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This research project aims at developing new applications for cashew nut shell liquid (CNSL) in the polymer field. Cashew is widely cultivated in the tropics and cashew nut is a very proteinaceous tasty product popular throughout the world. CNSL is a byproduct of the cashew nut processing industry. It is cheap, renewable and underutilized.

1.1 CASHEW NUT SHELL LIQUID

Cashew nut shell liquid (CNSL) occurs as a viscous liquid in the soft honeycomb of the shell of the cashew nut. Cashew nut is the crop of the cashew tree, *Anacardium occidentale* L. (1) native to Brazil. The plant may grow to 12 m in height. The tree also produces cashew apple, wood suitable for boats, charcoal etc., and a gum similar to gum arabic. Cashew nut is greenish gray in colour and is attached to the cashew apple, which when ripe is either bright yellow or red. The nut has two walls or shells, the outer one being smooth and somewhat elastic and olive green in colour before maturity. The honeycomb is housed between the inner and outer shells. The kernel is inside the shell and is covered with a brown skin known as testa. Industrial grade CNSL is reddish brown in colour. CNSL constitutes about 20-25% of the weight of the cashew nut.

![Diagram of Cashew Nut](image-url)
The main constituents of CNSL are phenolic compounds with long side chain substitution at the meta position. These compounds give most of the reactions of phenol and can be the basis for producing a number of polymeric substances of wide utility in industrial applications. CNSL being cheap can be a substitute for phenol in many applications. The use of CNSL in place of phenol is an excellent example of conservation of a synthetically derived substance and the utilization of a cheap agro by-product. In the modern context, CNSL occupies a position of importance because of its renewable nature (2). CNSL is abundantly available in many parts of the world, such as India, Brazil, Bangladesh, tropical regions of Africa and South America. In some of these regions, cashew is a popular plantation product, while some others import cashew nuts for processing.

Demand for CNSL stems from its numerous uses in many areas. Constituents of CNSL possess special structural features for conversion into specialty chemicals and high value polymers. This involves substantial value addition and the chemical transformation provides 100% chemically pure products.

India is the largest producer of raw cashew nuts in the world. The production of raw cashew nuts was 95,000 MT during 2003-04. The export of CNSL from India during 2003-04 was 7215 MT. Among Indian States, Maharashtra comes first in production of cashew nuts followed by Kerala and Andhra Pradesh. Export of CNSL from Kerala was 6784 MT during 2003-04 (3).

1.1.1. Composition

The earliest work published concerning the composition of cashew nut oil is by Staedeler (4). Since then many researchers have investigated the constitution of the oil (5-7). Naturally occurring CNSL contains mainly four components: cardanol, cardol, anacardic acid, and 2-methyl cardol. Figure 1.2 shows the chemical structure of these compounds.
Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during the roasting process, which converts anacardic acid to cardanol (8). The roasting process also leads to polymerisation, which accounts for 20-25% of polymeric substances in the oil. Crude CNSL is corrosive but becomes less so by decarboxylation and removal of H₂S during the refining process. The effect of processing parameters on the refining of CNSL has been studied (9).

The components of CNSL are themselves mixtures of four constituents differing in side-chain unsaturation, namely saturated, monoene, diene, and triene. The structures of the side chains of varying degrees of unsaturation occurring in the four major components of CNSL are identical. Fig. 1.3 shows the linear structures.

\[
\begin{align*}
C_{15}H_{31-n} = & \quad (CH_2)_n - CH = CH - CH_2 - \cdots - CH_2 - CH = CH \quad n=0 \\
& \quad (CH_2)_n - CH = CH - CH_2 - \cdots - CH_2 - CH = CH \quad n=2 \\
& \quad (CH_2)_n - CH = CH - CH_2 - CH = CH - CH_2 - CH_2 \quad n=4 \\
& \quad (CH_2)_n - CH = CH - CH_2 - CH = CH - CH_2 - CH \quad n=6
\end{align*}
\]

Fig. 1.3 Components of the side chain
Thus CNSL contains a total of 16 monomeric substances. CNSL is the only naturally occurring alkenyl phenolic substance.

Paul and Yeddanapally (10) identified the components of anacardic acid as 2-hydroxy-6-(n-pentadecyl)benzoic acid, 2-hydroxy-6-(n-pentadeca-8-enyl) benzoic acid, 2-hydroxy-6-(n-pentadeca-8,11-di-enyl)benzoic acid, 2-hydroxy-6-(n-pentadeca-8,11,14-trienyl)benzoic acid. Table 1.1 lists the constituents of anacardic acid as determined by various techniques.

Table 1.1
Composition of the constituents of anacardic acid as determined by various techniques (values are in wt %) (7)

<table>
<thead>
<tr>
<th>Constituents of anacardic acid</th>
<th>Technique employed</th>
<th>Low temp. crystallization</th>
<th>TLC-UV</th>
<th>TLC-grav</th>
<th>TLC-GLC</th>
<th>HPLC</th>
<th>TLC-mass spectrometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td></td>
<td></td>
<td>4</td>
<td>_</td>
<td>4</td>
<td>4.3</td>
<td>3.6  52.2-3</td>
</tr>
<tr>
<td>Monoene</td>
<td></td>
<td></td>
<td>15</td>
<td>38.7</td>
<td>38.4</td>
<td>38.3</td>
<td>33.4 18.19 25-33.3</td>
</tr>
<tr>
<td>Diene</td>
<td></td>
<td></td>
<td>44</td>
<td>16.3</td>
<td>17.3</td>
<td>17.3</td>
<td>19.9 16.5 17.8-32.1</td>
</tr>
<tr>
<td>Triene</td>
<td></td>
<td></td>
<td>37</td>
<td>45.1</td>
<td>44.1</td>
<td>40.4</td>
<td>42.4 41.62 36.3-50.4</td>
</tr>
</tbody>
</table>

Symes and Dawson (11) and Cornelius (12) identified the components of cardanol as 3-(n-pentadecyl)phenol, 3-(n-pentadeca-8-enyl)phenol, 3-(n-pentadeca-8,11-di-enyl)phenol, 3-(n-pentadeca-8,11,14-trienyl)phenol. Table 1.2 gives the composition of the constituents of cardanol.
Table 1.2
Composition of the constituents of cardanol as determined by various techniques (values are in wt %) (7)

<table>
<thead>
<tr>
<th>Constituents of cardanol</th>
<th>Technique employed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecular distillation</td>
<td>Argentated column</td>
</tr>
<tr>
<td>Saturated</td>
<td>_</td>
<td>5.4</td>
</tr>
<tr>
<td>Monoene</td>
<td>60</td>
<td>48.5</td>
</tr>
<tr>
<td>Diene</td>
<td>10</td>
<td>16.8</td>
</tr>
<tr>
<td>Triene</td>
<td>30.6</td>
<td>29.3</td>
</tr>
</tbody>
</table>

The same group of workers also identified the components of cardol as 5-(n-pentadecyl)1,3-benzene diol, 5-(n-pentadeca-8-enyl)1,3-benzene diol, 5-(n-pentadeca-8,11-di-enyl)1,3-benzene diol, 5-(n-pentadeca-8,11,14-trienyl)1,3-benzene diol,

The composition of the constituents of cardol is given in Table 1.3.

