DEVELOPMENT OF HIGH PERFORMANCE CASHEW NUT SHELL LIQUID (CNSL) BASED SURFACE COATINGS CROSS LINKED WITH STYRENE AND METHYLMETHACRYLATE

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Development of High Performance Cashew Nut Shell Liquid (CNSL) Based Surface Coatings Cross Linked with Styrene and MethylMethacrylate

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

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DEDICATION

This work is dedicated to my beloved late Dad, Mohammed Ahmed Noor, for instilling in me the virtues of courage and selflessness and for making me appreciate the value of education; to my beloved mum, Rehema Noor, my brothers, my sisters and the extended family for the love, encouragement and support and above all to God, the creator of all beings, Who provided strength, health, intellect and favor that saw me through this work.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF APPENDICES

ACRONYMS AND ABBREVIATIONS

AOAC   - Association of Official Analytical Chemists

ASTM   -American Society for Testing and Materials

BOD   - Biological Oxygen Demand

CNSL   - Cashew Nut Shell Liquid

Cp   -Centipoise

FAO   -Food and Agriculture Organization

FTIR   - Fourier Transform Infra Red

ICDC   - Industrial and Commercial Development Corporation

IDB   - Industrial Development Bank

JKUAT   - Jomo Kenyatta University of Agriculture and Technology

KCL   -Kenya Cashew Nut Limited

MMA   - Methyl Methacrylate

NCPB   - National Cereals and Produce Board

UV   -Ultra Violet

VMP   - Varnish Makers and Painters

VOC   - Volatile Organic Compounds

ABSTRACT

The unmitigated volume of cashew nut shells produced annually along the production line poses a challenge for waste disposal. In Kenya the waste cashew nut shells are used as fuel which results in heavy pollution to the environment through emission of heavy dark smoke with particulate matter. Cashew nut shell liquid (CNSL), is a dark reddish brown liquid extracted from cashew nut shells and is an excellent source of natural resins. Therefore, it is wise to extract as much of the CNSL prior to disposal. This will ultimately help reduce the environmental load for the residual portion of the shell. It is hoped that this project will contribute significantly towards addressing this problem and reversing the trend. Being renewable, CNSL offers much advantage over synthetic materials. This research aimed at developing high performance surface coatings based on cross linking CNSL by means of suitable monomers such as styrene and Methyl Methacrylate (MMA). A high performance resin was formed by addition of formaldehyde to a solvent solution of CNSL in the presence of a catalyst and modified with styrene and MMA at different mole ratios. Tests for pH, viscosity, relative density, adhesion, pencil hardness and drying time were determined using the simulated standard procedures of the Association of Official Analytical Chemists (AOAC) and American Society for Testing and Materials (ASTM). Both physico-chemical and performance characteristics of the formulations were compared with the standards and conclusions were drawn. The results indicated that the estimated relative density ($0.8691 kg/m^3$) of CNSL-based coating compared to that of standard commercial coating ($0.9294 kg/m^3$). The FTIR analysis established that decarboxylation of raw CNSL was successful because both the $\bar{\upsilon}_{max}$ O-H stretch and $\bar{\upsilon}_{max}$ C=O symmetrical stretch of the Carboxylic acid having $\bar{\upsilon}_{max}$ O-H, at 2596.0 cm^{-1} and $\bar{\upsilon}_{max}$ C=O at 1647.1 cm^{-1} frequencies respectively had been cleared. The average pH (6.07) of CNSL-based coating also compared well to the standard (6.08). The optimization of temperature and heating time was determined using physico-chemical and performance characteristics and

temperature of 70°C and heating time of 60 minutes were taken to be the optimum conditions. Polymerization was carried out under optimum conditions. Cross linking of the CNSL based coating with Styrene and MMA monomers, gave formulations with performance characteristics either improving or lowered, both adhesion and drying time properties were improved on different ratios of monomers that were added. Styrene monomers at lower ratios performed better in terms of adhesion and drying time, while MMA produced better formulations at higher ratios. Hardness characteristics for cross linked formulations were lowered compared to the standard. Generally, cross linking improved some performance characteristics and affected other characteristics negatively. Depending on the use of a given polymer, a suitable monomer can be used to effect the desirable performance characteristics. Successful implementation of the project would result into cleaner environment, job creation, increased returns to both producers and processors of the cashew nuts and net saving of foreign exchange to the country among other benefits. This research work was very successful as evidenced by the good results obtained. The study however, recommends further research to be done to determine other performance characteristics such as, impact resistance, corrosion resistance, flexibility and gloss.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 General Introduction

The cashew tree *Anacardium occidentale*, is a native plant of Brazil, where it is called by its Portuguese name *Caju* (the fruit) or *Cajueiro* (the tree). The tree grows in the coastal areas of Asia and Africa. Nowadays, it can also be found widely in other parts of tropical climates. The tree is indigenous to Central and South America and was introduced into East Africa during the sixteenth Century by the Portuguese (Mitchell & Mori, 1987). The cashew trees are evergreen trees, with an average height of not more than 30 feet (Plate 1.1).

Plate 1.1: Cashew tree

It grows abundantly in the tropics and is extensively found near the Equator, as it flourishes in extreme heat (Ohler, 1994). It is among the oldest cash crops in Kenya and yields even in poor soils and have excellent cash crop prospects for areas where other productive crops cannot grow well. Report by (Gibbon & Pain., 1981) state that many cashew trees are found growing wild and that the plant germinates poorly, those that are cultivated are propagated by seed which are planted at a rate of 2-3 per hole due to poor germination rates.

The major producing countries of cashew nuts are; Vietnam, Brazil, India, Nigeria and Indonesia accounting for estimated 68% of the global production. The production of cashew nut in Kenya compared to the major producing countries is very low at less than 1% of the global output. In 2008, the global output was reported at 3.1million metric tons (FAO Report, June 2008). Kenya has potential of producing up to 200,000 metric tons per annum.

In Kenya, the processing of cashew nuts started in a very small way at Kilifi in 1930. Five years later a primitive type of drum roaster was introduced where shelling, peeling and grading was done by hand in an open shed. In 1950 an improved type of drum roaster was installed and new drying ovens were built. This granted a great deal of economic stability to Kilifi District, which previously did not have a cash crop. Between 1960 and 1963, the processing was taken over by Mitchell Cotts Cashew Limited which was able to increase the processing capacity to 800 tons per year (Anon, 1971). In 1964 the government took over the business and placed it under the National Cereals and Produce Board (NCPB) in the Ministry of Agriculture which was later joined by the Industrial and Commercial Development Corporation (ICDC), Industrial Development Bank (IDB) and the Kilifi District Cooperative as owners. During this time the factory was able to process 1500 tons or about 30% of cashew nuts annually, the other 70% was exported to India for processing, which was an indication that the three main producing districts of Coast province namely Kilifi, Kwale and Lamu had stepped up their production capacity owing to the extension services by the ministry of Agriculture (Muturi & Arunga, 1988). In 1975 the Kenya Cashew Nut Limited (KCL) commenced operations and the plant's installed capacity was only 15,000 metric tons. The demand for cashew nut from Kenya was considerable and the main export markets were North America, Japan, Middle East, Europe and Australia. All raw nuts were supplied by the Kilifi District Cooperative Union to KCL, through the NCPB. The factory was privatized in 1993 and continued under the same name. The crop was marketed through farmers' cooperative societies, traders and agents. The Liberalization of marketing of

cashew nuts took place in 1997/1998. The factory closed down in 1998 but it was later reopened after being take over by the Millennium Nut limited.

The cashew tree is one of the economically important crops in Kenya, and is a multi-purpose plant. The tree is known for its various products that include; cashew apple, cashew nut (kernel) and CNSL. It also yields gum which is used together with the bark for medicinal purposes (Achal, 2002). Among these, two most important parts in commercial use are the cashew nut for human consumption and the CNSL for various industrial and medicinal applications.

1.2 Cashew fruit or Cashew apple

Cashew apple is a bell-shaped pseudo carp which holds the nut below it (Figure 1.1). It is in fact the false fruit that develops from the cashew flower stalk (Akinwale, 2000).
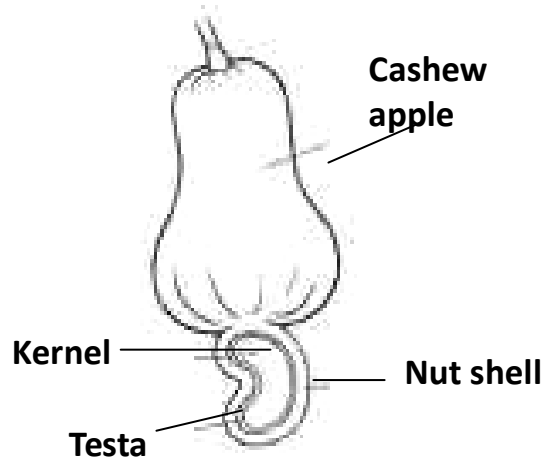
Figure 1.1: Cross section of cashew apple and nut

It ripens into a yellow and/or red color and is about 5-11 cm in length. The fruit is edible, juicy, nutritious, pungent, sweet to taste and high in vitamins A and C. Fresh fruit, the cashew apple has more vitamin C than guavas, mangoes and oranges per 100 g. However, they are quite perishable and only used locally unless preserved. It can be preserved in syrup, candied, sun-dried, stewed, and made into jams, chutneys, vinegar, wine, brandy, gin, pickles, and juices. In Brazil, fresh cashew apples are packed in trays and marketed in retail fresh produce outlets (Winterhalter *et al*., 1990).

1.3 Cashew kernel

Cashew kernel is the main product of the cashew industry. It is a popular snack. Due to its distinctive sweetness and crispiness, it is easily found in the markets throughout the year for consumption. The kernel (Plate 1.2) is a high value nut used for human consumption. Researchers found that the vegetable proteins contained in cashew kernels stand at par with milk, eggs and meat. Besides, it also contains a high concentration of much needed acids in the right proportions. A cashew kernel contains 47% fat, 82% of this fat is unsaturated fatty acids (Rosengarten & Frederic, 1984).

Plate 1.2: Cashew kernels

Some of the common fatty acids present in cashew kernel are; oleic acid (73.8%), stearic acid (11.24%) and linoleic acid (7.7%). The unsaturated fatty acids help in lowering blood's cholesterol level, (Azam-Ali & Judge, 2001).

1.4 Cashew nut shell liquid (CNSL)

Cashew nut shell liquid (CNSL) is a by-product of cashew industry obtained from the soft honeycomb structure of the shell of cashew nut. It appears as a reddish brown viscous liquid with a characteristic smell, quite unlike other vegetable oils. It is opaque and immiscible with water but miscible with most organic solvents (Plate 1.3). (Ras *et al*., 2003)
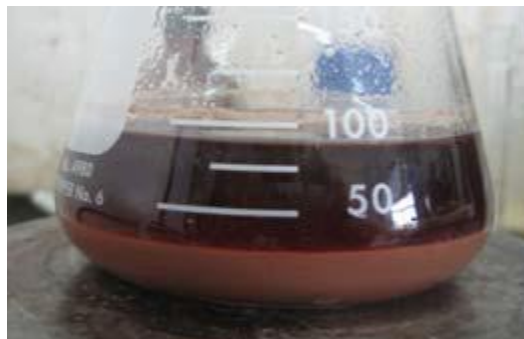
Plate 1.3: CNSL extract

The world availability of CNSL is approximately 50 kiloton per annum (FAO Report, June 2008). CNSL is essentially a mixture of phenolic compounds namely anacardic acid, cardol, cardanol and 2-methlycardol (Scheme 1.1). These natural products could serve as alternative source of phenolic compounds from petrochemical industry (Tyman & Bruce, 2003). CNSL is not a triglyceride and contains a high proportion of phenolic compound; in the natural state, it serves as a protection to kernel against insect attacks. When used in combination with kerosene or diesel oil, it is an effective insecticide against mosquito larvae and when made into varnish, it provides preservation to wooden floors and fine carved woods, protecting them from insect destruction. For many years, fishermen have used this liquid to waterproof and preserve their fishnets, fishing lines and boats.
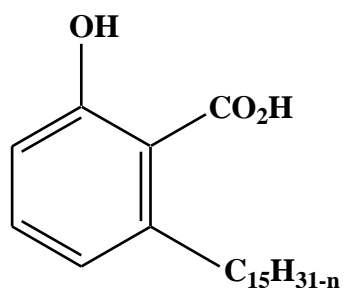
Anacardic acid (82%)
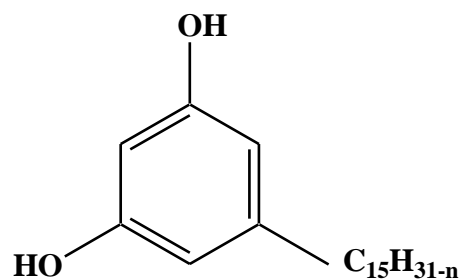
Cardol (13.8%)
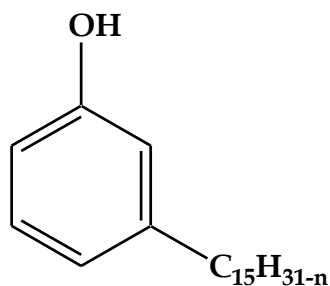
Cardanol (1.6%)

Methyl cardol (2.6%)

n=0 (3 %)

n=1 (34-36 %)

n=2 (21-22 %)

n=3 (40-41 %)
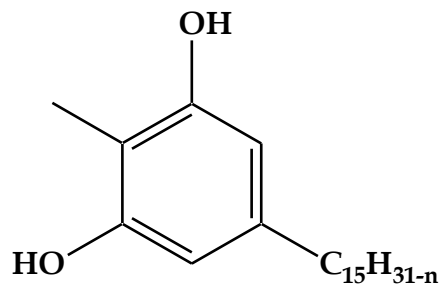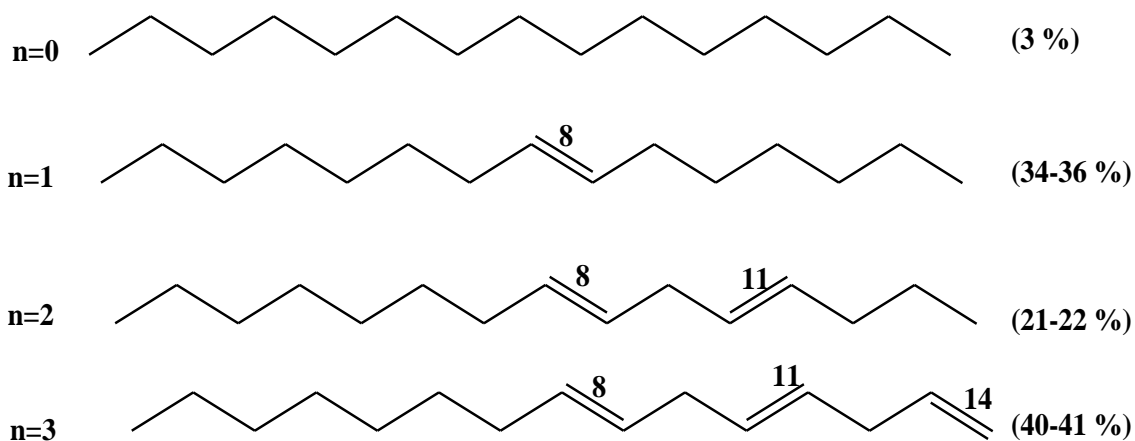
Scheme: 1.1: Main Chemical Fractions of CNSL with their percentage by weight

(Tyman & Bruce, 2003)

With recent advances in chemical technology, CNSL is finding many new industrial applications. It is used commercially as a phenolic raw material for the manufacture of resins and plastics. In particular, it is used as a friction modifier in the manufacture of brake lining and clutch facing. It has the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer. It is also used in rubber compounds, where it acts as reinforcing fillers, whose tensile strength, hardness and abrasion resistance are improved. The resins from CNSL are used in laminating paper, cloth and glass fibers, or impregnating materials where oil or acid

resistance is required. Other uses include the manufacture of lacquers, paints, printing inks, electrical insulation material, anti-corrosive for metals, water proofing compounds and adhesives (Menon *et al.,* 1985).

