rate at which the glass transition temperature builds up as well as on the extent to which the cure process of the resin proceeds. Misra and Pandey [6] observed a similar relationship. Overall, It is the curing temperature rather than formaldehyde concentration, which is responsible for the increase in the glass transition temperature.

It was observed that the T_g reaches maximum at 10-min. curing time (ln t of around 2.3) at CNSL-formaldehyde concentration ratio of 1:2 and 140 °C when the resin is cured with and without HMTA (Figs 4, 6, 8). A lower curing temperature 110 °C and the same reactant ratio increased the curing time to around 60-min (ln t of 4) (Fig. 6) while increasing CNSL-formaldehyde ratio without HMTA gave a curing time of around 16-min. (ln t of 2.8) (Fig. 8).

The same CNSL-formaldehyde concentration ratio and curing temperature with and without HMTA gave a curing time of 5-min (ln t of 1.6) (Figs 5, 7, 9). However, lowering the curing temperature increased the curing time to around 60-min while increasing the reactants ratio at 140 °C without HMTA lowered the curing time to around 16-min. (ln t of 2.8) (Fig. 9). The curing time of different formulations of CNSL-formaldehyde resin is between 5–60 minutes [3, 8].

3.2. Infrared spectroscopy analysis

The infrared spectra of the neat and alkali catalysed CNSL–formaldehyde resin polymerised with and without HMTA at room temperature is shown in Fig. 10. The phenolic hydroxyl band is observed at 3418 cm^{-1}, 3423 cm^{-1} and 3424 cm^{-1} in the neat CNSL and in the alkali polymerised CNSL without and with HMTA respectively. However, the decrease in intensity of these peaks, which is more in the CNSL-formaldehyde resin with HMTA than without HMTA (Fig. 10), is due to the diminishing phenolic hydroxyl groups that has occurred as a result of CNSL reaction with formaldehyde. The peaks at 3009 cm^{-1} and 2854 cm^{-1} are the —CH stretching aromatic and aliphatic groups respectively [7]. The —CH_2 peaks are found at 2926 cm^{-1} while the —CH_3 peaks are seen at 2854 cm^{-1} and are confirmed by the presence of their deformative peaks at 1382 cm^{-1} and 1458 cm^{-1} respectively in the neat CNSL and the polymerised CNSL with and without HMTA [6]. The band at 1382 cm^{-1} in the neat CNSL shifts to 1384 cm^{-1} in the polymerised CNSL.

The band observed at 1718 cm^{-1} in the CNSL–formaldehyde resin without HMTA is due to water molecules resulting from the condensation reaction of the phenolic groups or from the sodium hydroxide and formaldehyde solutions. This peak vanishes when HMTA is added implying that HMTA might also be acting as a dehydrating agent. The peak at 1590 cm^{-1} is due to the skeletal vibrations of the aromatic —C=C— linkages. The peak found at 1120 cm^{-1} is associated with the presence of the aromatic ether linkages, which are not possible when phenol-formaldehyde reactions are carried out under alkaline conditions. This means that a pH closer to acidic conditions may have developed during the polymerisation process.

The vinyl vibrations between 997–823 cm^{-1}, at 695 cm^{-1}, and the band at 723 cm^{-1} and 780 cm^{-1} are due to the side chain —C=C— double bonds. These peaks have completely vanished in the formaldehyde-polymerised CNSL with and without HMTA indicating that polymerisation has taken place through the double bonds in the side chain. Similar results have been reported [8].

4. Conclusions

The change in the glass transition temperature shown by DSC as the reaction proceeds to complete conversion of the CNSL–formaldehyde resin, is a useful physical parameter, which indicates the extent of cure of the resins. The experiments were carried out changing the CNSL-formaldehyde ratio and temperature with and without HMTA. It can be deduced that the curing mode is more progressive when hexamethylenetetramine is added compared to without HMTA. This is observed by comparing Figs 4 and 6 for the T_g and Figs 5 and 7 for the extent of cure. It may be concluded that different curing temperatures alters the rate of increase of the glass transition temperature and hence, the cure characteristics of the CNSL-formaldehyde resin under alkaline conditions regardless of the amount of formaldehyde used. It has also been observed that there is a strong relationship between the change in the glass transition temperature and the extent of cure of the alkaline catalysed CNSL-formaldehyde resin.

FT-IR results show that the formaldehyde reduces the intensity of the phenolic peak indicating that phenolic hydroxyl groups have reacted. By adding HMTA the phenolic peak diminishes more rapidly. The disappearance of the peak at 1718 cm^{-1} with HMTA shows the removal of water molecules, which may have the advantage of reducing the amount of voids in the resin and hence in composites with CNSL resin matrices.

The absorption band appearing at 1384 cm^{-1} in polymerised CNSL is due to the methylene group ($-CH_2$) linking the phenol rings in the CNSL-formaldehyde resin with and without HMTA. This implies that the band observed at 1382 cm^{-1} in the neat CNSL which shifts to 1384 cm^{-1} in the polymerised CNSL indicates the presence of a naturally occurring polymeric material in the CNSL. The appearance of many $-C{=}C-$ double bonds than any other bonds (Fig. 10) shows the presence of more diene in the CNSL used in this work than monoene and triene components.

The understanding of thermal characteristics of the CNSL resin curing is essential for materials selection; design and manufacture of natural fibre reinforced composite material.

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