Table 1.3
Composition of the constituents of cardol as determined by various techniques (values are in wt %) (7)

<table>
<thead>
<tr>
<th>Constituents of cardol</th>
<th>Technique employed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TLC-GLC</td>
<td>TLC-mass spectrometry</td>
</tr>
<tr>
<td>Saturated</td>
<td>0.3</td>
<td>0.24</td>
</tr>
<tr>
<td>Monoene</td>
<td>8.1 9.6</td>
<td>10.74</td>
</tr>
<tr>
<td>Diene</td>
<td>21.9 25.2</td>
<td>20.64</td>
</tr>
<tr>
<td>Triene</td>
<td>69.7 62.2</td>
<td>68.39</td>
</tr>
</tbody>
</table>

Tyman (6) established the components of 2-methyl cardol as 2-methyl-5-(n-pentadecyl)1,3-benzene diol, 2-methyl-5-(n-pentadeca-8-enyl)1,3-benzene diol,
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2-methyl-5-(n-pentadeca-8,11-di-enyl)1,3-benzene diol, 2-methyl-5-(n-pentadeca-8,11,14-trienyl)1,3-benzene diol.

The relative proportions of the saturated and unsaturated constituents of 2-methyl cardol are shown in Table 1.4.

Table 1.4

Composition of the constituents of 2-methyl cardol as determined by various techniques (values are in wt %) (7)

<table>
<thead>
<tr>
<th>Constituents of 2-methyl cardol</th>
<th>Technique employed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TLC-GLC</td>
</tr>
<tr>
<td>Saturated</td>
<td>1.66</td>
</tr>
<tr>
<td>Monoene</td>
<td>13.9</td>
</tr>
<tr>
<td>Diene</td>
<td>18.5</td>
</tr>
<tr>
<td>Triene</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Table 1.5 gives typical compositions of natural and technical CNSL.

Table 1.5

Phenolic composition of natural and technical CNSL (values in wt %) (7)

<table>
<thead>
<tr>
<th>Component</th>
<th>Natural CNSL</th>
<th>Technical CNSL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol</td>
<td>1.2</td>
<td>62.86</td>
</tr>
<tr>
<td>Cardol</td>
<td>11.31</td>
<td>11.25</td>
</tr>
<tr>
<td>2-methyl cardol</td>
<td>2.04</td>
<td>2.08</td>
</tr>
<tr>
<td>Polymer</td>
<td>20.3</td>
<td>23.8</td>
</tr>
<tr>
<td>Anacardic acid</td>
<td>64.93</td>
<td></td>
</tr>
</tbody>
</table>

The phenolic nature of the constituents of CNSL along with varying degrees of unsaturation in the side chain makes it a highly polymerisable substance amenable to a variety of polymerisation reactions. Of overriding importance, however, is the condensation reaction with active methylenes that formaldehyde exemplifies. This leads to a phenol-formaldehyde type condensation.
1.1.2. Extraction

A process for extracting CNSL has been patented in India in September 1961 (13). Traditionally, a number of methods are employed to extract the oil from the nuts. Often a particular region follows a technique by convention rather than by deliberate choice. The following are the popular methods currently employed for the extraction of the oil (6).

a. Hot oil bath method

The raw nuts are passed through a bath of hot CNSL at 180-200°C. The outer part of the shell bursts open and releases CNSL. About 50% of the oil is thus recovered. This process makes the disintegration of nuts easy, without adversely affecting the quality of the kernels. Improvements over this basic technique include initial surface wetting and dipping in water at 20-25°C and subsequent steam treatment prior to exposure to the hot CNSL bath. The excess moisture content of 7-10% of the weight of the nuts causes the cells to burst, with the result that the oil oozes into the bath. Another 20% could be extracted by passing the spent shells through an expeller and the rest by a solvent extraction technique. The expeller oil can be upgraded by acid washing followed by centrifugation and heating.

b. Roasting method

Sudden exposure to higher temperature from ambient is the basis of this method. The shells are charred during this process, producing an explosive pressure in the cellular structure, which forces the liquid out of the shell. In drum roasting the nuts are heated at high temperature in a rotating drum and then shelled. One variation of this method is abrading at 100-300°C for about 1 hour and subsequent roasting at 400-700°C in an inert atmosphere. In yet another patent, the nuts are first abraded and then treated with moisture and heated in an infrared oven. Finally they pass through a high frequency electric field, where the liquid flows out. Often this technique is employed in conjunction with an expeller, where the oil is expelled from the shells to an extent of 90%.
c. Miscellaneous methods

CNSL is expelled by exposing the shell to superheated steam at temperatures ranging from 150°C to 300°C (14). Extraction of the oil by solvents such as benzene, toluene, petroleum hydrocarbon solvents or alcohols (15) or with supercritical CO₂ and water are other reported techniques (16). Report of a power operated cashew nut sheller has also appeared (17).

1.1.3. Refining

Sulfides, nitrogenous materials, and minerals contained in crude CNSL directly affect the quality of the oil. Hence CNSL is often subjected to chemical treatment with substances such as hydrocarbon sulfates and sulfuric acid before industrial use. Several acid treatment processes have been found to reduce the poisoning or vesicant action. Aqueous solutions of acids such as hydrochloric acid, sulfuric acid, acetic acid, chloroacetic acid or phosphoric acid, or acid sulfates such as sodium hydrogen sulfate are employed for this purpose. This performs two important functions: mineral salts of ammonium, calcium and potassium are precipitated and there is a reduction in the content of skin vesicant present in CNSL. The chemical treatment is accompanied by the evolution of hydrogen sulfide. The reduction in sulfur content has been found to correspond roughly to the removal of the agent responsible for the skin irritation. Treatment with amines or with hydroxides of the metals of group IA or IIA has been found to reduce the cardol content.

The refined CNSL can be readily distilled under reduced pressure or hydrogenerated, both processes leading to products with good colour stability. Steam treatment of H₂SO₄ treated CNSL followed by distillation has been found to deodorize the oil to a substantial extent.