1.5 Extraction of CNSL from cashew nut shell

Cashew nut processing industry involves several steps such as pre-grading, drying, peeling, grading, and packaging. In the peeling stage, the shell is separated after the removal of kernels. The sheer volume of cashew nut produced annually poses a challenge for waste disposal of cashew nut shell generated during processing of the nut. Research and development have shown that valuable chemicals can be extracted from the shell. Therefore, it is wise to extract as much of the CNSL prior to disposal. This ultimately helps reduce the environmental load for the residual portion of the shell. There are three main methods to obtain this liquid; thermal extraction, screw pressing method and solvent extraction as shown in (Figure 1.2). For the purpose of this work solvent extraction was adopted because it gives off most of CNSL compared to other two methods. (Edoga *et al*., 2006)

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                        ┌─────────────────────┐
                        │    Raw materials    │
                        │  Cashew nut shells  │
                        └─────────────────────┘

┌──────────────┐                                    ┌──────────────┐
│   Cleaning   │ ◄──────────────────────────────►   │   Reduced    │
│              │                                    │     size     │
└──────────────┘                                    └──────────────┘

┌──────────────┐        ┌──────────────────┐        ┌──────────────┐
│ Extracted by │        │Thermal Extraction│        │   Solvent    │
│              │        │                  │        │  extraction  │
│  Screw press │        │        at        │        └──────────────┘
└──────────────┘        │                  │
                        │   200-250⁰C      │        ┌──────────────┐
┌──────────────────┐    └──────────────────┘        │CNSL + Solvent│
│CNSL + Contamination│                              └──────────────┘
└──────────────────┘
                                                    ┌──────────────┐
┌──────────────┐                                    │Distilled solvent│
│Separated and │                                    │  from CNSL   │
│ Demoistured  │          ┌──────────────┐          └──────────────┘
└──────────────┘ ───────► │  Pure CNSL   │ ◄────────
                          └──────────────┘
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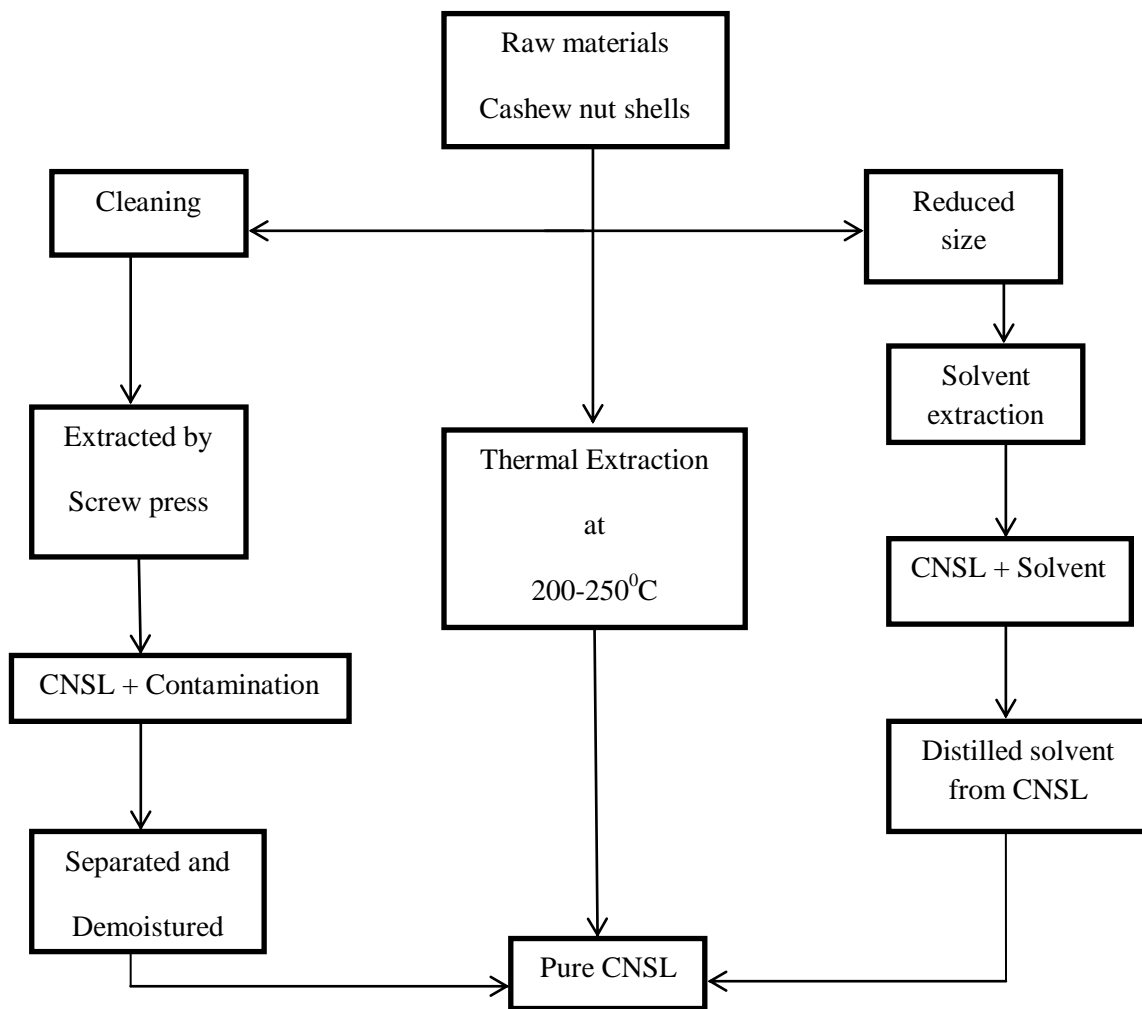
Figure 1.2: Flow diagram for extraction of CNSL from cashew nut shell

1.5.1 Solvent extraction method

The oil in the residue after solvent extraction is less than 1% by weight (Edoga *et al.*, 2006). In the preparation step, the contamination remaining is removed by the use of magnetic device. Cashew nut shell is then reduced to small sizes to facilitate drying and extraction. The organic solvent is added to the cashew nut shell. CNSL is then extracted

in the solution. The solution is separated from the solid particles and brought to boil off the solvent, which is subsequently condensed for reuse in the process (Gedam & Sampathkumaran, 1986). The percentage yield of CNSL varies with the extraction process. Indian native method of roasting nuts and collecting the expelled liquid is reported to yield about 50% of total oil content. Extraction with hot oil bath method gives about 85–90% of total CNSL in India. Superheated steam treatment and collection of condensate method improves the yield further by 2% (Edoga *et al.*, 2006).

CNSL is often considered as a good and cheap natural source of unsaturated phenols, which are excellent monomers for polymer production. Nowadays, cashew nut is one of the key commodities in the international trading markets including Kenya. Unfortunately, little attention has been paid to the utilization of abundantly available by-product of the industry. Raising public awareness is necessary for locals to take advantage of this natural resource, which is part of supporting economic self-sufficiency in line with Kenya's Vision 2030.

1.6 Statement of the Problem

From the FAO report of June 2008, Kenya has the potential of producing over 200,000 metric tons of cashew nuts annually which translates to over 50,000 metric tons of waste cashew nut shells. Disposal of the cashew nut shells and CNSL presents environmental hazards; when used as fuel in industries they release dark sooty smoke rich in particulate matter which pollutes the environment heavily. When used as landfills the heavy CNSL oozes out into the water bodies raising the Biological Oxygen Demand (BOD) which affects the aquatic ecosystem. Therefore the extraction of the CNSL from waste cashew nut shells prior to the disposal and the alternative use of CNSL in the production of high performance surface coatings will alleviate environmental pollution effects.

1.7 Justification

The current practice in Kenya where the cashew nut shell is burnt to generate fuel heavily pollutes the environment. This research aims at producing an alternative use of cashew nut shells thus alleviating environmental pollution, both air and water. The extraction of CNSL from the waste cashew nut shells provides one of the richest natural phenolic materials with innumerable applications in polymer based industries. Apart from alleviating environmental pollution, the alternative use of cashew nut shells is expected to increase returns to both the producers and processors of cashew nuts leading to creation of employment for many deserving job seekers thus contributing to a better economy for the country.

1.8 Null Hypothesis

Surface coatings developed from modified CNSL does not compare favorably in quality to commercially available coatings.

1.9.0 General Objective

To develop high performance surface coating based on modified cashew nut shell liquid (CNSL) from waste cashew nut shells.

1.9.1 Specific objectives

   i.   Extraction of CNSL from milled shell
  ii.   To determine physico-chemical properties of CNSL and CNSL based surface coatings.
 iii.   To develop surface coatings from CNSL through optimization of temperature and time of polymerization.
  iv.   To develop surface coatings from CNSL modified with suitable monomer/s.
   v.   To carry out performance tests to ascertain the quality of the developed products.

1.10 Aromatic Phenols and Cardanol

Synthetic high performance polymers are constantly being modified and improved for current and future need. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry. In this regard CNSL, an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production (Akinhanmi *et al.,* 2008). Considerable research work has been done by scientists all over the world to find out the multifarious uses of CNSL. Recent investigations (Table 1.1 and Table 1.2) have revealed that the constituents of CNSL possess special structural features and desirable physico-chemical characteristics which allow it to be chemically transformed into specialty and high value polymers. (Lomonaco *et al.*, 2009).

The cashew nut shell comprises some 50% of the weight of the raw nut, the kernel represents 25% and the remaining 25% consists of the natural CNSL; a viscous reddish brown liquid (Tyman & Bruce, 2003). Report by (Ohler, 1994) state that fresh CNSL contains anacardic acid of about 90% by weight. Anacardic acid is a derivative of salicylic acid, which readily decarboxylates upon heating and converts to obtain anacardol or cardanol (Scheme 1.2). Cardanol is the component that is responsible for the aforementioned applications of CNSL (Ganesh *et al*., 2006). The remaining 10% of CNSL consists of cardol, a resorcinol derivative having a long unsaturated hydrocarbon chain (Akinhanmi *et al.,* 2008).

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Table 1.1: Brazilian and Indian Standards for CNSL

Properties	Brazilian standard[2]	Indian Standard (IS840)[1]
Appearance	Dark brown liquid	Dark brown liquid
Nature	Viscous liquid	Viscous liquid
Specific gravity (Kg/M^3)	0.943-0.968	0.950-0.970
Moisture content (% by weight)	Max 1	Max 1.0
Iodine value Wij's method (mg iodine/100g)	Min 200	250
pH 25°C	Min 6.0	5-10
Viscosity at 30°C, centipoises (Cp)	Max 600	Max 300
Acid value, g/100 g KOH	0-15	Max 14

Sources: [1] Bola Raghavendra Kanath & Sons (2003); [2] Amber wood Trading Ltd. (2003).

Cardanol, a natural alkyl phenol from CNSL is a potential natural source for biomonomers. Today, it cannot even be said to have found its niche in terms of an appropriate industrial application. Cardanol is a phenolic compound with a C15 aliphatic chain in the Meta position, obtained from CNSL (Kumar *et al*., 2002). The name cardanol is used for the decarboxylated derivatives obtained by thermal decomposition of any of the naturally occurring anacardic acid (Scheme 1.2). This includes four compounds because the composition of the side chain varies in its degree of unsaturation.
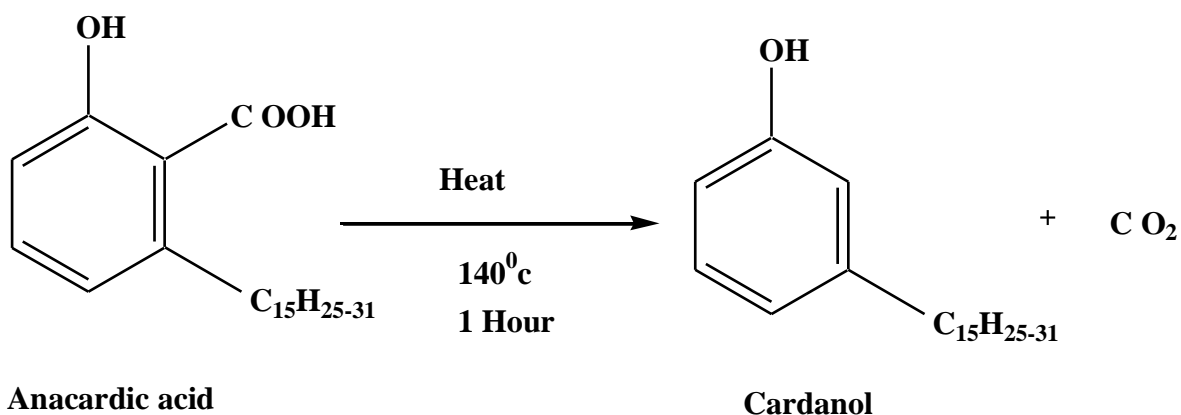
Scheme: 1.2: Decarboxylation of Anacardic acid (Tychopoulas *et al.*, 1990)

The structure of tri-unsaturated cardanol given below is the major component (41%). The remaining cardanol is 34% mono-unsaturated, 22% bi-unsaturated, and 2% saturated (Cornelius, 1966).
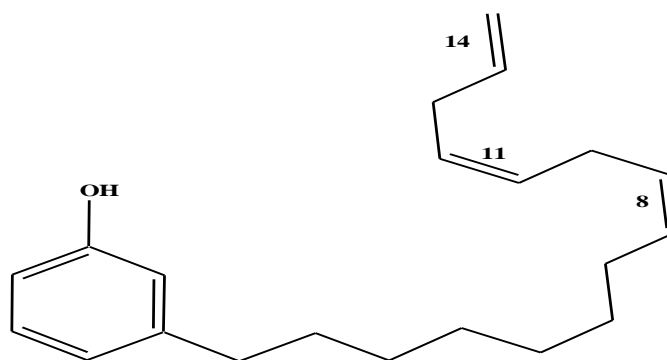
Structure of tri-unsaturated cardanol

1.11 Functionality of the side chain of cardanol

Functionality is the number of reaction sites where cross linking can occur. In order to determine the functionality of a given compound, the composition of the side chain in

terms of the saturation or unsaturation should be known. The following formula was used to determine the functionality (average double bond) of a given compound, (Cornelius, 1966).

$$\text{Functionality} = A \times \% \; E + B \times \% \; E + C \times \% \; E + D \times \% \; E$$
$$\text{where} \quad A = \text{Tri}- \text{unsaturation}$$
$$B = \text{Bi}- \text{unsaturation}$$
$$C = \text{Mono}- \text{unsaturation}$$
$$D = \text{Saturation}$$
$$E = \text{Abundance}$$

The functionality of a tri-unsaturated cardanol can be computed using the data given above;

$$\text{Functionality} = 3(0.41) + 2(0.22) + 1(0.34) + 0(0.02)$$
$$= 1.23 + 0.44 + 0.34 + 0.00$$
$$= 2.01$$

The Functionality of cardanol is 2, indicating that it can easily polymerize. Therefore the knowledge of average double bond is very important in polymer formation. Cardanol is hydrophobic and remains flexible and liquid at very low temperatures; its freezing point is below −20 °C, it has a density of 0.930 g/ml, and boils at 225 °C under reduced pressure (10 mmHg), (Eromosele *et al.,* 1994).

Table 1.2: Indian Standard Specifications for Cardanol, (Akinhanmi *et al.,* 2008)

Properties	Indian Standard (IS 840)
Color	Pale Amber
pH at 25 ^{o}C	6.16
Specific Gravity @ 30 ^{0}C	0.927 – 0.934
Viscosity @ 30 ^{0}C (Cps)	45.0 – 60.0
Iodine value (mg iodine/100g)	210 – 230
Acid value g/100 g KOH	1.9-2.0
Moisture content (%)	Negligible

1.12 Reactivity of CNSL

CNSL undergoes all the conventional reactions of phenols. Cardanol is a major fraction of commercial CNSL and only differs from phenol in that it has in addition a C15 side chain. CNSL can be polymerized through the following processes; Additional polymerization through the side chain double bonds using cationic initiators such as sulphuric acid or diethylsulphate (Antony, 1990), or condensation polymerization through the phenolic ring with aldehydic compounds such as the formaldehyde condensation reaction of phenols (Scheme 1.3) that give rise to phenolic polymers (Calo *et.al*, 2007). CNSL can also undergo polymerization after chemical modification to introduce specialty properties (Odin, 1991).
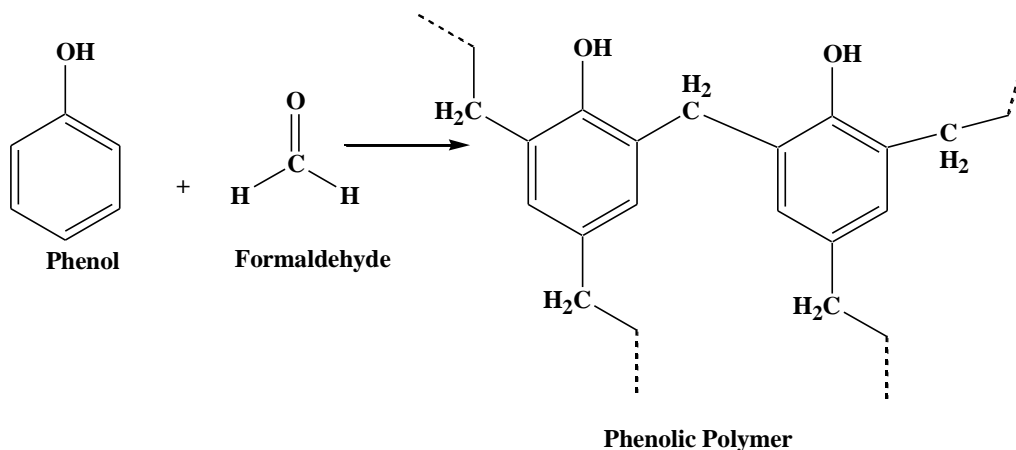
Scheme: 1.3: Formaldehyde Condensation Reaction of Phenols, (Calo *et.al*, 2007)

1.12.1 Polymerization of CNSL

CNSL can be polymerized by a variety of techniques. The unsaturation in the side chain can be the basis for addition polymerization using free radicals or ionic initiators (Mary & Thachil, 2001). Acids such as sulphuric acid (H_2SO_4) and hydrochloric acid (HCI) can

give polymeric products. The phenolic properties of CNSL are utilized to make condensation polymers by reaction with formaldehyde (Frechet *et.al*, 1994). These polymers are similar to the product of phenol and formaldehyde condensation but shows less reactivity during synthesis and later during cross linking. Both resole and novolac type resins can be made as shown in the structures below.

$R=C_{15}H_{31-n}$
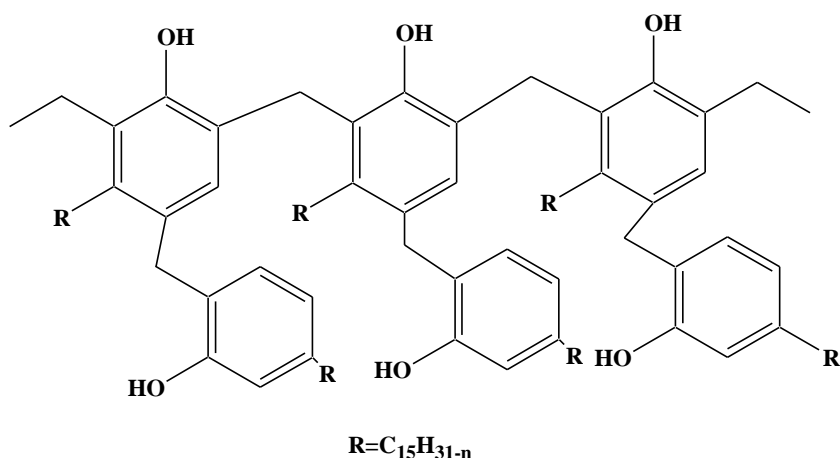
Chemical structure of Resole resin made from cardanol

In the presence of acid catalyst and with less formaldehyde, the resin has no reactive methylol groups and therefore is incapable of condensing with other molecules on heating in the absence of hardening agents. To complete resinification, more formaldehyde is added, resulting in cross linking. The final structure of the novolac product shown below, has also been given by (Tyman & Bruce, 2003).

$R=C_{15}H_{31-n}$
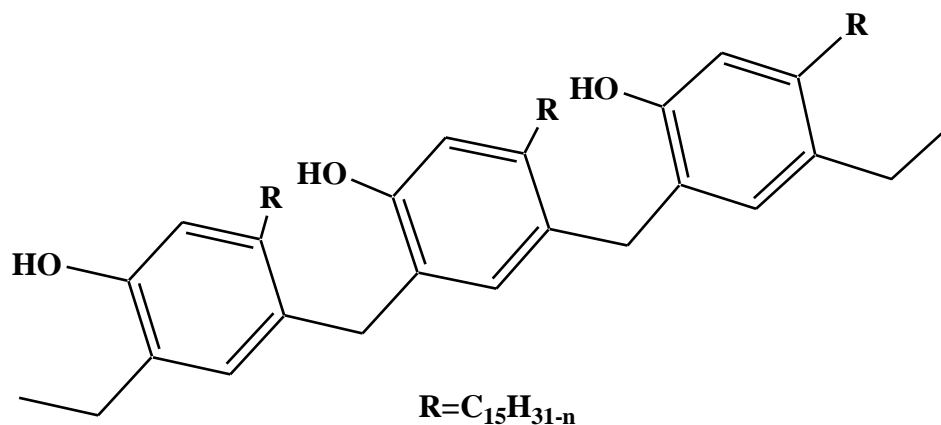
Chemical structure of Novolac resin made from cardanol

It is observed that condensation of CNSL takes place at one of the ortho positions and the para position of the phenolic ring. Condensation does not occur at the ortho position between the side chain and the OH group. The expected reaction scheme for the novolac product is given below (scheme 1.4). This is deduced by considering the final polymer structure and the reaction of phenol under similar conditions.
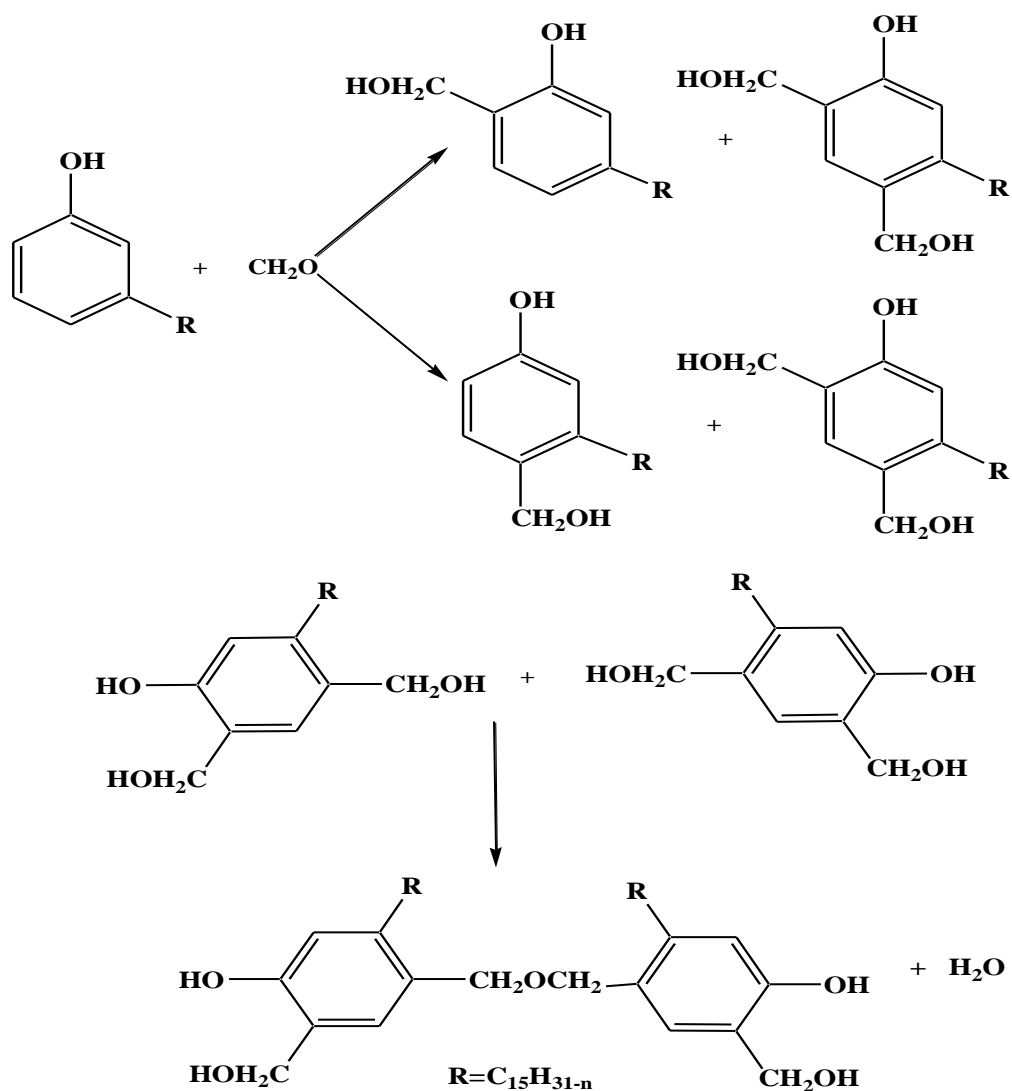
Scheme: 1.4: Polymerization scheme of CNSL using acid catalysts

The condensation in this case is more difficult because of the immiscibility of CNSL and formaldehyde (HCHO) layers and the steric hindrance caused by the lengthy side chain. Longer processing times are needed and the reaction product is a mushy, high viscosity substance, which tends to solidify at comparatively low degrees of polymerization. In certain applications, a preliminary step of polymerization through the side chain is done before condensation polymerization (Calo *et.al*, 2007).

When CNSL is heated to 200^0C or above, it undergoes polymerization. Cationic, anionic or oxidizing agents can accelerate the process. Alkalis can also be used as catalysts for the polymerization of CNSL by heat. The first step is usually the reaction of phenolic hydroxyl with the alkali, and the compound thus obtained acts as a catalyst for the polymerization. Mono or dialkyl sulphates in concentrations of about 2% have been used to polymerize CNSL at about 160^0C. The advantage of using alkyl sulphates is that metal present as impurities in CNSL are precipitated out during polymerization (Antony *et al.,* 1990).

1.13 Surface coatings

Surface coatings are mixtures of film-forming materials with or without pigments, solvents, and other additives, which, when applied to a surface and cured or dried, yield thin films that are functional and often decorative (Muturi, 1987). Surface coatings include paints, drying oils and varnishes, synthetic clear coatings, and other products whose primary function is to protect the surface of an object from the environment. These products can also enhance the aesthetic appeal of an object by accentuating its surface features or even by concealing them from view (Kurkarni *et al.,* 1964).

All coatings whether used for corrosion protection, to provide good aesthetics or a pleasing appearance, or for any other purpose will contain a film-forming material. This material may be organic or inorganic and, after application, may form a hard, impervious film, a soft porous film, or combinations in between. Furthermore, the film-forming material may be clear (unpigmented) or filled with a variety of different

pigments, which provide color, opacity, gloss, and other properties, depending on its function (Guionnet *et al*, 1999).

When the film-forming material (resin) contains pigments, it is called a binder. The binder will hold the pigment particles together and to the substrate over which it has been applied. When the binder (resin plus pigment) is dissolved in a solvent to make it liquid, the combination (solvent, binder, and pigment) is considered to be a vehicle. The term vehicle comes from the ability to transport and apply the liquid to the surface being coated. Once on the surface, the solvent evaporates and the vehicle becomes a pigment-binder system.

Application properties of the paint usually are characterized by the vehicle in a liquid condition. The viscosity, rate of solvent evaporation, and consistency of the wet coating are most important during application. After application, the pigments determine the corrosion-inhibitive properties and, generally, the color and some flow control properties of the applied coating. The binder determines the weather ability of the coating, its environmental resistance, and the coating's ability to function in a given environment. The required surface preparation, and often the application equipment and techniques, are determined by the binder (Thachil & Unnikrishnan, 2006).

Most surface coatings employed in industry and by consumers are based on synthetic polymers that is, industrially produced substances composed of extremely large, often interconnected molecules that form tough, flexible, adhesive films when applied to surfaces (Muturi, 1987).

1.13.1 Film-Forming Mechanisms

The principal mechanisms by which binders form films are reaction with oxygen from the air, evaporation of the solvent from the vehicle, or chemical cross linking. The coating film attained by these mechanisms can be either thermoplastic or thermosetting. Thermoplastic materials deform and soften on exposure to heat. Thermoset materials do not deform and remain hard upon heat exposure. Each type of coating resin or binder is categorized by; its film-forming mechanism, different types of pigments, and the various

solvent families. Drying oils are an integral part of some coating formulations, and they as well as driers aid in the drying reaction (Odin, 1991).

1.13.1.1 Oxidation and Chemically cross-linked (thermoset)

Thermoset coatings, by definition, are coatings that are "set," and are non-deformable when exposed to elevated temperatures. Thermoset coatings achieve their characteristic "set" and the ability to resist heat deformation by virtue of a three dimensional cross linking. This cross linking is achieved by co-reacting two or more monomers, with at least one monomer having a functionality of three or greater, and the other a functionality of at least two. This film-forming mechanism involves a chemical reaction combining monomers to create polymers. The reactions can consist of the same kind of monomer units reacting to form homopolymers or different monomer units reacting to form copolymers or tripolymers (Odin, 1991). After cross linking, and depending on the type and extent of cross linking, the resin system is solvent resistant, ranges from tough and flexible to hard and brittle, and does not significantly deform on the application of heat. Polymerization reactions are becoming increasingly important in the formulation of modern VOC-compliant coating systems (Mary & Thachil, 2003).