Physical constants of CNSL before and after chemical treatment are summarized in Table 1.6 (18).
### Table 1.6 (18)

<table>
<thead>
<tr>
<th>Physical components of the oil before and after chemical treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw oil</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Iodine no., Wijs</td>
</tr>
<tr>
<td>Refractive index, 20°C</td>
</tr>
<tr>
<td>Specific gravity, 25°C</td>
</tr>
<tr>
<td>Saponification value</td>
</tr>
<tr>
<td>Viscosity at 25°C, cp</td>
</tr>
<tr>
<td>Acetyl value</td>
</tr>
</tbody>
</table>

### 1.1.4. Physical properties

CNSL is dark viscous oil with a characteristic smell, quite unlike other vegetable oils. It is opaque and when applied as a thin film, is reddish-brown in color. It is immiscible with water but miscible with most organic solvents. CNSL has germicidal and fungicidal properties. It is used traditionally as a cure for acne vulgaris of the feet in Kerala. Table 1.6 gives some of its physical properties.

### 1.1.5. Reactions of CNSL

The chemical structure of CNSL is such that it can take part in a large number of reactions. A few reviews have appeared summarizing the known reactions of CNSL (6, 19). The reaction schemes given in the following sections are based on cardanol, the major constituent of CNSL.

#### a. Decarboxylation

As mentioned earlier, anacardic acid decarboxylates on heating to cardanol. Fig. 1.4 shows the chemical changes taking place during decarboxylation (19).

![Decarboxylation of CNSL](image-url)
b. Hydrogenation (20)

Hydrogenation is usually carried out using hydrogen and catalysts such as copper, nickel, palladium and platinum (Fig. 1.5).

\[
\text{OH} \quad \text{C}_{15} \text{H}_{31-n} + n\text{H}_2 \xrightarrow{\text{Cu, Ni, Pa, Pt}} \text{OH} \quad \text{C}_{15} \text{H}_{31}
\]

**Fig. 1.5 Hydrogenation of cardanol**

c. Polymerisation

CNSL can be polymerized by a variety of techniques. The unsaturation in the side chain can be the basis for addition polymerisation (21-23) using free radicals or ionic initiators. Acids such as H₂SO₄, HCl, paratoluene sulphonic acid (PTSA) etc. can give polymeric products. CNSL can be polymerized using salts such as zinc chloride, stannic chloride, ferrous sulphate, aluminium sulphate, boron trifluoride and salts of iron, cobalt, nickel, boron, chromium, lead, silver, mercury, manganese, etc. These salts are generally used to the extent of 1-6%.

The phenolic properties of CNSL are utilized to make condensation polymers by reaction with formaldehyde, furfural, HMTA, etc. (24-26). These polymers are similar to the product of phenol and formaldehyde condensation but shows less reactivity during synthesis and later during crosslinking. Both resole and novolac type resins can be made.

\[
\text{R=C}_{15} \text{H}_{31-n}
\]

**Fig. 1.6. Resole resin made from cardanol (7)**
In the presence of alkaline catalysts and with more formaldehyde, the methylol phenols condense either through methylene linkages or through ether linkages. In the case of resole type polymers, the structure of the final product has been studied by Tyman (7) (Fig. 1.6). Working back from this structure and in analogy with similar reactions for phenol the reaction scheme leading to this final crosslinked network can be given as shown in Fig. 1.7.

Fig. 1.7. Polymerisation of CNSL using alkali catalysts.
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 crosslinking. The final structure of the novolac product has also been given by Tyman (Fig. 1.8).

\[ R = \text{C}_{15} \text{H}_{31-n} \]

**Fig. 1.8. Novolac resin made from cardanol (7)**

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 in Fig 1.9. This is deduced by considering the final polymer structure and the reaction of phenol under similar conditions.

The condensation in this case is more difficult because of the immiscibility of CNSL and 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 polymerisation. In certain applications, a preliminary step of polymerisation through the side chain is done before condensation polymerisation.
Fig. 1.9. Polymerisation of CNSL using acid catalysts.

Similar reactions can be conducted with hydrogenated cardanol and the product converted to methyl ether and then oxidized with KMnO₄, giving a substituted acid. (Fig. 1.10).

Fig. 1.10. Condensation of hydrogenated cardanol followed by etherification and oxidation.
Mishra and Pandey have investigated the kinetics of alkali catalyzed formaldehyde condensation after thoroughly reviewing the results previously reported by various workers (27). O'Conner and Blum have studied the thermal stability of some formaldehyde condensate resins (28).

The structure and properties of CNSL novolac resin prepared using succinic acid as a catalyst has been investigated (29). The synthesis and characterization of a large number of resins using different hydroxy aromatic compounds, formaldehyde, furfural, and substituted aromatic compounds like CNSL. in the presence of acid and base catalysts have been studied (30, 31).

Oxidation polymerisation using acid oxidizers such as HNO₃ can also give polymers, which have proved to be excellent for surface coatings and paper/fabric impregnation (32). CNSL on treatment with copper, lead, aluminium etc. undergoes polymerisation. The air drying qualities of CNSL were found to improve by this. Enzymatic polymerisation of alkyl phenols derived from CNSL has been carried out in a dioxan-water mixture (33).

When CNSL is simply heated to 200°C or above, it undergoes polymerisation. Cationic, anionic or oxidizing agents can accelerate the process. Alkalis can also be used as catalysts for the polymerisation 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 polymerisation (19).

Mono or dialkyl sulphates in concentrations of about 2% have been used to polymerize CNSL at about 160°C. The advantage of using alkyl sulphates is that metal present as impurities in CNSL are precipitated out during polymerization (34).

**d. Sulfonation** (35)

CNSL derivatives can be sulphonated to yield alkyl aryl sulphonate acid or their metal salts. The reaction is carried out using concentrated H₂SO₄ at 108°C. The reaction scheme shown in Fig. 1.11 employs hydrogenated cardanol.
Introduction

To prevent polymerisation during sulphonation, an aryl or alkali group is substituted for hydrogen and the double bonds of the aliphatic side chain are saturated by hydrogenation before treatment with the acid.

e. Nitration (19)

Direct nitration of cardanol or CNSL leads to simultaneous oxidation and polymerisation. By nitration of hydrogenated cardanol, 4-nitro compound and 6-nitro compound were obtained. Nitroderivatives of cardanol are very efficient antioxidant for gasoline, mineral hydrocarbons, petroleum products and lubricating oils (Fig. 1.12) (36-38).

f. Halogenation (39)

Halogenation of CNSL can be accomplished with comparative ease. For example, chlorine gas can be passed through CNSL dissolved in kerosene to obtain
15% (w/w) chlorination. Chlorinated CNSL reacts with active methylenes at a faster rate and are more flame resistant. The halogenation is accompanied by polymerisation and thickening and a large exotherm.

g. Etherification (40)

\[
\begin{align*}
2 
& + \quad \text{R}_2\text{SO}_4 \\
& \rightarrow 2 
& + \quad \text{H}_2\text{SO}_4
\end{align*}
\]

\[\text{C}_{15}\text{H}_{31} \quad \text{C}_{15}\text{H}_{31}\]

Fig. 1.13. Etherification of cardanol.

Cardanol can be reacted with dialkyl sulphates in presence of alkalis to give dialkyl cardanols. Fig. 1.13 shows the chemical changes during etherification.

h. Esterification (41)

Cardanol can be reacted with acid chlorides in the presence of alkalis to give cardanol esters. Thus benzoyl chloride gives benzoyl cardanol (Fig. 1.14). Various other esters of industrial importance have also been reported (38).

\[
\begin{align*}
\text{OH} 
& + \quad \text{C}_6\text{H}_5\text{COCl} \\
\text{C}_{15}\text{H}_{31} 
& \rightarrow 
\text{OCOC}_6\text{H}_5 
& + \quad \text{HCl}
\end{align*}
\]

\[\text{C}_{15}\text{H}_{31} \quad \text{C}_{15}\text{H}_{31}\]

Fig. 1.14. Esterification of CNSL.
i. Epoxidation (42)

Epoxidation of the phenolic group can be accomplished by the reaction of CNSL with epichlorohydrin. The chemical changes during this reaction are shown in Fig. 1.15. Epoxy resin can also be prepared from glycidyl ethers by reaction with CNSL.

![Chemical reaction]

Fig. 1.15. Epoxidation of cardanol.

According to Kamath et al., reaction product of cardanol and phenol when reacted with epichlorohydrin produced epoxy resin which claimed to be superior to conventional epoxy resin (43)

j. Miscellaneous reactions

Pillai and co-workers (44-50) have investigated the phosphorylation of cardanol and the prospective applications of the products. Urethanes have been synthesized from CNSL as in the case of other hydroxy compounds, by reaction with isocyanates (51). CNSL can be converted to acetals by reaction with compounds like dimethyl acetal in presence of acids (19). Isocyanates have been prepared from hydrogenated cardanol (52). Azo dyes are made by the reaction of phenols with primary aromatic amines after diazotization of hydrogenated cardanol (53). By reacting CNSL with triethylene-tetramine, phenolic polyamines can be prepared (54). Benzotriazole derivatives are prepared from hydrogenated cardanol by diazotizing with aromatic amines followed by reduction. Syrenation of CNSL resin can be done by reacting styrene with CNSL hexamine condensate (55).

1.1.6. Applications

Polymers derived from CNSL have certain outstanding properties which make them unique for many applications. The most attractive aspect of CNSL as a
starting material is its low cost. The polymer shows flexibility due to internal plasticization resulting from the presence of the long side chain. This long aliphatic side chain also gives water resistance. It has low fade characteristics, which make it a desirable component of brake lining formulations. It is compatible with a wide variety of polymers such as alkyds, melamines, polyesters etc. Its ready solubility in a number of common solvents makes it a natural choice for a large number of surface coating applications. There have been a number of reviews on the applications of CNSL-based materials (56-82).

**Consumption of CNSL by Indian Industry (Estimated) in 2003 (Mega tons)**

<table>
<thead>
<tr>
<th>Application</th>
<th>Estimated Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brake linings</td>
<td>1200-1400</td>
</tr>
<tr>
<td>Paints and varnish</td>
<td>600-800</td>
</tr>
<tr>
<td>Lamination</td>
<td>900-1000</td>
</tr>
<tr>
<td>Foundry</td>
<td>400-500</td>
</tr>
</tbody>
</table>

**a. Brake linings and clutch facings**

CNSL and cardanol based resins have found extensive uses in automotive brake lining applications as binders/friction property modifiers. CNSL polymers are a natural choice for this application because of an excellent blend of properties such as low hardness, abrasion resistance, longer retention of breaking efficiency, low fade characteristics, better water repellence and low cold wear (83, 84)

Addition of friction dust gives a silent braking action, which is highly desirable in modern times. About 12,000-15,000 tons of brake linings are produced for use in motorcars every year in the country. With increasing use of automobiles, there is an expanding market for brake lining applications.

In brake lining materials, two types of CNSL products are used:

1. CNSL resin as a partial substitute for phenolic resin to reduce cost and
2. CNSL based friction material (friction dust) to modify the friction and wear properties of brake linings.
Modified CNSL resin can substitute phenolic resin totally and meet all the specifications of brake linings. Additionally it improves impact properties and reduces fade.

Friction dust is added to brake linings to modify the frictional and wear properties of brake linings. It also provides properties similar to that of CNSL matrix resin. Formulations for excellent fade characteristics, enhanced thermal stability, good resistance to noise, high resistance to hygroscopy, corrosion resistance, rust resistance and low brake noise have been reported (85-100). Friction dust is generally prepared by crosslinking CNSL formaldehyde resin with hexamine / paraformaldehyde and powdering the product to the required specifications. Modified friction dust for applications in 'hot wear' conditions can be prepared from modified CNSL resin.

**b. Surface coatings**

The chemically stable nature of CNSL, the solubility of the resin in various solvents, the inherent hydrophobicity and chemical resistance, the film forming nature, anti-termite, anti-microbial properties, and a high degree of unsaturation make CNSL polymers highly suitable for surface coating applications. The formulation and manufacture of various classes of paints based on CNSL have been described by Ramanujam (101).

Films of high heat resistance, corrosion resistance, excellent electrical properties, anti-corrosive, water and solvent resistance properties, water based coatings etc. can be formulated from CNSL. CNSL based surface coatings possess excellent gloss and surface finish with optimum levels of toughness and elasticity. Because of the dark colour its uses are restricted to anticorrosion primers, black enamels, paints to prevent marine growth on structures, etc (102). Transparent resin from CNSL that can be used as a base for paint of all colours has been developed (103).

CNSL resins give excellent lacquers with decorative and protective properties. Lacquers from CNSL have been used as surface coatings for wood, porcelain, metal ware and so forth (104-115). The dried film of this lacquer is superior to ordinary oil paints in resistance against oils, grease, moisture and
chemicals. Lacquers for special applications such as screen lacquering and gold lacquering are prepared from CNSL.

CNSL resin based varnishes possess good insulating properties apart from their high water repellence and low dielectric properties. Although CNSL and its resins are highly susceptible to fire and burn easily, they can be successfully made fire resistant by incorporating flame retardant agents chemically or flame retardant fillers physically.