Thermoset coating dry and cross link by reaction with oxygen from the atmosphere. All such coatings in this class contain drying oils that consist mainly of polyunsaturated fatty acids. The drying oil frequently is combined with a resin, usually by cooking or heating to enhance water and chemical resistance. The curing reaction is accelerated by the presence of metallic salts as driers (Mary & Thachil, 2001). After application, the coating dries by solvent evaporation. However, to attain maximum chemical and moisture-resistance properties, the oil must react with oxygen from the air to cross link, cure, and further harden. The auto-oxidation reaction occurs at a relatively fast rate shortly after application of the wet paint and it continues throughout the life of the coating, although at a much slower rate (Ras *et al*, 2003).

1.13.1.2 Solvent evaporation (thermoplastic)

The solvent within which the resin is dissolved or emulsified may be water or an organic solvent. The liquid resin returns to a solid material when the solvent evaporates. The coating is formed as a result of solvent evaporation and drying, with no attendant cross linking or polymerization (Odin, 1991). Solvent-based coating systems that dry solely by solvent evaporation without chemical cross linking such as vinyls and chlorinated rubbers have their usage severely restricted because of VOC regulations. These resins must be dissolved in relatively high amounts of noncompliant solvents to be formulated into a corrosion-resistance protective coating. Principal coatings in this class are acrylic lattices, solvent cutbacks, and hot melt bituminous coatings and vinyl coatings (Frechet *et al*, 1994).

1.13.2 Binders/Resins

The binder, sometimes called a resin, and a suitable solvent are combined to form the vehicle. Pigment particles then are dispersed and mixed into the liquid resin, and the paint is packaged, usually in a can or pail, for sale. Upon use, the liquid paint is applied by brush, roller, or spray after which the solvent volatilizes, the liquid resin dries or cures, and the pigment particles "bind" together to the surface being painted. Binders may be natural or synthetic resins and may be organic or inorganic. The binder used in a particular coating system is primarily responsible for the coating's chemical, water, and UV light-resistant properties (Mary & Thachil, 2001).

1.13.3 Natural resins

Natural resins are derived from tree exudations, fossilized vegetable remains, or insect secretions. Natural resins generally are cooked with drying oils to make varnishes with faster drying rates, higher gloss, and harder films than can be attained from the oil alone. Some were used as a sole binder in so-called spirit varnishes, i.e., the resin was simply dissolved in volatile solvents. When applied to a surface, the solvent evaporated from the spirit varnish leaving a film of the resin on the substrate. This type of drying

mechanism involves no substantial chemical change and is typical of what today is called lacquer (Calo *et.al*, 2007).

1.13.4 Oil-based alkyds

Alkyd resins are derived as a reaction product of polyhydric alcohols and polybasic acids. Alkyds use a polybasic acid derived from semi-drying or drying oil so the resin formed can undergo auto-oxidation at any temperature. This definition also includes polyester resins, of which alkyds are a specific type. The properties of alkyd coatings predominantly are the result of the properties of the drying oil used in the manufacture of the alkyd resin. Drying time, hardness, color, and moisture sensitivity all depend on the drying oil, its type, and the degree of unsaturation. Alkyd coating systems should not be used in immersion or in environments in which the coating will be subjected to prolonged wetting, dampness, or condensing humidity (Knop & Pilato, 1985). Because drying oils are saponified by alkalies, they should not be applied to alkaline surfaces, including applications over galvanizing as a result of the alkaline nature of zinc hydroxide which is a corrosion product of zinc or concrete, mortar, and most cementitious surfaces as a result of inherent alkalinity because of the use of lime as a component of cement (Strong & Kock, 1974).

1.13.4.1 Alkyd modification

Alkyds are perhaps the most widely used industrial protective coating by virtue of their ease of application, relatively low cost, color stability, and good weather ability in most atmospheric environments; therefore coating formulators should seek to improve properties of the drying oil alkyd by modification with other resin types. Although these modifications somewhat increase the cost of the coating system, improved properties usually result and make the modification cost effective (Thachil & Unnikrishnan, 2006).

1.13.4.2 Phenolic modification

Modification with a phenolic resin improves gloss retention, water, and alkali resistance. Phenolic alkyd resins have performed satisfactorily in water immersion, a service in which non-phenolic modified alkyd resins are not suitable. (Mary & Thachil, 2003)

1.13.4.3 Methyl Methacrylate modification

Methyl Methacrylate monomer whose chemical structure is shown below, gives the hardest thermoplastic polymer, and acrylate monomers yield the softest product. Copolymers of acrylic and methacrylic esters are used extensively for exterior acrylic emulsion paints. Vinyl acetate acrylic copolymers also are popular, particularly for interior use. The acrylic constituent upgrades water and alkali resistance, film flexibility, and durability; and it act as a permanent plasticizer for the vinyl acetate (Fay *et al.,* 2004).
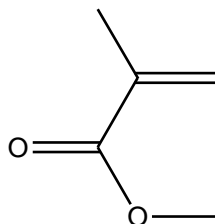
Chemical structure of Methyl Methacrylate

1.13.4.4 Styrene-acrylic modification

Styrene-acrylic waterborne systems in which the styrene whose chemical structure is shown below is copolymerized with lower alkylacrylates have gained in importance. They are characterized by high gloss and good gloss retention. When properly formulated, they dry quickly and develop good film hardness. Styrene acrylic systems are used primarily as interior house paints or as coatings for relatively mild interior industrial service conditions. These coatings may yellow on exterior exposure and do not have good moisture resistance. They are used as concrete block fillers (Mary & Thachil, 2003).
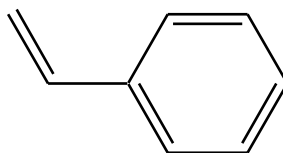
Chemical structure of styrene

25

1.13.5 Driers

Driers are materials that promote or accelerate the curing or hardening of drying oil paints (Strong & Kock, 1974). Drying of oil-based paints by auto-oxidation is affected considerably by temperature and the presence of certain catalysts. Driers act as a catalyst to aid in both surface and through drying of drying oil paints. Driers are considered metallo-organic materials that can be classified as surface driers and through driers (Gibbon & Pain, 1981). The metal constituent is lead, cobalt, zinc, or manganese; the organic radical of the metallo-organic drier is usually a naphthenate derived from naphthenic acid. Surface driers are compounds of cobalt and manganese. The use of these materials will cause a surface of the drying oil paint to rapidly set to a near solid, but the underlying paint does not reach this advanced state of oxidation. In thick films an uneven hardening will cause wrinkling; therefore, through driers should be used in conjunction with surface driers. Through driers are metallo-organic compounds of lead, cadmium, zinc, or zirconium. When used in conjunction with surface driers, through driers help cause auto-oxidative cross linking through the cross-section of the film.

1.13.6 Drying Oils

An oil is classified as drying oil if its iodine value is greater than 140 mg iodine/100g and when if spread out in the air as a thin layer, it changes from a liquid to a solid film with a great strength, toughness, and hardness (Strong & Kock, 1974). If a drying oil is reduced or dissolved in a solvent and pigmented, a drying oil coating results. Not all oils are drying oils. The drying ability depends on the molecular structure of the various chemical compounds that make up the oil. Specifically, the oil must have polyunsaturated fatty acids, commonly ethylene carbon double bonds. When combined with oxygen and accelerated by metallic driers, auto-oxidative polymerization occurs and transforms the oil from a liquid to a solid (Knop & Pilato, 1985).

Fatty vegetable oils that exhibit proper drying oil characteristics can be formulated into paints or protective coatings. Linseed oil is one of the most widely used drying oils obtained from pressing the flax seed. Raw linseed oils dry too slowly for most purposes; therefore, they require processing and the addition of driers to hasten the hardening rate

(Gibbon & Pain, 1981). CNSL has its iodine value above 140 mg iodine/100g which is an indication that it is highly unsaturated and therefore can be applied in the production of surface coatings among other applications thereby adding value to otherwise waste material.

1.13.7 Solvents

A solvent is defined as a substance, usually a liquid, which will dissolve and change a solid to a solution. In the coating industry, solvents are considered any volatile liquid formulated into paint, even though it may not have solvency power (Mary & Thachil, 2001). Some liquids are diluents and, even though the diluent may not have solvency power, it may enhance the solvency of other solvents in the paint. Water is the universal solvent, except for its use as a dispersant in emulsion coatings, but it is not used as a paint solvent in durable coatings. Organic solvents impart low water sensitivity and are the solvents of choice when dissolving solid resins (Mary & Thachil, 2003).

The purpose of any solvent in paint industry is to dissolve solid paint constituents, reduce viscosity, and render the paint fluid enough that it can be satisfactorily applied. The solvent is undesirable after application and must evaporate from the drying coating film. In addition to enabling application of the coating material, solvents must be able to wet the substrate being coated and penetrate into and help the coating seal any crevices, voids, or depressed irregularities. Also, the solvent must volatilize fast enough to prevent runs and sags in the drying coating film. However, a solvent that is too volatile can cause solvent pops, loss of gloss, dry spray, poor surface wetting and penetration, and poor film flow and inhibit cure (Thachil & Unnikrishnan, 2006). Virtually all coating formulations use a blend of solvents to achieve optimum properties. Some solvents within the blend will evaporate fast, enabling the drying paint to set quickly. Other solvents may dry slower and provide wettability and penetrability. Ultimately, all solvents should evaporate to allow the coating to achieve hardness, cure, and final properties. Solvents can be categorized according to their chemical composition. The most commonly used categorization subdivides solvents into classes called turpentine, hydrocarbons, ketones, esters, alcohols, and glycol ethers.

1.13.7.1 Hydrocarbon solvents

Hydrocarbon solvents are obtained from both petroleum and coal tar sources. Petroleum hydrocarbon solvents are the lighter and more volatile fractions from the distillation of crude oil. Coal tar hydrocarbons are distillation products from coke oven byproducts. Hydrocarbon solvents may be classified as aliphatic or aromatic. Aliphatic hydrocarbons are straight or cyclical carbon-hydrogen containing liquids that are nonpolar in character and exemplified by mineral spirits, "varnish makers and painters" (VMP) naphtha, and other materials such as hexane and heptane. For the most part, these solvents have poor to moderate solvency for all but oil-modified coatings. Their solvency can be increased by blending them with various amounts of other, more powerful solvents such as aromatic hydrocarbons or ketones. Aliphatic hydrocarbons are generally the least expensive of all solvents and can be obtained in a wide range of evaporating rates. Aliphatic solvents are considered the least toxic of any of the solvent classes, although as with any other solvent; gloves, respirators, and protective clothing should be used by individuals applying paints containing these solvents. Naphthenic hydrocarbons are aliphatic hydrocarbon solvents, but with a cyclical ring molecular structure. The naphthenic solvents are midway between the aliphatic and aromatic solvents in solvency power. Naphthenic solvents are used in alkyd and epoxy ester coatings and asphaltic and coal tar-containing coatings (Mary & Thachil, 2001).

1.13.8 Coatings made from CNSL and its derivatives

CNSL and its products have a significant role to play in surface coating development; it is renewable and thus offers much advantage over synthetic materials (Mary & Thachil, 2003). The preparations of polymer materials by emulsion, suspension or solution polymerization and other techniques follow well-known procedures (Billmeyer, 1984), which have been developed through many years of extensive research. Petrochemical and natural products are the principle sources of monomers used in polymerizations. While petrochemicals cannot be sustained as they become either expensive or highly depleted leading to economic and environmental problems, natural products are renewable. Thus, it is necessary for the polymer industry to look for renewable monomer

sources and CNSL is one of the natural products that have both unsaturated hydrocarbon and phenols compounds which may serve as a supplement monomer resource in the polymer industry. CNSL is branded as natural or technical depending on the method of extraction. The former is obtained by solvent extraction while the latter by thermal extraction. CNSL can take part in ether linkage (Gedam & Sampathkumaran, 1986), usually in an alkaline medium forming useful compounds such as ethyl ether cardanol and cardanoxy acetic acid (Scheme 1.5), both of which have wide applications in the manufacture of paints, binders, varnishes and many other products (Lomonaco *et al.*, 2009).
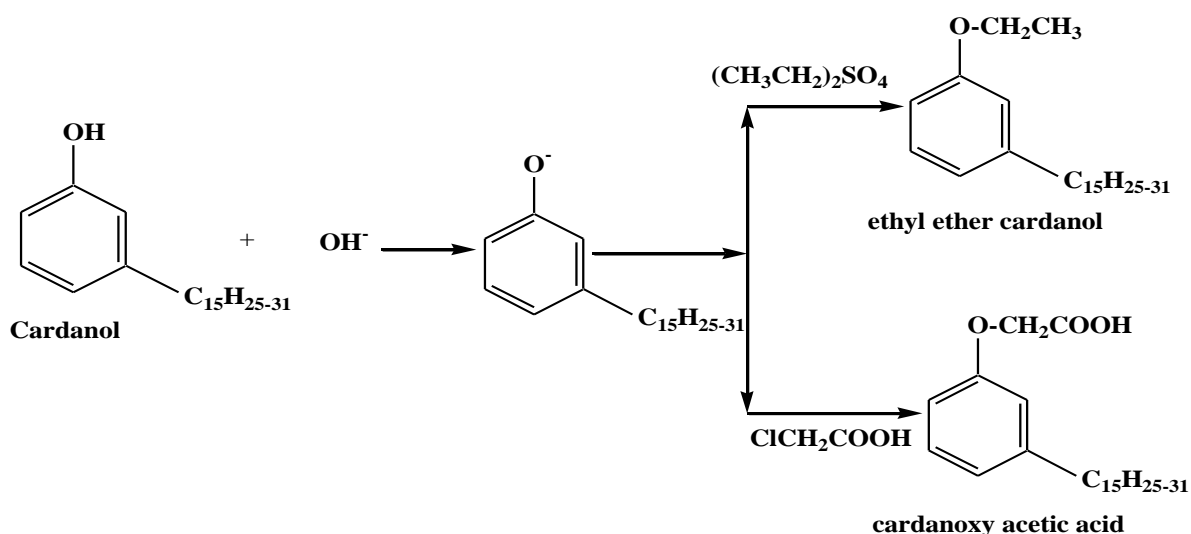
Scheme: 1.5: Formation of CNSL Ether Linkage, (Gedam & Sampathkumaran, 1986)

The coatings developed from CNSL and its derivatives have many advantages such as; improved flexibility, reduced brittleness, good electrical resistance, better water repellence, improved alkali and acid resistance, compatibility with other polymers, termite and insect resistance (Mahanwar & Kale, 1996).

CHAPTER TWO

2.0 MATERIALS AND METHODS

2.1 Study area

The cashew nut shells were collected from the Kenya Nut Company located in Thika town 40 Km from Nairobi City. The dry shells are by-products, and are stored in the company`s warehouse (Plate 2.1). The dry shells are used as fuel in boilers to generate steam used in processing the nuts. The shells were sampled and brought to the laboratory in gunny bags and stored at room temperature and room pressure in a metallic drum. All organic solvents and chemicals used in the analysis were procured from Kobian Kenya Limited. The reagents used were both analytical and general purpose grade.