CNSL resins singly or in combination with other resins show excellent water and weather proofing properties and can be used for protection of roofs. Shirsalkar and Sivasamban have prepared anticorrosive paints based on CNSL, which have been found to be suitable for ships hulls and other such applications (116-117). The coating withstands alkalinity normally encountered with cathodically protected steel hulls. Rust inhibiting zinc rich primers can be prepared from CNSL. Coatings giving tough elastic films are reported from CNSL-glycerine reaction products (118).

c. Foundry

The phenolic nature of CNSL facilitates the use of resin derived from it in place of conventional phenolic materials used in the foundry industry. The fire retardant and ablative properties associated with the phenolic structure are responsible for this. CNSL is being used as a substitute for linseed oil in the manufacture of foundry core oil used as binder in foundry. CNSL resin imparts good scratch hardness to sand cores after baking them. It also provides resistance to moisture and weathering, good green strength and surface finish to moulded articles (119). Modified CNSL resin when used as core binder is found to improve collapsibility of the core and enhances bench life and anti-damp behaviour in comparison to conventional core binders (76).

d. Laminates

CNSL based resins improve the resistance to heat, the bonding with reinforcement materials and the flexibility of laminates while reducing brittleness and age hardening. Resins for laminated products are made from CNSL and phenol by reaction with aldehydes. Modified phenolic resins are used for making laminates
with good dimensional stability and warp resistance. Metal-polymer laminates of high inter laminar shear strength have been developed from CNSL (120).

e. Miscellaneous applications

CNSL forms the basic raw material for a vast number of industrially important chemicals. Patents and reports cite a number of applications such as antioxidants, bactericides, fungicides, disinfectants, insecticides, dispersing and emulsifying agents, dye stuffs, ion exchange resins, surfactants, stabilizers, curing agents etc (121-145). Lipid nanotubes can be prepared from CNSL (146). Applications of CNSL in adhesives and rubber compounding are discussed in sections 1.2 and 1.3

1.2 CNSL BASED ADHESIVES

1.2.1 Adhesives

An adhesive is a substance that bonds two substrates by surface attachments. Adhesives can be categorized both in terms of their chemical composition or polymer type and their physical forms. Adhesive compositions include a number of additives such as plasticizers, tackifiers and fillers in their formulation. To enhance performance primers and coupling agents are sometimes employed.

Advantages of adhesive bonding are (1) they permit bonding of materials that are impractical to join in other ways (2) possibility of joining dissimilar materials (3) uniform stress distribution in the joints (4) enhanced environmental protection (5) resistance to vibration and shock (5) better aesthetic appeal (6) higher speed of production and lower cost etc.

On the other hand, adhesives can be sometimes relatively expensive, have high temperature limitations, often require surface preparation and require jigs, presses or other fixtures to hold parts in place until the adhesive cures (147-150).

a. Ingredients

The components of an adhesive mixture are usually determined by the need to satisfy application properties of the adhesive or properties required in the final joint.
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1. **Binder** - The basic component of the adhesive formulation is the binder which provides the adhesive and cohesive strength in the bond. It is usually an organic resin but can be a rubber, an inorganic compound or a natural product.

2. **Diluent** – It is employed as a solvent vehicle for other adhesive components and also to provide viscosity control which makes a uniformly thin adhesive coating possible.

3. **Catalysts and hardeners** – These are curing agents for adhesive systems. Hardeners chemically combine with the binder material. The ratio of hardener to binder sometimes determines the physical properties of the adhesive. Catalysts are also employed as curing agents for thermosetting resins to reduce cure time and increase the crosslink density of the synthetic polymer.

4. **Accelerators, inhibitors and retarders** - These substances control the curing rate. Accelerators speed up the curing rate by combining with the binder. An inhibitor arrests the curing reaction. Retarder slows down the curing reaction and prolongs the storage or working life of the adhesive.

5. **Modifiers** - These are chemically inert ingredients added to adhesive compositions to alter their end use or fabrication properties. Modifiers include fillers, extenders, thinners, plasticizers, stabilizers and wetting agents.
   
   i. **Fillers** are non adhesive materials which improve working properties, strength or other qualities of the adhesive bond.
   
   ii. **Extenders** have some adhesive properties and are added as diluents to reduce the concentration of other adhesive components and thereby the cost of the adhesive.
   
   iii. **Thinners** are volatile liquids added to modify the consistency or other properties.
   
   iv. **Plasticizers** are incorporated to provide the adhesive bond with flexibility.
   
   v. **Stabilizers** are added to increase its resistance to adverse service conditions.
   
   vi. **Wetting agents** promote interfacial contact between adhesive and adherend by improving the wetting and spreading qualities of the adhesive.
b. Elastomer based adhesives

These materials are based on synthetic or naturally occurring polymers having superior toughness and elongation but lower modulus. Curing procedures vary depending on the type and form of adhesive. These adhesives can be formulated for a wide variety of applications, but they are generally used for their high degree of flexibility and superior peel strength.

These adhesives are used in unstressed joints on lightweight materials. So they cannot be considered as structural adhesives. They are particularly advantageous for joints in flexure. Most of these adhesives are modified with synthetic resins for bonding rubber, fabric, foil, paper, leather and plastic films.

1. Natural rubber (NR)

NR is the most widely used of all elastomers in pressure sensitive adhesives. NR adhesives display excellent flexibility, rich initial tack and good tack retention. The most suitable grade of raw rubber for making adhesive solutions is pale crepe.

2. Styrene butadiene rubber (SBR)

Styrene butadiene rubbers are copolymers of styrene and butadiene. They do not have outstanding adhesive properties but are cheaper and have better heat ageing properties than NR. SBR absorbs less water and reinforced compositions have higher strength retention.

3. Nitrile rubber (NBR)

These materials are predominantly random copolymers of butadiene and acrylonitrile. Usually the copolymer contains enough acrylonitrile so that good resistance to oil and grease is obtained. The adhesive properties improve with increasing acrylonitrile content. NBR adhesives have outstanding shelf stability and high temperature properties. Because of the high polarity of nitrile rubbers, they show good adhesion to surfaces such as textile, paper and wood.
4. Butyl rubber (IIR)

Butyl rubber is a copolymer of isobutylene with a small amount of isoprene. This elastomer is non-crystallizing, has a largely saturated backbone, and is available in a wide range of molecular weights. Butyl adhesives are mainly used in sealants and caulks where resistance to oxidative degradation is important.

5. Chloroprene

Chloroprene is often used in contact cements. The basic components of the adhesives are the elastomer and about 30-35 phr reactive phenolic resin. The more rigid the rubber and complete the crystallization the shorter the open time and greater the ultimate peel strength of the bond. More details are given in Section 1.2.2

c. Thermostet adhesives

Because thermostetting adhesives are densely crosslinked when cured their resistance to heat and solvents is good and they show little elastic deformation under load at elevated temperature. Bonds are ordinarily good to 93-260°C. Creep strength is good and peel strength fair. The major application is for stressed joints at somewhat elevated temperatures. Most materials can be bonded with thermostetting adhesives, but the emphasis is on structural adhesives.