Plate 2.1: Cashew nut shells at the factory warehouse

2.2 Sample preparation and extraction of cashew nut shell liquid

The shells were milled using a disintegrator plant mill, Nogueira Make, Model No: DPM-4 (Plate 2.2). Solvent extraction method (Muturi & Arunga, 1988) was used to extract CNSL from the ground shells using *n*-hexane as the solvent. A volume of 2.5 L of n-Hexane were employed per 750 grams of shells. The mixture was stirred to ensure the release of air and proper contact between the solvent and the shells and was left to stand for a period of 24 hours. The solvent was used to extract CNSL from 3 batches of ground shells resulting into a CNSL rich solvent known as miscella. The miscella was decanted from the shells and left overnight to settle out the very fine particles, followed by filtration using a Buchner funnel and vacuum pump. The solvent (n-Hexane, boiling

point 65ºC) was distilled off and recovered for re-use using a Buchi rotavapor, Model No: R 200 (Appendix 4). The weight of CNSL was determined and recorded. The residual CNSL was heated to temperatures ranging from (135ºC-140ºC) for one hour or until the frothing stops at the oil surface to allow for the decarboxylation of anacardic acid (Scheme 1.2).

Plate 2.2: Disintegrator plant mill

2.3 Formulation of coatings

The method described by Muturi (1984) was adopted for production of the coatings. Hundred (100) grams of decarboxylated CNSL were weighed and heated to about 70ºC, 90ºC, and 110ºC respectively using a magnetic stirrer for 30 min, 60min and 90min respectively with 1.0g of concentrated sulphuric acid and 3.0 g of distilled water. Three replications were done at each temperature in order to increase the precision of the results. The mixture was cooled to about 40ºC after which 150 g of white spirit was added and refluxed for one hour at 60ºC. After refluxing, 25 g of 40% aqueous solution of formaldehyde was added followed by addition of driers consisting of 1.0 g of Lead naphthenate (32%) and 0.6 g of cobalt naphthenate (30%). The coating formulations formed were left to stand for one day to ensure completion of the reaction. Physico-chemical tests were then carried out to determine the average pH, specific gravity and viscosity.

31

2.4 Cross linking of CNSL based coatings with styrene and MMA monomers

The CNSL coating formulated at the optimum conditions of temperature and heating time was cross linked using two monomers; Styrene and Methyl Methacrylate (MMA). The method described by Muturi (1984) was adopted for the production of the CNSL based surface coatings, with few modifications as described above. The optimum conditions of temperature at $70^{o}C$ and heating time of 60 minutes was employed. Three formulations were made for each monomer at different mole ratios based on the weight of the CNSL Coating, Styrene and MMA. These ratios were; CNSL Coating: Monomer; 1:3, 1:6 and 1:12, which were coded as follow;

Styrene: CNSL ratio 12:1 was coded as SCNSL3, Styrene: CNSL ratio 6:1 was coded as SCNSL2, Styrene: CNSL ratio 3:1 was coded as SCNSL1, MMA: CNSL ratio 12:1 was coded as MCNSL3, MMA: CNSL ratio 6:1 was coded as MCNSL2, MMA: CNSL ratio 3:1 was coded as MCNSL1

The CNSL based coating formulation was weighed into a beaker and heated to the optimum temperature using a hot plate, this time an iniator; 1 % lauryl peroxide was added followed by the addition of weighed monomer as per the mole ratio, each of these formulations was heated on a hot plate for an optimum time of 60 minutes and temperature of $70^{o}C$ while stirring using a magnetic stirrer. After 60 minutes (1 hour) had elapsed, the cross linked coating formulation was allowed to cool and stand for one day to ensure completion of the reaction. Performance tests were then carried out to determine the hardness, adhesion, drying time and iodine value.

2.5 Determination of moisture content using Dean and Stark apparatus

The recommended method of the Association of Official Analytical Chemists (AOAC, 1990) was adopted in determining the levels of moisture content. The sample of 100 ml and 100 ml of petroleum spirit were mixed in a round bottomed flask and fitted with the Dean and Stark apparatus (Plate 2.3).

Plate 2.3: Dean and Stark apparatus for determining the moisture content

2.6 Determination of viscosity using capillary viscometer

The viscosity of the sample was determined using capillary viscometer (appendix 3). (Eromosele & Paschal, 2002). The water bath was set at 40^0C and the capillary viscometer was mounted on a clamp and inserted in the water bath. Ten milliliters (10 mls) of distilled water was measured and put in the viscometer using a pipette and allowed to warm up to 40 ^{0}C. On the other end of the viscometer, pipette filler was inserted and allowed to suck the water to the mark. A stop watch was started at the point the water was at the upper mark and allowed to run till the water touched the lower mark on the viscometer. The time duration was taken and recorded in triplicates. Similar procedure was done but now with the samples instead of water. The viscosity was calculated from the formula given below:

$$\text{Viscosity} = \frac{\text{time (seconds) of sample} \times \text{dynamic viscosity of water at } 40^{\circ}\text{C}}{\text{time (seconds) of water}}$$

The dynamic viscosity for water at 40^0C=**0.65**

2.7 Determination of iodine value

Iodine value was obtained by the method of (Strong & Kock, 1974). In this method, 0.5 grams of sample was weighed in a 250 ml glass stoppered flask and dissolved in 10 ml of chloroform, a similar amount of chloroform was added to a similar conical flask containing no sample (blank). A volume of 25 ml of the Wij´s solution was added into the flask containing the sample and an equal volume into the blank. Each flask was shaken vigorously and allowed to stand in dark for half an hour. The solutions in each flask were diluted with 70 ml of water and 25 ml of 10 % KI solution. The solutions were titrated using standard 0.1 M sodium thiosulphate solutions. Two to three drops of Starch solution indicator were added when the yellow colour nearly disappeared by the addition of the thiosulphate. The solution was titrated up to the end point when the blue colour formed by addition of starch had finally disappeared. This procedure was repeated in triplicates for each sample. The iodine value was calculated from the formula shown below:

$$\text{Iodine value} = \frac{(a-b) \times c \times 12.692}{d}$$

where, a = mls of thiosulphate required by blank

b = mls of thiosulphate required by sample

c = Molarity of thiosulphate

d = weight of sample

2.8 Determination of Relative Density at 30^{0}C

The weight of empty pycnometer was determined using the analytical balance and recorded, the pycnometer was then filled with distilled water and the weight determined using the analytical balance. The samples were put into a dry pycnometer and the weight determined using the analytical balance. This procedure was repeated in triplicates for each sample. The relative density of the sample was obtained using a pycnometer at 30 ºC and calculated from the formula given below (AOAC, 1990).

$$\text{Relative Density} = \frac{e - f}{g - f}$$

$$\text{where, } e = \text{weight of pycnometer with sample}$$
$$f = \text{weight of empty pycnometer}$$
$$g = \text{weight of pycnometer with water}$$

2.9 Determination of pH

A pH meter of Combo Gro´check make from Hanna Instruments, Model No HI991404 was calibrated using buffer 4 and 7 and used to determine the pH of the samples. pH was then measured by inserting the probe of the pH meter into the sample and three values taken. (Atkins & Julio, 2006).

2.10 FTIR analysis

FTIR spectra were determined using a Shimadzu Model 8400 Spectrophotometer. A small quantity of the sample was smeared on a KBr plates and ran in an FTIR machine where various peaks were recorded. (Coates, 1996).

2.11 Determination of acid value

A weight of 1.3 gram of the sample was accurately measured into a 250 ml conical flask. A volume of 25 ml of diethyl ether and 25 ml of ethanol were mixed and introduced into the conical flask and three drops of phenolphthalein indicator added. The solution was shaken so that the fatty acids present in the oil dissolved. This solution was titrated with 0.1M aqueous KOH while shaking. This procedure was repeated for other samples in triplicates (Devine & Williams 1961).

2.12 Performance tests- Film Characterization

The coated panels were examined for adhesion test, pencil hardness, and drying time by standard methods. The mild steel panels were first degreased in alkali solution and subsequently swabbed with xylene to remove any type of oily material or contaminant. After the xylene has evaporated, panels were burnished with emery paper as per Indian Standards (Patel & Naji, 2010). Panels were again washed with xylene after burnishing to remove any trace of emery paper particles or metal particles. As soon as the panels were dry, coatings were applied on them using Bird Film Applicator (002) without any delay.

2.12.1 Adhesion test

Adhesion of films to substrate was determined by employing cross-hatch adhesion test according modified method from ASTM D-3359. Cross hatch adhesion test was carried out on dry film by using a Cross hatch cutter (Appendix 1), 10 parallel lines 1mm apart from each other were cut on the film. Another set of such lines at right angles to previous lines was superimposed to give a pattern of squares consisting of 100 squares with each square having 1 mm side length. The film was then brushed lightly using a soft brush to remove any detached flakes of coatings. An illuminated magnifier was used to aid in the inspection of the grid area for removal of coating from the substrate. The adhesion results were rated in accordance with the ASTM classification (Table 2.1).

Table 2.1: ASTM Classification for Adhesion Test

Classification	% of area removed	Remarks	Ratings
5B	0% none	Excellent	5
4B	Less than 5%	Very Good	4
3B	5-15%	Good	3
2B	15-35%	Fair	2
1B	35-65%	Poor	1
0B	Greater than 65%	Very poor	0

2.12.2 Pencil scratch hardness test

Pencils of various degrees of hardness are moved over the surface under a fixed pressure and angle to the surface (Plate 2.4). The degree of hardness of the pencil which damages the surface is taken as a measurement of scratch hardness (Table 2.2). In this method which complies with ASTM D3363 IS 101, pencils having different hardness were used. The pencil having hardness ranging from 6B (soft) to 6H (hard) were prepared by hand rubbing it on fine abrasive paper. The pencil was held approximately at an angle of 45° to the film and with uniform pressure pulled down over the length of the film (Appendix 2). The test was repeated till a pencil with specific hardness was able to cause either superficial trace or causing destruction down to the substrate. The hardness of that pencil was then reported as the hardness of coating.

Plate 2.4: Pencil Hardness Tester

Table 2.2: ASTM Classification for Pencil Scratch Hardness Test

Pencil type	Classification	Ratings
6H	Hard	2
5H	Hard	2
4H	Hard	2
3H	Hard	2
2H	Hard	2
H	Hard	2
F	Hard	2
HB	Soft	1
B	Soft	1
2B	Soft	1
3B	Soft	1
4B	Soft	1
5B	Soft	1
6B	Soft	1

2.12.3 Drying time

The coating sample was applied to the test panels using a Gardco Microm Film applicator supplied by Gardner Company. Immediately the drying time recorder (Plate 2.5) was placed on the test panel and the clean 0.9525 cm weighted teflon stylus was lowered gently into position. The desired drying time was selected, then the drying time recorder was switched on and the stylus begun to be drawn along the test panel. After the selected time cycle was complete, the drying time recorder stopped automatically. The test panel was evaluated using the supplied time template to determine the stages of drying time. A clear time template was placed over the circular area scribed by stylus and appropriate scale number of minutes or hours required for the film to cure was noted, this procedure was repeated for other samples in triplicates. The character of the track by the 0.9525 cm teflon ball stylus relate to the drying of the film (ASTM D-5895). The results obtained were recorded alongside the room temperature because temperature is an important factor that affect the drying time of films.

Plate 2.5: Drying time recorder

2.13 Data analysis and presentation

All tests were carried out in triplicates and the results obtained expressed as Mean ± standard deviation. The data generated during the research was stored in excel worksheet and represented as bar charts for comparison purpose. Both physico-chemical characteristics and performance characteristics data obtained were compared with standards and conclusions were drawn.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

3.1 Extraction Yield

The cashew nut shell comprises about 50% of the weight of the raw nut, the kernel represents about 25% and the remaining 25% consists of the natural CNSL (Tyman, 1979). The average percentage yield obtained in this work (21.203±0.387%) was slightly less than the theoretical yield of CNSL and the shortfall was attributed to the oozing out of some CNSL to the floor during storage at the factory (Plate 2.1).

3.2 Physico-chemical characteristics of CNSL and decarboxylated CNSL

The physico-chemical characteristics of cashew nut shell liquid are presented in (Table 3.1). The oil extracted from the cashew nut shell was dark brown in color which compared well to the Indian Standards. The relative density was found to be 0.9995 ± 0.003kg/m^3, which indicated that the CNSL was less dense than water. It was found to be a viscous liquid with viscosity value of 160.71±0.02 Centipoises. Moisture content of CNSL was found to 0.55%. This value was comparable to both the Indian and Brazilian standards as reported by Bola Raghavendra Kanath and Sons (2003) and Amber wood Trading Ltd. (2003). The low moisture was an indication that the oils could have longer shelf life. The iodine value was high at 211.703±0.001 mg iodine/100g which was above (>140 mg iodine/100g) specified as drying oils (Strong & Kock, 1974). The high iodine value was an indication that the oil contained high degree of unsaturation therefore, it could be classified as drying oil and could find application in paints, varnishes and surface coatings. The total acidity expressed as the acid value takes into account the contribution of all the constituent fatty acids in the oil (Ekpa & Ekpe, 1995). This is a quality control parameter employed by paint manufacturers to monitor the concentration of acids in resins. The pH of CNSL was found to be 6.09±0.02 and compared well with both the Indian and Brazilian standards (Table 1.1).

Table 3.1: Physico-Chemical characteristics of raw CNSL

Parameter	Range of values[1]
Appearance	Dark brown liquid
Nature	Viscous liquid
Relative density (kg/m^3)	0.9995±0.003
Viscosity at 40°C (Cp)	160.71±0.02
Iodine value (mg iodine/100g)	211.703±0.001
Moisture content (%)	0.55±0.05
Acid value, g/100 g KOH	12.64±0.01
pH at 25°C	6.09±0.02

Sources: [1] Results obtained for raw CNSL

The result of relative density of raw CNSL and decarboxylated CNSL did not compare (Table 3.2). CNSL has a high relative density because it has anacardic acid as the major fraction. There is intermolecular attraction between the electronegative oxygen atom and the partially positive hydrogen atom of the phenol core; as a result the molecules are closely packed together. A large mass occupies the same volume of the density bottle and hence a high relative density. The decrease in relative density in decarboxylated CNSL is due to the release of carbon dioxide gas from anacardic acid during decarboxylation, which has a smaller relative density than the raw CNSL. The molecules

are not closely packed together as there are no strong dipole-dipole attractions. The viscosity values of the raw CNSL and decarboxylated CNSL did not compare (Table 3.2). The raw CNSL has the –COOH group in the ortho position of the phenol core and therefore there is strong dipole–dipole attraction between the partially positive charged hydrogen atom and the strong electronegative oxygen atom resulting in the formation of intramolecular hydrogen bonding which makes the molecule to be entangled together as it flows down the capillary tube as a result the shear rate increases and thus a high viscosity in the raw CNSL as compared to decarboxylated CNSL.