1. Epoxies

The principal epoxies used for commercial adhesives are the reaction products of epichlorohydrin with dihydroxy compounds and include bisphenol A, novolacs and aliphatic glycols. Novolac based epoxies have functionalities greater than two and sometimes over five. They give adhesives of higher crosslink density and consequently, high heat resistance. The wide acceptance of epoxy adhesives is based on its high adhesion to many substrates, low shrinkage and creep, ability to formulate 100% solids and a large number of possible coreactants (151). Epoxies are used to bond metals, glass, ceramics, plastics, wood, concrete and other surfaces.

2. Amino resins

The condensation product of formaldehyde with urea or melamine is the important members of the amino resin class. The largest application of urea
formaldehyde resin is in bonding wood, principally in the manufacture of particleboard. In the furniture industry UF resin finds use as inexpensive adhesives. Consumption of melamine resins is about 1/5 that of urea resins because of the cost differential. Melamine resins are used where light color, resistance to solvents and abrasion are required.

3. Polyesters

Polyester hot melt adhesives are prepared by copolymerisation of multiple diacids or glycols. The principal use of polyester hot melt adhesives is in shoe and textile industries. Unsaturated polyesters which require a catalytic cure are used for the bonding of polyester substrates.

4. Silicones

Silicone adhesives are mainly used in construction industry because of their excellent physical properties, high elongation, chemical inertness and heat resistance.

5. Polyurethanes

Polyurethane adhesives are reactive adhesives, fully formed polymers applied from solution or used as films and aqueous dispersions. In reactive adhesives, the usual isocyanates used are toluene diisocyanate and diphenyl methane- 4, 4'-diisocyanate. Depending on the molar ratio of isocyanate to OH groups, the prepolymers may be either isocyanate or hydroxyl terminated. The isocyanate terminated prepolymers are usually applied from solution. Curing takes place by reaction with moisture often with the help of multifunctional compounds.

d. Thermoplastic adhesives

These materials do not crosslink during cure. So they can be resoftened repeatedly with heat. Thermoplastic adhesives are not ordinarily recommended for use over 66°C, although they can be used up to 90°C in some applications. These materials have poor creep resistance and fair peel strength. They are used mostly in unstressed joints and designs. The materials most commonly bonded are nonmetallic, especially wood, leather, cork and paper. Thermoplastic adhesives are not generally used for structural applications.
1. Ethylene copolymers

These materials are copolymers of ethylene and vinyl acetate. The most important ethylene copolymers for adhesive use are ethylene vinyl acetates (EVA) those containing 25-40% by weight of vinyl acetate. A high VA content in the copolymer leads to greater solubility, high tack in the adhesives, better adhesion to polar surfaces and better low temperature performance. EVA hot melt adhesives are used in bookbinding and pressure sensitive adhesives.

2. Polyamides (nylons)

Polyamides are employed as single component hot melts. A number of hot melt polyamides are produced by copolymerisation of multiple diacids or diamines. Polyamide hot melt adhesives are used in packaging textiles and in furniture, shoe and electronic industries. Excellent adhesion to plasticized PVC, porous materials and metals are reported for polyamides.

3. Poly (vinyl acetate)

PVAc is almost always used in emulsion form. The largest adhesive application of PVAc is in bonding paper. PVAc adhesives are used in bookbinding, bag seaming, tube winding, cup adhesives, remoistenable adhesives on stamps and envelopes, and for bonding various films to cellulosic materials. Polyvinyl alcohol derived from PVAc is used as a component of PVAc emulsions.

4. Poly (vinyl acetal)

Two commercial resins of this type of materials, poly (vinyl formal) and poly (vinyl butyral) are produced by the reaction of poly (vinyl alcohol) with formaldehyde and n-butyraldehyde respectively. They are used in structural bonding, primarily of metals, and for the manufacture of automotive safety glass. Poly (vinyl butyral) combined with plasticizers, extending resins and waxes are used as interlayer in laminated automobile safety glass. It currently dominates this area internationally.
5. Acrylics

Acrylic adhesives are derived from acrylate or methacrylate esters. An important industrial application of acrylic emulsions is in bonding nonwoven fabrics. Acrylates are used very widely in pressure sensitive adhesives. The principal constituents of these adhesives are either butyl or octyl acrylate, along with polar monomers such as acrylic acid or acrylamide.

Advantages of acrylic adhesives are tolerance for oily and otherwise poorly prepared surfaces, rapid bonding at room temperature, low shrinkage during cure, high peel and impact strength combined with excellent shear strength, good environmental resistance and elevated temperature properties (152).

e. Adhesive alloys

These are made by combining resins of two different chemical nature chosen from the thermosetting, thermoplastic or elastomeric classes. The thermosetting resin, chosen for high strength, is plasticized by the second resin, making the alloy tougher, more flexible and more resistant to impact. The adhesive utilizes the most important properties of each component material. They are commonly available as solvent solutions and as supported and unsupported films.

Adhesive alloys used include epoxy – phenolic, epoxy – polysulphide, epoxy – nylon, nitrile – phenolic, neoprene – phenolic, vinyl – phenolic, polyvinyl acetal – phenolic etc.

1.2.2 Neoprene adhesives

Polymer structure of neoprene is determined by the manner in which the monomer 2 chloro-1, 3-butadiene reacts with the growing polymer chain. Upon polymerisation, chloroprene may take any of four isomeric forms shown in Fig.1.16

\[
\begin{align*}
H & \quad \text{Trans 1, 4 addition} \\
\text{Cl} & \quad \text{Cis 1, 4 addition}
\end{align*}
\]
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**Fig. 1.16 Structure of neoprene**

The proportions of these configurations in the polymer determine the amount of crystallization (trans 1, 4) and reactivity towards vulcanization (1, 2 addition). Rapid bond strength development of neoprene adhesives is associated with crystallization of trans configuration in which there is no side group bulkier than chlorine atom.

**Different grades of neoprene are**

*Neoprene AC*: General purpose, quick setting adhesive elastomer containing about 90% trans 1,4. It has good stability and cohesive strength.

*Neoprene AD*: Similar to AC with better colour and viscosity stability.

*Neoprene AF*: Carboxylated, slow crystallizing rubber, develops cohesive strength rapidly and has excellent resistance at elevated temperatures.

*Neoprene HC*: The most rapidly crystallizing type and hence suitable for cold setting, heat sealable adhesives.

*Neoprene FB and FC*: Slow crystallizing, high viscosity fluid elastomer.

*Neoprene AT*: Highly reactive peptizable polymer that can be used as a base for pressure sensitive adhesives requiring high peel strength and flame resistance.

*Neoprene AG*: High gel polymer, provides improved application properties.

*Neoprene AH*: Dispersable, non crystallizing, chemically peptizable polymer.

*Neoprene W*: General purpose elastomer, non crystallizing, contains 85% trans 1,4 segments, good tack and low cohesive strength.

Neoprene adhesives are used as elastomeric binders because of high bond strength, bonding range, high ultimate strength and creep resistance, adhesion to
many surfaces, durability, flexibility, chemical resistance and resistance to burning. Strength of neoprene is associated with crystallization as the polymer is deposited from solution (153). Rapid bond strength development of neoprene contact adhesives is associated with crystallization resulting from high level of trans configuration in which there are no side groups bulkier than chlorine atom. The temperature and solvent resistance can be considerably increased by additional crosslinking with phenolic resins which also improves tack and adhesion. Thermal resistance is enhanced further by addition of bivalent oxides of the second main group and subgroup metals such as calcium and zinc. By increasing the amount of resin the heat resistance is raised, the elongation reduced and therefore brittleness of the adhesive layer enhanced. A 40-45% resin level seems to be the best compromise.

CR types with medium or strong crystallization tendency are preferred. CR is soluble in aromatic chlorinated hydrocarbons, in some esters, ketones and also in mixtures of certain non-solvents. The nature of the phenolic resin used influences the open time and peel strength to a great extent. The content of methyl groups and dimethylene ether bridges are the key factors which have to be coordinated with the crystallization tendency of CR. If the crystallization rate is high non-or less basic reactive phenols is of advantage (154).

A typical neoprene contact adhesive contains 100 parts neoprene, 45 parts t-buty1 phenolic resin, 5 parts MgO, 2 parts ZnO and an antioxidant. Phenolic resin first reacts with MgO in the presence of water resulting in a three dimensional system. MgO also functions as an acid acceptor. Neoprene contact cements have important uses in shoe industry, automotive and construction industry.

1.2.3 Phenolic adhesives

Phenolics are condensation products of phenol and formaldehyde. A large variety of phenolic resins are possible depending on (1) choice of phenol, (2) P: F ratio (3) type and amount of catalyst used (4) time and temperature of reaction.

Phenolic adhesives employed are provided either as one component, heat curable liquid solutions or powder, or as liquid solutions to which catalysts must be added. In general phenolic resin exhibits adhesive functions in all kinds of applications. Their adhesion to most materials is very good due to the marked
polarity of the phenolic structure. Disadvantages are their brittleness, the high curing temperature and pressure required and the limited shelf life of resol grades.

In structural adhesives, the phenolic resin for metal/metal and metal/rubber bonding are combined with elastomers or thermoplastics. By these combinations the characteristic properties of both can be utilized and specific requirements met by the ratio of resin and elastomer. As soft components polyvinyl acetate, NBR, polyamides and polyacrylates are preferred. The elongation, elasticity and resilience of the phenolic resin is improved considerably especially at low temperature by this binding. The toughening action of such polymer blends is attributed to chemical reaction and the morphology of the cured system. Because of the limited solubility of the thermoplastic or elastomeric component a discrete, discontinuous phase develops in the cured phenolic matrix. Crack propagation is considerably minimized by the two-phase system and the impact strength therefore improved.

Adhesives based on neoprene and NBR exhibit high green strength and excellent adhesion to various substrates. The strength, temperature and creep resistance can be improved and adhesive cost reduced by the addition of phenolic resins. Chloroprene adhesives yield high peel strength and have outstanding green strength properties. Nitrile adhesives exhibit excellent oil and grease resistance.

An important use of phenolic adhesives is in wood bonding where water resistance is required. Phenolics may be formulated as water dispersions, where penetration into the cell structure of wood is important for the formation of permanent bonds. Resorcinol-formaldehyde condensates are also used as wood adhesives. Resorcinol resins cure at room temperature under mildly alkaline conditions and are therefore used for wood bonding applications.

Unmodified phenolics are mainly used as primers, to prepare metal surfaces for bonding and as binders for such varied products as glass wool insulation mats, foundry sand, abrasive wheels and brakelining composites. Phenolic resins are also used in the manufacture of abrasive devices such as grinding wheels and sand papers. Laminates of various fabrics are prepared by impregnating the sheets with phenolic resin (155).
Other phenols used are cresol, p-nonyl phenol, p-phenyl phenol, p-tertiary butyl phenol, p-amyl phenol and p-octyl phenol. Phenols substituted at either the ortho or para positions are only difunctional, hence the resins are incapable of crosslinking to a useful thermoset structure. The meta substituted isomer is trifunctional and therefore crosslinking will occur.

1.2.4 CNSL based adhesives

The high polarity and inherent tackiness of phenolic materials and the ease with which liquid to solid conversion can be accomplished make CNSL a desirable starting material for adhesive formulations (156).

There are many reports and patents describing the use of CNSL polymers in adhesives. In these formulations resins derived from CNSL by various polymerisation and/or modification techniques are employed. Details are given in (157).

CNSL based adhesives exhibit admirable properties to meet the growing demand for quality and durability in bonding plywood. Low grade wood impregnated with CNSL resin shows remarkable upgrading of quality. These resins are used for the preparation of particleboards, bamboo boards, coconut leaf based boards etc. where both quality and cost effectiveness could be simultaneously achieved.

Polymerisation of CNSL with H₂SO₄ as the catalyst followed by compounding with aldehyde type hardeners leads to cold setting adhesives (158). Polymerized CNSL obtained using HCl, HNO₃, MnO₂, maleic acid or stearic acid as catalyst was found to be a good plywood adhesive (158). Alkali catalyzed CNSL-phenol- formaldehyde condensates compounded with CuCl₂ or CaCO₃ are excellent adhesives for plywood (160). Cold setting adhesives meeting Indian Standards specifications have been prepared from alkali catalyzed CNSL-phenol-formaldehyde resin and p-toluene sulphonic acid (161). Cure time of adhesives obtained from CNSL, phenol and formaldehyde was reduced when KMnO₄ was used as accelerator (162). CNSL modified phenol-formaldehyde resins have been reported as useful adhesives for heat bonding metals to polymers (163). Heat curable adhesives have been prepared using a formulation consisting of CNSL resin and epoxy resin (164). Polymerisation of CNSL mixed with
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paraformaldehyde has been used as cements for corrosion resistant tanks (165). An increase in self adhesion strength with storage time was observed for PCNSL modified NR (166).

In this study, adhesives consisting of resins derived from CNSL and neoprene rubber have been investigated for rubber-to-rubber, rubber-to-metal and metal-to-metal bonding.