There was no comparison in the moisture content of the raw CNSL and decarboxylated CNSL as shown in (Table 3.2). This is because decarboxylation process requires high temperature of 140 ^oC, at this elevated temperatures water undergoes evaporation. The iodine values of raw CNSL compared well with that of the decarboxylated CNSL because both had iodine value greater than 140 mg iodine/100g which is an indication that the oil contained high degree of unsaturation (Strong & Kock, 1974), as shown in (Table 3.2). The acid values of raw CNSL did not compare with the values obtained for the decarboxylated CNSL. According to Mahanwar and Kale (1996), raw CNSL that has an acid value >10 was not suitable for resin production, because it will produce a viscous liquid with very low resin content. The high acid value causes an acid-alkaline reaction with an alkaline catalyst, in the formation of resol from cardanol. The pH value shows that the raw CNSL was acidic due to the fact that the anacardic acid content in the liquid was very dominant, however, heating the raw CNSL decomposed the anacardic acid into cardanol and carbon dioxide (Scheme 1.2). The pH for the decarboxylated CNSL was found to be 6.29±0.03, this value compared closely with the pH of cardanol at 6.16 as reported by Akinhanmi *et al.,* (2008) (Table1.2 and Table 3.2). Decarboxylation process converts all the anacardic acid (82%) to cardanol, initially at (1.6%) to a total of (83.6%) by the pyrolysis of the –COOH group. In this project decarboxylated CNSL was used to develop surface coatings, because of its desirable qualities, especially the low acidity and high iodine value as compared to the raw CNSL (Table 3.2).

Table 3.2: Comparison of the Physico-Chemical Characteristics of decarboxylated

CNSL and Raw CNSL

Parameter	Decarboxylated CNSL	Raw CNSL
Color	Brown liquid	Dark brown liquid
Relative density at 25^oC, kg/ m^3	0.965±0.005	0.9995±0.003
Viscosity at 40^oC, cps	46.56±0.06	160.71±0.02
Acid value, g/100 g KOH	1.73±0.02	12.64±0.01
Iodine value, mg/100 g	231.2±1.1	211.703±0.001
pH at 25^oC	6.29±0.03	6.09±0.02
Moisture content (%)	Negligible	0.55±0.05

3.3 FTIR Spectrum of CNSL

Interpretation of infrared spectra was done by referring to a correlation map for identification of groups in the infrared spectra. Area between $\bar{\upsilon}_{max}$ 1400-4000 cm^{-1}, the left side of the spectrum, is an area particularly useful for identification of functional groups. This area indicated absorptions that are caused by the extension modes. Areas to the right of $\bar{\upsilon}_{max}$ 1400 cm^{-1} have the extension mode or the bent up which causes simultaneous absorptions. In this area usually correlation between a band and a specific functional group cannot be drawn accurately, although each organic compound has a unique absorption in the particular area (Fessenden & Fessenden 1991; Young 1996).

Aromatic compounds show useful characteristic infrared bands in five regions of the mid-infrared spectrum. The C–H stretching bands of aromatic compounds appear in the $\bar{\upsilon}_{max}$ 3100–3000 cm^{-1} range, so making them easy to differentiate from those produced by aliphatic C–H groups which appear below $\bar{\upsilon}_{max}$ 3000 cm^{-1} (Barbara, 2004). In the

$\bar{\upsilon}_{max}$ 2000–1700 cm^{-1} region, a series of weak combination and overtone bands appear and the pattern of the overtone bands reflects the substitution pattern of the benzene ring. Skeletal vibrations, representing C=C stretching, absorb in the $\bar{\upsilon}_{max}$ 1650–1430 cm^{-1} range. The C–H bending bands appear in the regions $\bar{\upsilon}_{max}$ 1275–1000 cm^{-1} (in-plane bending) and $\bar{\upsilon}_{max}$ 900–690 cm^{-1} (out-of plane bending). The bands of the out-of-plane bending vibrations of aromatic compounds are strong and characteristic of the number of hydrogen in the ring, and hence can be used to give the substitution pattern (Barbara, 2004).

The FTIR spectrum of CNSL (Figure 3.1) had absorption bands in $\bar{\upsilon}_{max}$ 4000-500 cm^{-1} areas. The peak of absorption of C-H stretch that indicated an aromatic compound appeared at a $\bar{\upsilon}_{max}$ 3008.7 cm^{-1} frequency. The peak that appears at frequency of $\bar{\upsilon}_{max}$ 2923.9 cm^{-1} indicated the presence of Methylene C-H symmetrical stretch of long aliphatic chains of the phenolic compounds. The spectrum appearing at $\bar{\upsilon}_{max}$ 2596.0 cm^{-1} indicated O-H stretch of the carboxylic acid (Coates, 1996). The C=O symmetrical stretch of the carboxylic acid showed the absorption peak appearing at $\bar{\upsilon}_{max}$ 1647.1 cm^{-1}, while the peak that appeared in the $\bar{\upsilon}_{max}$ 1450.4 cm^{-1} frequency indicated the Methylene C-H bend for long aliphatic chains (Table 3.3).
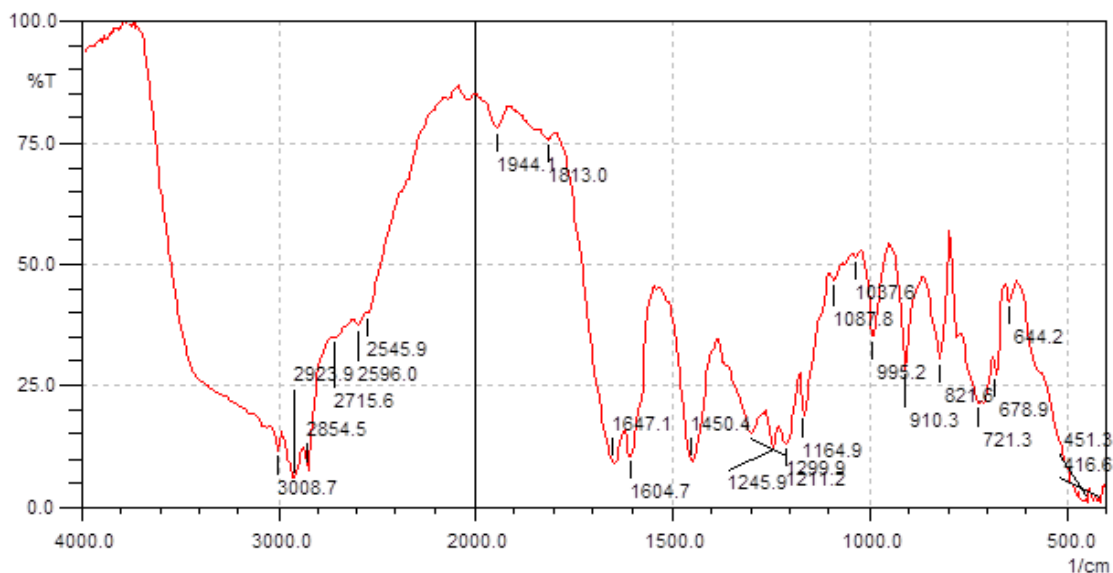
Figure 3.1: FTIR spectrum of raw CNSL

The FTIR interpretation for the raw CNSL spectrum is summarized in Table3.3, below;

Table 3.3: Interpretation of FTIR spectrum for raw CNSL

Frequency ($\bar{\upsilon}_{max}$)	Interpretation
3008.7 cm^{-1}	C-H stretch , Aromatic
2923.9 cm^{-1}	Methylene C-H symmetrical stretch, long aliphatic chain.
2596.0 cm^{-1}	O-H stretch, carboxylic acid
1647.1 cm^{-1}	C=O symmetrical stretch, Carboxylic acid
1450.4 cm^{-1}	Methylene C-H bends; long aliphatic chain.

The FTIR spectrum of decarboxylated CNSL (Figure 3.2) had absorption bands in $\bar{\upsilon}_{max}$ 4000-500 cm^{-1} areas. The peak of absorption of OH group that indicated phenolic compounds appeared at a $\bar{\upsilon}_{max}$ 3332.8 cm^{-1} frequency. The peak that appeared at frequency of $\bar{\upsilon}_{max}$ 3008.7 cm^{-1} indicated the presence of C-H stretch of the aromatic compounds (Barbara, 2004). The spectrum appearing at $\bar{\upsilon}_{max}$ 2923.9 cm^{-1} indicated a methylene C-H symmetrical stretch of long aliphatic chain. The C=C stretch of the conjugated aliphatic chains has the absorption peak appearing at $\bar{\upsilon}_{max}$ 1604.7 cm^{-1}, while the peak that appeared in the $\bar{\upsilon}_{max}$ 1454.2 cm^{-1} frequency (Table 3.4) indicated the C=C-C stretch of the aromatic ring (Barbara, 2004).
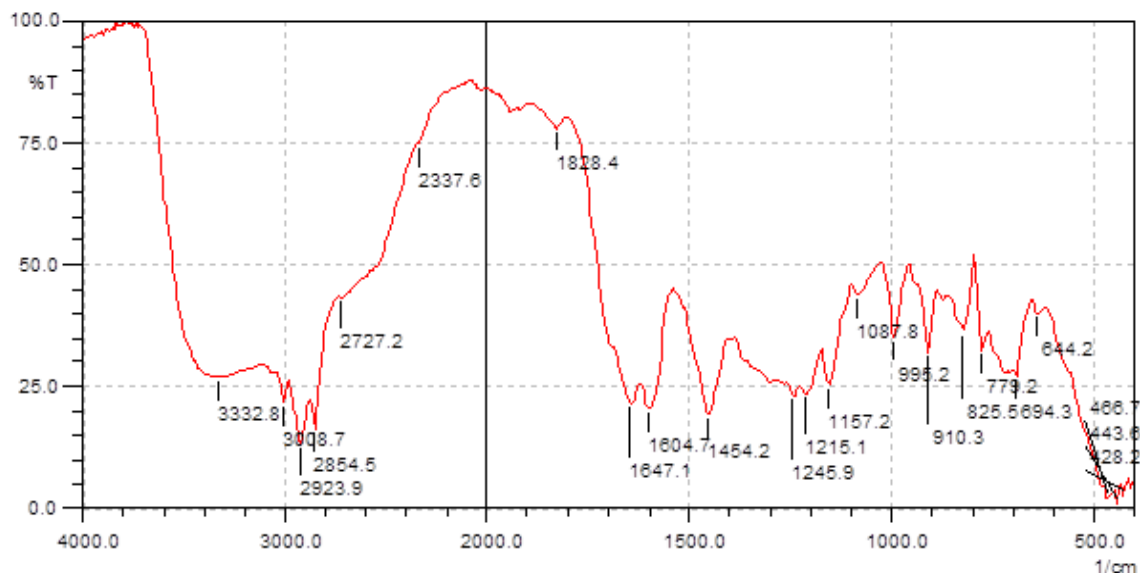
Figure 3.2: FTIR spectrum of decarboxylated CNSL

The FTIR interpretation for the decarboxylated CNSL spectrum is summarized in Table 3.4, below;

Table 3.4: Interpretation of FTIR spectrum for decarboxylated CNSL

Frequency ($\bar{\upsilon}_{max}$)	Interpretation
3332.8 cm^{-1}	O-H stretch, phenolic
3008. 7cm^{-1}	C-H stretch , Aromatic
2923.9 cm^{-1}	Methylene C-H symmetrical stretch, long aliphatic chain
1604.7 cm^{-1}	C=C stretch, conjugated aliphatic chain
1454.2cm^{-1}	C=C-C stretch, aromatic ring

From the FTIR analysis it was established that decarboxylation of CNSL was successful because both the O-H stretch and C=O symmetrical stretch of the Carboxylic acid having absorption spectra at, $\bar{\upsilon}_{max}$ 2596.0 cm^{-1} and $\bar{\upsilon}_{max}$ 1647.1 cm^{-1} frequencies, respectively had been cleared (Figure 3.2).

3.4 Optimization of temperature and heating time for the preparation of CNSL based surface coatings

The physico-chemical characteristics of CNSL based surface coating are presented in (Table 3.5). The CNSL based surface coatings were prepared at three different temperatures; 70°C, 90°C and 110°C at three different heating times for each temperature; 30, 60 and 90 minutes respectively. A conventional surface coating product from the market was used as a Standard. The physico-chemical characteristics of standard coating and those of the samples were determined and compared. These results were used to find out the best conditions of temperature and heating time that produced a formulation that does not have significant difference with the standard coating, these were the optimum conditions.

Table 3.5: Physico-chemical characteristics of CNSL- based surface coating

Formulation Temperature (^{o}C)	Time (Mins)	Relative density (kg/m^3)	pH at 25°C	Viscosity (Cp)	Iodine value (mg iodine/100g)
Formulation at 70	30	0.8783±0.006	6.275±0.04	7.472±0.001	171.09±0.006
	60	0.8704±0.004	6.305±0.02	7.8295±0.04	162.97±0.01
	90	0.8703±0.003	6.35±0.07	7.523±0.03	160.94±0.03
Formulation at 90	30	0.8681±0.003	5.895±0.007	5.3785±0.05	163.22±0.01
	60	0.8652±0.004	6.07±0.14	7.2305±0.001	153.83±0.02
	90	0.8658±0.001	6.04±0.08	7.8955±0.01	146.97±0.007
Formulation at110	30	0.8691±0.004	6.00±0.01	7.467±0.002	173.63±0.02
	60	0.8659±0.004	6.035±0.21	6.9935±0.13	167.79±0.01
	90	0.8687±0.007	6.02±0.04	7.236±0.15	141.89±0.01
Standard Formulation		0.9294±0.002	7.01±0.02	156.21±0.03	162.90±0.02

3.4.1 Relative density of the CNSL- based surface coatings

The relative density for all the formulations was lower compared to the standard, which indicates that the formulations were less dense than the standard. However, formulation made at the temperature of 70 ^{o}C and heating time of 30 minutes gave better relative density compared to the other formulations (Figure 3.3).
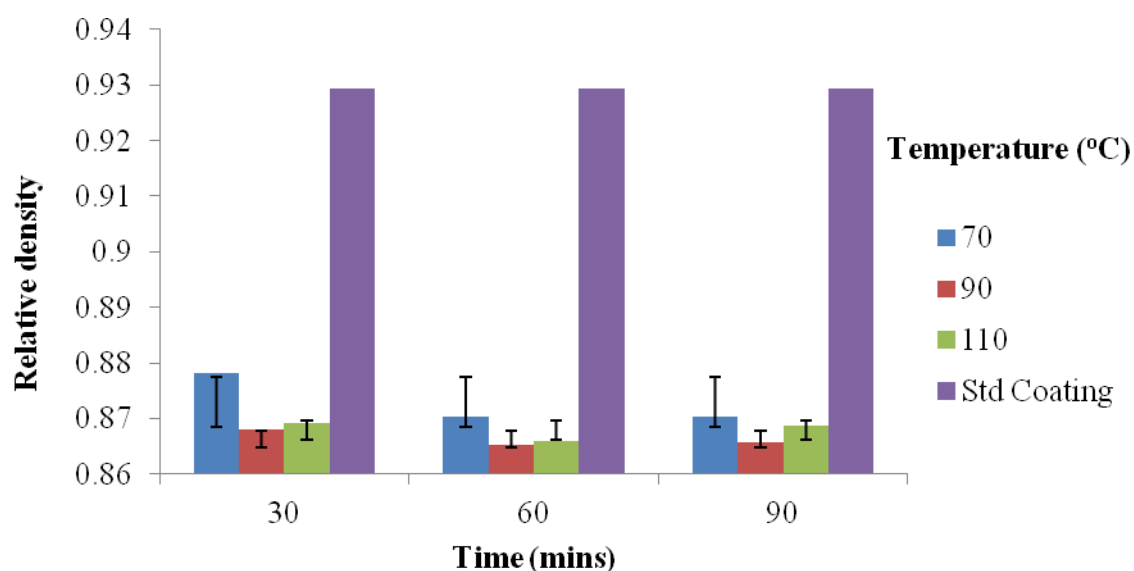
Figure 3.3: Effect of temperatures and heating times on relative density of CNSL-based surface coating formulations

3.4.2 Viscosity of the CNSL- based surface coatings

The coating formulations had very low viscosities and did not compare with the standard coating (Table 3.5). The standard coating had viscosity value of 156.21±0.03 Centipoises. However, formulations made at 90 ^{o}C and heating time of 90 minutes gave the highest viscosity value of 7.8955±0.01 Centipoises, followed by the formulation made at 70 ^{o}C and heating time of 60 minutes which gave the viscosity value of

7.8295±0.04 Centipoises compared to other formulations (Figure 3.4). The viscosity of the formulations increased with the increasing temperatures up to 110°C and also decreased as the heating time increased (Figure 3.4). The optimum viscosity was found to be at 70 ^{o}C and heating time of 60 minutes which gave the viscosity value of 7.8295±0.04 Centipoises. The large difference in the viscosities between the standard coating and other formulations can be attributed to the amount of solvent used during the polymerization reaction and whether the CNSL act as a reactive diluent for alkyd coatings.

Decarboxylated CNSL has varied carbon chains ($C_{15}H_{25-31}$) attached to phenol core. The condensation polymerization reaction at lower temperature is more difficult because of the immiscibility of CNSL and formaldehyde (HCHO) layers and the steric hindrance caused by the lengthy side chain. Longer processing times are needed and the reaction product is a mushy, high viscosity substance, which tends to solidify at comparatively low degrees of polymerization (Calo *et.al*, 2007). At higher temperatures, the decarboxylated CNSL probably has more straight side chains than that resulted at lower temperatures. Polymerization reactions involves the cross linking of the side chains, the more the heating time the higher the rate of polymerization reactions which result in more branched molecules that cannot approach closer enough for all atoms to reach the Van der Waals distance and this will cause low viscosity (Mary & Thachil, 2001).
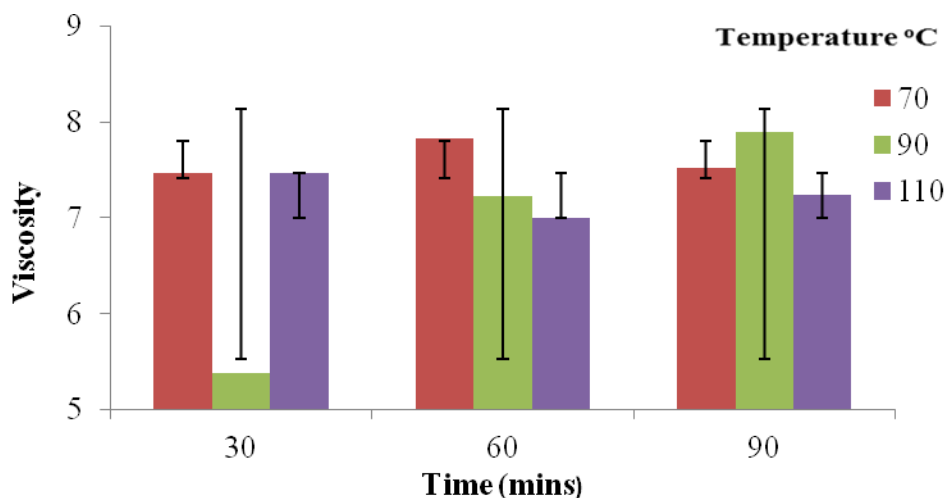
Figure 3: Effect of temperatures and heating times on viscosity of CNSL- based surface coating formulations

3.4.3 pH of the CNSL- based surface coatings

The pH values shows that most coating formulations were weakly acidic; pH ≤ 6 and that of the standard coating was neutral at pH = 7.01±0.02. The best formulation based on the pH was those close to neutral and this was observed from two sets of formulations; those made at temperature of 70°C and heating times of 60 and 90 minutes (Figure 3.5) with pH values as; 6.305±0.02 and 6.35±0.07 respectively. At lower pH the sample reacts with an alkaline catalyst in the formation of resol from cardanol, which slows down the polymerization reactions. This therefore proposes a lower heating temperature of 70°C and 60 minutes of heating time as the optimum condition for better polymerization based on the pH of the formulations.
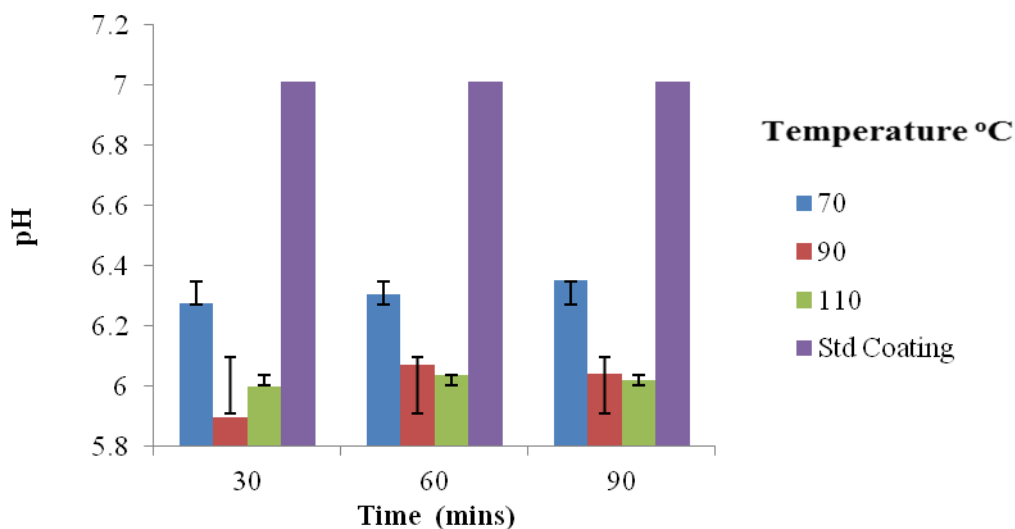
Figure 4: Effect of temperatures and heating times on pH of CNSL- based surface coating formulations

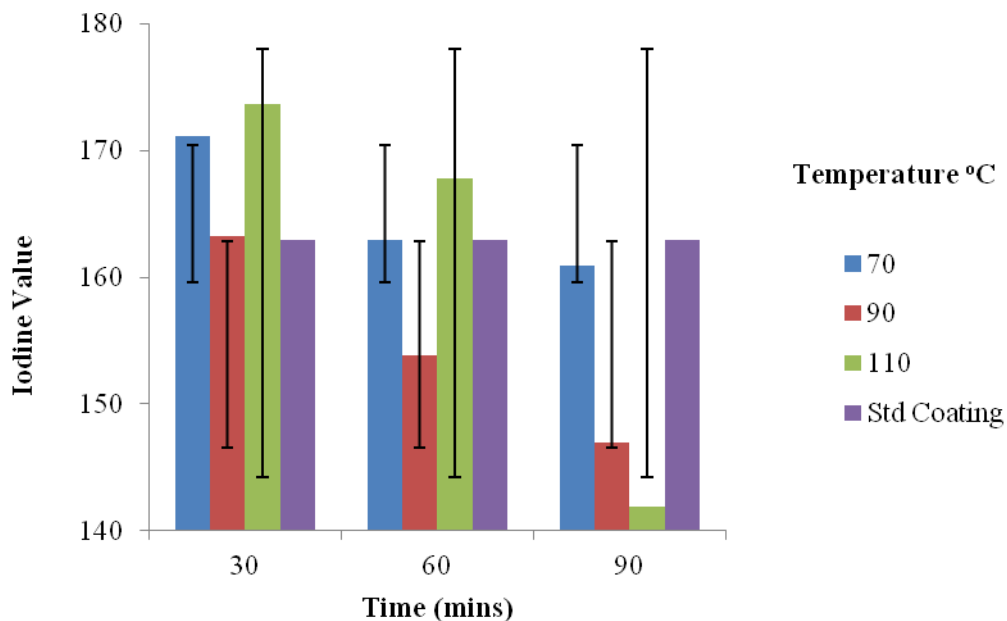### 3.4.4 Iodine value of the CNSL- based surface coatings

Iodine value for the formulation made at the temperature of 70°C and heating time of 60 minutes was found to be; 162.97±0.01 and compared very well with the value obtained for the standard coating; 162.90±0.02. Iodine values of the other coating formulations were relatively the same in all the treatments, ranging from 141.89±0.01 to 173.63±0.02 (Table 3.5). Higher temperatures and increased heating times resulted in coating formulations with reduced iodine values (Figure 3.6). This is an indication of the extent of polymerization reactions, a lower iodine value indicate faster polymerization reaction while a high iodine value implies a higher number of double bonds which in practice favors further polymerization reactions at the cross linking stage. This information is very important because it forms the basis by which the cross-linking reaction can be carried out.

Figure 3.6: Effect of temperatures and heating times on iodine value of CNSL- based surface coating formulations

3.5 Performance characteristics of CNSL Based surface coatings

3.5.1 Adhesion test for the formulated surface coatings

The adhesion performance rating for the coating formulations was comparable to that of the standard coating (Table 3.6).

Table 3.6: Effect of temperatures and heating times on adhesion rating of CNSL- based surface coatings

Polymerization Temperature (^{o}C)	Heating Time (mins)	Classification	Remarks	Ranking
	30	3B	Good	3
70	60	4B	Very good	4
	90	3B	Good	3
	30	4B	Very good	4
90	60	4B	Very good	4
	90	4B	Very good	4
	30	3B	Good	3
110	60	3B	Good	3
	90	4B	Very good	4
Standard Coating		5B	Excellent	5

Figure 3.7, compares the results of the adhesion performance rating of different coating formulations to that of the standard. The formulations formed at the temperature of 90 ^{o}C had very good adhesion properties similar to the formulations at 70°C and 110°C at the heating time of, 60 minutes and 90 minutes respectively. This result implies that if formulations are made at temperature of 70°C and 60 minute of heating time, a very good coating that adheres well to the substrate are produced. This will reduce the amount of energy to be consumed and therefore reduces the cost of production.
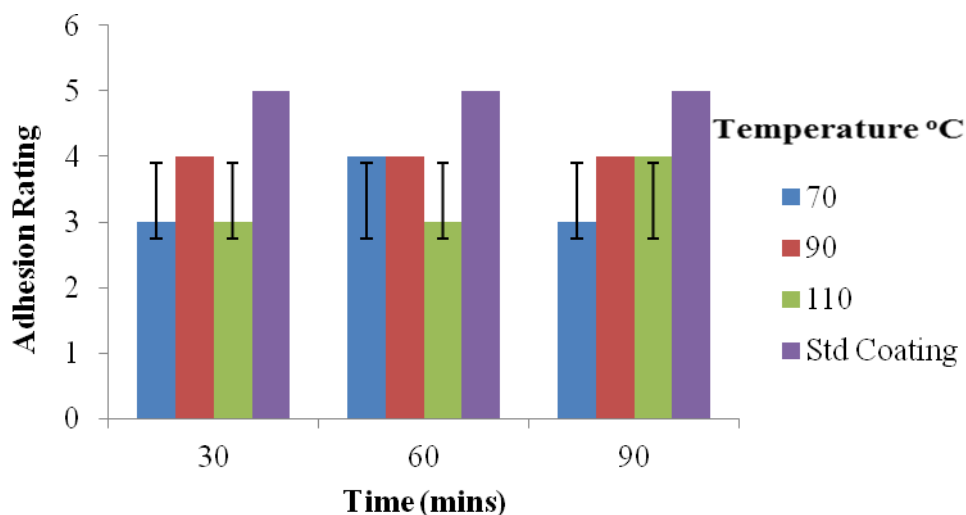
Figure 5: Effect of temperatures and heating times on adhesion rating of CNSL- based surface coatings

3.5.2 Pencil Hardness test for the formulated surface coatings

The Hardness rating for the coating formulation prepared at a temperature of 70^0C and heating times of, 30, 60 and 90 minutes was comparable to that of the standard coating (Table 3.7).

Table 3.7: Effect of temperatures and heating times on Hardness rating of CNSL- based surface coatings

Polymerization Temperature (^{o}C)	Heating Time (mins)	Classification	Remarks	Ranking
	30	f	Hard	2
70	60	f	Hard	2
	90	f	Hard	2
	30	2b	Soft	1
90	60	f	Hard	2
	90	2b	Soft	1
	30	2b	Soft	1
110	60	2b	Soft	1
	90	2b	Soft	1
Standard Coating	-	f	Hard	2

However the hardness rating for the coating formulations at 90^{0}C and 110^{0}C varied slightly from that of the standard coating. Figure 3.8 shows a summary of the hardness rating of the formulated coating and that of the standard. This data supports the optimum conditions of temperature at 70°C and heating time of 60 minutes as proposed by other parameters.
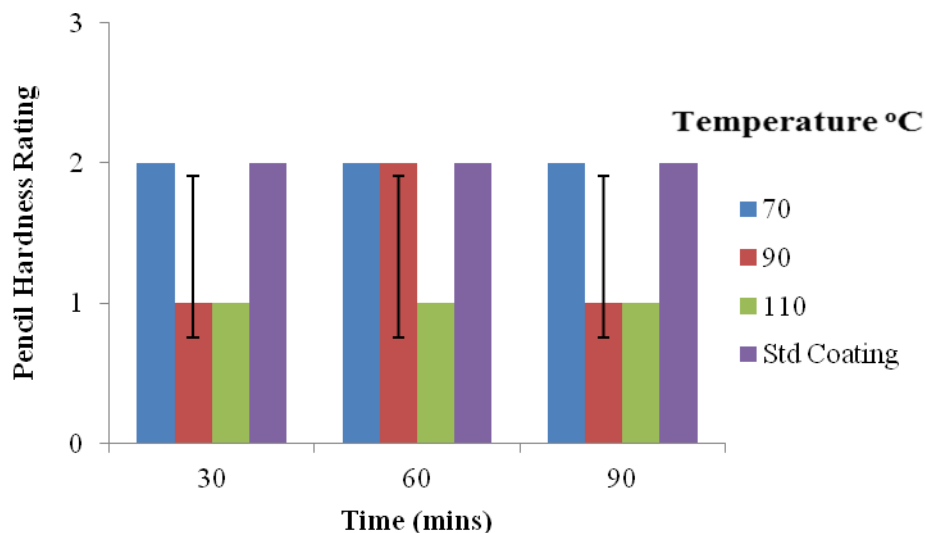
Figure 3.8: Effect of temperatures and heating times on Hardness rating of CNSL-based surface coatings

3.5.3 Drying Time test for the formulated surface coatings

The results for drying time showed that the formulation at temperature of 70^{0}C and heating time of 60 minutes gave comparable results to that of the standard coating however, drying time for the formulations prepared at higher temperatures of 90 ^{0}C and 110 ^{0}C gave a reduced drying time of $\leq$ 4 hours, this could be attributed to the fact that more solvent molecules are lost at higher temperatures and higher chances of a complete polymerization process (Table 3.8 and Figure 3.9).

Table 3.8: Effect of temperatures and heating times on drying time of CNSL-based
surface coatings

Polymerization Temperature (^{o}C)	Heating Time (mins)	Drying Time (Hours)
70	30	8.5
	60	8.0
	90	6.5
90	30	4.0
	60	4.0
	90	4.0
110	30	5.5
	60	3.8
	90	2.0
Standard Coating	-	8.0

According to the ASTM D-5895, temperature is among important factors in considering the drying time of films. The drying ability depends on unsaturation of the various chemical compounds that make up the formulation. When the formulated surface coating combines with oxygen and accelerated by metallic driers, auto-oxidative polymerization occurs and transforms the formulation from a liquid to a solid (Mary & Thachil, 2001).
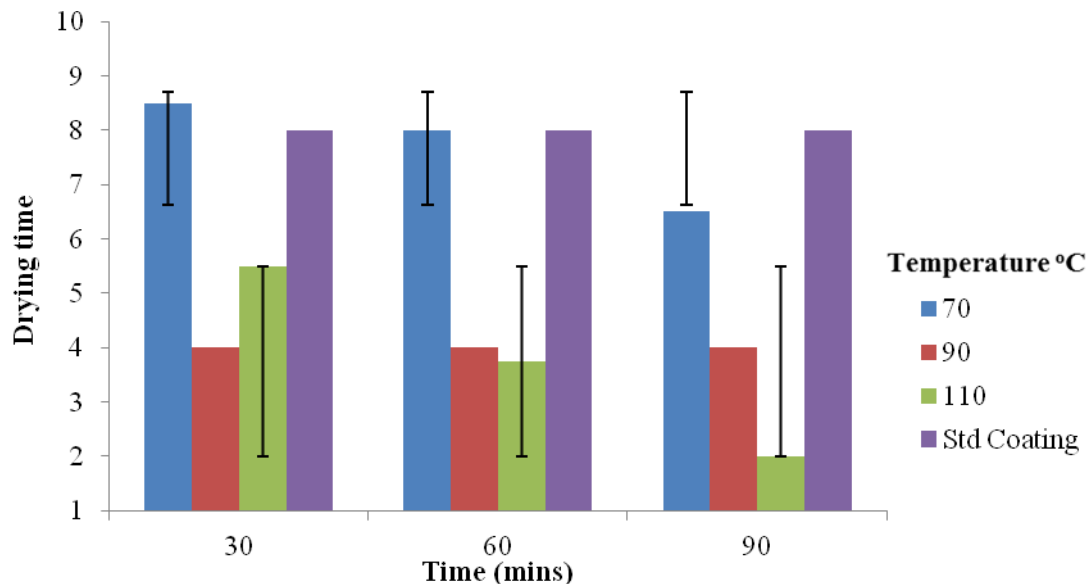
Figure 6: Effect of temperatures and heating times on drying time of CNSL- based surface coatings

Both the physico-chemical and performance characteristics carried out confirms that the optimum conditions of temperatures and heating times for the polymerization of CNSL based surface coatings are 70°C and 60 minutes respectively. Generally many initiators have operational heating time not exceeding one hour (Fay *et al.,* 2004), this argument supports the optimum conditions as indicated by the parameters that were tested. At higher temperatures above 70°C, a higher rate of polymerization reaction takes place due to increased production of free radicals.

3.6 Performance characteristics of cross linked CNSL based surface coatings

Surface coatings cross linked with styrene and MMA were made at the optimum conditions of temperature and heating time of 70°C and 60 minutes respectively. Their performance characteristics were determined and compared to both the standard coating and also with the coating formulation made at optimum conditions before cross linking with either MMA or styrene. The finding of this research noted that by cross linking the CNSL coatings with styrene and MMA at different mole ratios, the performance

57

characteristics of the formulation was affected significantly. Drying time of all cross-linked formulations was improved, while adhesion and hardness properties became poor compared to the standards (Table 3.9).

Table 3.9: Drying time, pencil scratch hardness and adhesion tests of the cross-linked surface coatings

Sample	Drying Time (H	Adhesion Test			Pencil Hardness Test		
		Classification	Remarks	Ranking	Classification	Remarks	Ranking
SCNSL3	3.5	3B	Good	3	2B	Soft	1
SCNSL2	3.25	3B	Good	3	2B	Soft	1
SCNSL1	2	4B	Very good	4	HB	Soft	1
MCNSL3	3.25	3B	Good	3	6B	Soft	1
MCNSL2	2.5	2B	Fair	2	HB	Soft	1
MCNSL1	2	2B	Fair	2	2B	Soft	1
Std Coating	8	5B	Excellent	5	F	Hard	2
70°C, 60 mins	8	4B	Very good	4	F	Hard	2

3.6.1 Adhesion Test for the cross linked Surface Coatings

The adhesion tests for different formulations was investigated and found out that different ratios of monomers imparted different adhesion characteristics, with the Styrene CNSL cross linked coating at ratio 1:3; SCNSL1, giving a very good adhesion, but as the styrene ratio increased (SCNSL2 and SCNSL3) the adhesion properties became poor (Table 3.9), MMA had the opposite trend, the adhesion properties improved as the ratio of MMA increases from MCNSL1 to MCNSL3 (Table 3.9 and Figure 3.10). The results shows that lower ratio of styrene caused more cross linking network which improved adhesion properties of the coating formulation. Higher ratios yielded formulations with poor cross linking network with poor adhesion properties.

3.6.2 Pencil Hardness Test for the cross linked Surface Coatings

The results for pencil hardness for the cross linked formulations did not compare to those of the standards. This implies that when the coating formulations were cross linked with MMA and styrene at different monomer ratios they resulted into soft polymers (Table 3.9 and Figure 3.10), according to Mary and Thachil (2003), acrylate monomers yield the softest products. The hardness and softness of a polymer is determined by the chain mobility. Soft polymers wiggle past and around each other more frequently than hard polymers. It has been found out that cross linking the coating formulation with MMA and styrene at any given ratio increased the chain mobility resulting to soft polymers.

3.6.3 Drying Time Test for the cross linked Surface Coatings

The drying time for all the cross linked coatings ≤3.5 hours did not compare with the standard coatings at 8 hours (Table 3.9 and Figure 3.10). Styrene and MMA cross linked coatings gave improved drying time at lower ratios, this in essence implies that cross linking lowers the drying time of coating formulations. The results shows that lower ratio of styrene caused more cross linking network which improved drying time of the coating formulation. Higher ratios yielded formulations with poor cross linking network and longer drying time. Mary and Thachil (2003), agrees that when styrene monomers are properly formulated, they dry quickly and develop good film hardness.
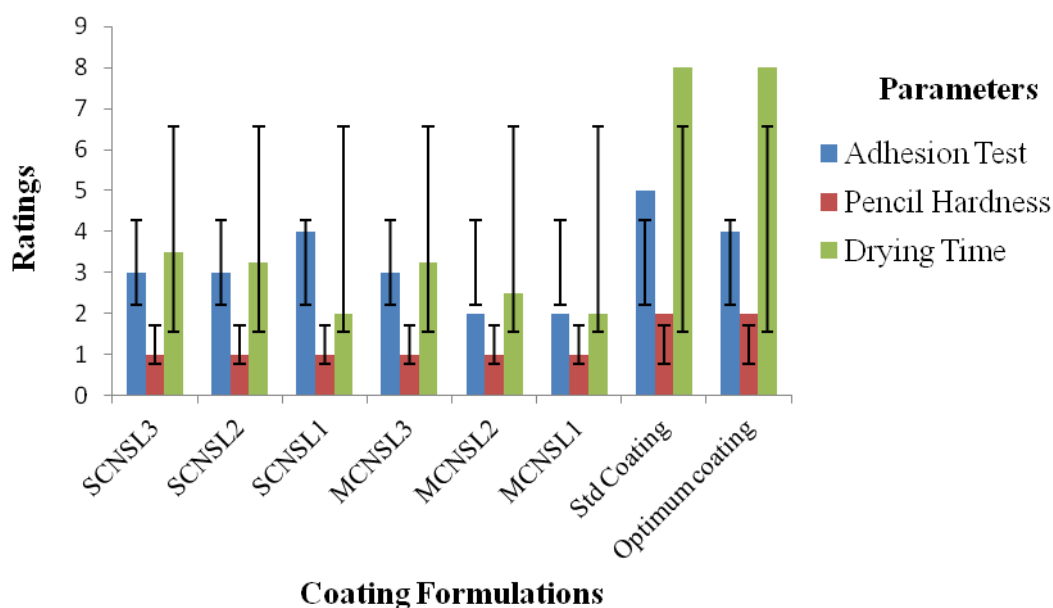
Figure 3.10: Effect of modification of CNSL based surface coatings with different ratios of styrene and MMA monomers on; adhesion, pencil scratch hardness and drying time of the cross linked surface coatings

3.6.4 Iodine value for the cross linked Surface Coatings

The iodine values for most of the cross linked formulations compared closely to the standard formulation (Table 3.10), however, Styrene: CNSL formulation with mole ratio 3:1, gave the highest iodine value at 184.80 ± 0.02 (Table 3.10), which could be attributed to the lower ratio of styrene monomer, this was an indication that there were fewer cross links and high unsaturation. Styrene: CNSL formulation gave comparable iodine value to that of the standard formulation. At lower ratios, the amount of styrene may not be enough to completely cross link all the unsaturated bonds, this will in turn show a higher iodine value, at higher ratios the amount may be sufficient to cause higher cross links. The MMA formulations had lower iodine values compared to the standards.

Table 3.10: Iodine value of the cross-linked surface coating

Sample	Coding	Iodine value (mg/100g iodine)
Styrene: CNSL Coating; Ratio 12:1	SCNSL3	165.50±0.03
Styrene: CNSL Coating; Ratio 6:1	SCNSL2	169.82±0.01
Styrene: CNSL Coating; Ratio3:1	SCNSL1	184.80±0.02
MMA: CNSL Coating; Ratio 12:1	MCNSL3	153.83±0.01
MMA: CNSL Coating; Ratio6:1	MCNSL2	160.94±0.03
MMA: CNSL Coating; Ratio 3:1	MCNSL1	152.81±0.01
Std Coating	-	162.9±0.02
Optimum Coating	-	162.97±0.01

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The average percentage yield of CNSL was slightly less than the expected yield; the shortfall was attributed to the oozing out of some CNSL to the floor during storage at the factory. This challenge can be mitigated by either, storing the cashew nut shells in metallic drums; this will help to collect the CNSL that oozes out.

From the research findings it was established that the coating formulations had comparable physico-chemical characteristics to the standard coating in terms of pH, relative density, but had a variation in viscosity, however the viscosity can be improved by reducing the volume of the solvent used.

The optimization of temperature and heating time was achieved successfully using physico-chemical and performance characteristics; a temperature of $70^{o}C$ and heating time of 60 minutes were taken to be the optimum conditions.

Cross linking of the CNSL based surface coating with Styrene and MMA monomers was successful giving formulations with performance characteristics either improving or lowered compared to the standard coatings, both adhesion and drying time properties were improved on different ratios of monomers that were added. Styrene monomers at lower ratios (SCNSL1) performed better in terms of adhesion and drying time, while MMA produced better formulations in terms of adhesion at higher ratios (MCNSL3) and the best drying time at lower ratio (MCNSL1). Hardness characteristics for cross linked formulations were lowered compared to the standard. Formulations that were cross linked with styrene monomer gave better adhesion properties than those cross linked with MMA while formulations that were cross linked with MMA gave better drying time than those cross linked with styrene. Cross linking with both MMA and styrene gave soft polymers at any given ratio. Generally, cross linking improved some performance characteristics and affected other characteristics negatively. Depending on the use of a given polymer, a suitable monomer can be used to effect the desirable

performance characteristics. The findings of this research reveals that the surface coatings developed from cross linking the CNSL with styrene and MMA monomers at different mole ratios compared favorably in quality to the commercial coatings and some qualities like drying time even improving more than those of commercial coatings. These findings therefore provides a viable opportunity for commercial exploitation of cashew nut shells while at the same time mitigating pollution effects always associated with burning of cashew nut shells. Exploitation would also result to increased returns to the stakeholders of the cashew nut industry.

Recommendations

Further research work should be done to determine other performance characteristics such as, impact resistance, corrosion resistance, flexibility and gloss of the cross linked CNSL based surface coatings as well as determine if the cross linked CNSL based surface coatings can be used as reactive diluents for alkyd coatings in order to reduce the use of solvents and improve viscosity.

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APPENDICES

Appendix 1: Plate for adhesion test

Appendix 2: A plate of pencil Hardness test
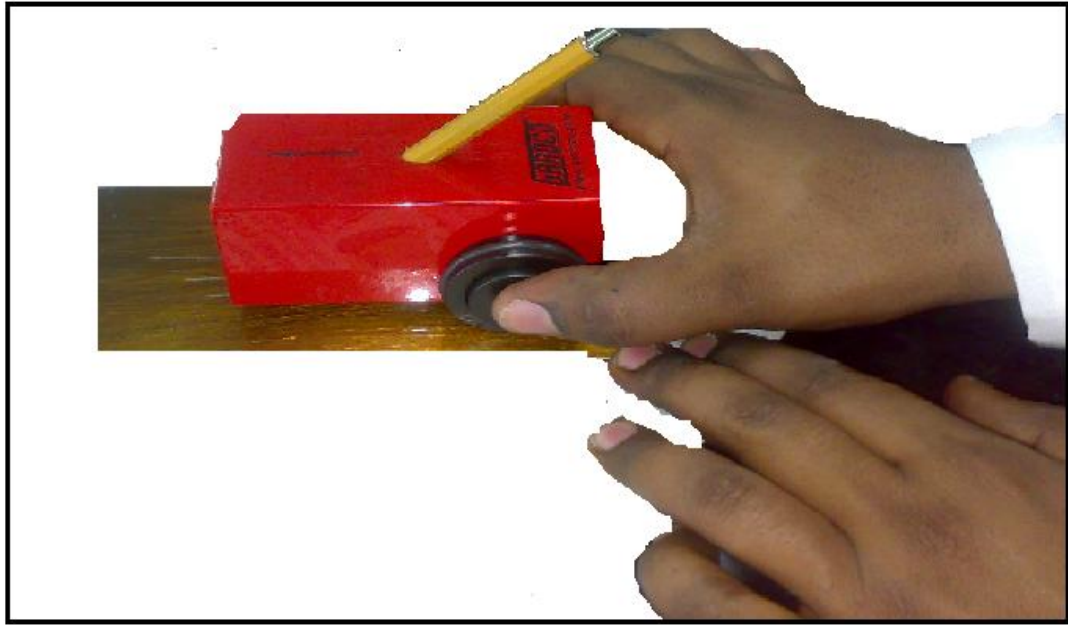
Appendix 3: A plate for viscosity test

Appendix 4: A plate of rotary evaporator