1.3 AGE RESISTORS FROM CNSL

The incorporation of CNSL has been found to improve the properties of rubber products. It aids processing and enhances the vulcanization properties (68). It also helps the incorporation of ingredients into rubber, increases its resistance to moisture, resistance to crack and cut and thermal stability.

1.3.1 Mechanism of ageing

The ageing of polymers occurs through a free radical process. Any form of energy — heat, light or mechanical stress can break polymer bonds to form carbon radicals (C) to start the degradation process. In the presence of oxygen, peroxy radicals (COO.) are formed. The peroxy radical abstracts hydrogen from the polymer to generate another carbon radical and a hydroperoxide (COOH). The hydroperoxide decomposes under heat to form two or more free radicals, an alkoxy radical (CO ') and a hydroxyl radical (HO '). Each of these radicals can abstract a hydrogen atom from the polymer backbone to form yet more carbon radicals. Each time additional free radicals are generated. Two free radicals can combine to terminate each other, which results in new crosslinks. Polymers with many double bonds provide many attachment sites for polymer radicals, leading to many crosslinks. These polymers become stiff and brittle consequently.

Other polymers undergo reversion or chain scission during ageing. Scission is favoured in polymers that are branched or have many side groups. During ageing alkoxy or carbon radicals are generated which undergo beta scission or unimolecular cleavage to lower molecular weights. These polymers degrade by becoming soft and tacky.
The exposure of rubber products to elevated temperature during the service life will result in gradual degradation of the product so that ultimately it may no longer fulfill its function. The rate at which this degradation takes place will be greatly accelerated under aerobic conditions, heat acting as catalyst for the oxidation process (167).

Various ageing processes are

a. **Oxidative ageing** – Oxidation of rubber vulcanizates is technologically important since the absorption of only a small amount of oxygen (1%) by rubber vulcanizates results in considerable change in physical properties. Natural and synthetic rubbers are attacked by oxygen and the reaction is accelerated by heat, light and the presence of certain metallic impurities which catalyze the decomposition of peroxides to form free radicals.

b. **Accelerated oxidation in the presence of heavy metal compounds**

Many heavy metal compounds, like copper and manganese have a catalytic action on the oxidation of rubber vulcanizates. Even traces of (0.001 wt %) copper and manganese compounds are able to accelerate the oxidation of rubber vulcanizates

c. **Heat ageing in the absence of oxygen**

Various reactions can take place in the absence of oxygen—thermal decomposition of crosslinks, continuation of inter or intramolecular network or shifting of crosslinks without change in the total numbers

d. **Fatigue**

When rubber is subjected to prolonged mechanical stress changes, cracks will slowly develop in the material and they grow until they lead to complete breakage of the article. Higher temperature and higher frequency of stress change accelerate crack formation.

e. **Ozone crack formation**

When vulcanizates are exposed to weather conditions in a static extended mode, cracks appear perpendicular to the direction of the applied stress. Small amounts of ozone in the atmosphere are the cause. Without extension of the
vulcanizates cracks are not formed. A critical extension has to be exceeded in any case before cracks show up. With increasing extension, the number of cracks formed per unit area and time increases rapidly. The speed of ozone crack formation depends on temperature and humidity of air. Totally saturated elastomers are ozone resistant.

f. Crazing effect

When an unstressed vulcanizate is exposed to weather, especially prolonged sunlight, unoriented cracks can develop on the surface. The surface can, after prolonged irradiation become brittle.

g. Frosting phenomena

Frosting is caused by the action of warm, moist, ozone containing atmosphere on vulcanizates.

1.3.2 Phenolic age resistors

Age resistors react with the agents oxygen, ozone, light, weather and radiation which are responsible for the deterioration process. This in turn prevents or slows the polymer breakdown, improves the ageing qualities and extends the service life of the product involved (168).

Phenolic resin can give thermally stable crosslinks. The service life of sulphur cured vulcanizates can be improved by using PF resins. In the case of certain rubbers like IIR, NBR and SBR phenolic resin leads to crosslinking of the rubber and this improves the ageing behaviour. CNSL based resins are prospective candidates for this modifying action on rubbers. Retention of tensile modulus, tensile strength and elongation at break of natural rubber vulcanizates containing phosphorylated CNSL (PCNSL), 2-ethyl hexyl diphenyl phosphate and aromatic oil after ageing has been investigated (169,170). The vulcanizates containing PCNSL showed good retention of tensile properties after ageing due to the post-curing reactions during the ageing period (171). The effect of addition of paraffin oil, vegetable oil, castor oil and CNSL to natural rubber compounds has been compared in terms of the mechanical properties (172). Polymerized CNSL has been recommended as a substitute for DOP, DBP for nitrile rubber and neoprene rubbers (173). CNSL- phenol- formaldehyde resin when incorporated into rubber
articles improves resistance towards cracking and action of ozone (174). Sulphur vulcanized NR containing CNSL possesses greater resistance towards oxidation (175). The formation of a network bound antioxidant (78) or the formation of phenolic sulfides in situ during the vulcanization (79) have been used to explain the antioxidant activity of CNSL derivatives in natural rubber vulcanizates. The steric effect due to long tail substituents, has been also reported as an important factor (50). The alkyl substituents could trap both alkyl and peroxy radicals and increase antioxidant activity (80). CNSL condensed with formaldehyde has been recommended as an effective antioxidant for SBR (176). Cardanol is used as vulcanizing agent for IIR (177). Modification of NR with 10-15 phr of PCNSL resulted in improvement in tensile properties along with a lower degree of stress relaxation at high shear ratios and strain levels (178). Bromo derivatives of PCNSL improved the flame retardant characteristics of NR vulcanizates (179). Rheological studies on blends of NR and PCNSL indicates the plasticizing effect of PCNSL and good compatibility between NR and PCNSL (180). PCNSL lower the activation energy of vulcanization of NR (181).

In this study, CNSL is used in the resin form as well as naturally occurring oil for modifying the ageing properties of various elastomers.

1.3.3 Other age resistors

a. Antioxidants

Antioxidants are substances that retard oxidation by atmospheric oxygen at moderate temperatures. Oxidation by atmospheric oxygen is a free radical chain reaction and can be inhibited at initiation and propagation steps.

All commercial important antioxidants fall into four classes (182) - amines, phenols, metal salt of dithioacids and bound antioxidants.

1. **Amine antioxidants** are strong protective agents but discolor and stain to various degrees. Examples are diphenylamine, naphthylamine, alkylamine, quinoline, phenylenediamine etc.

2. **Phenol** is less discoloring than amines. Most of the commercial antioxidants are of this type. eg. styrenated phenol, 2,2,4 - trimethyl-1,2-dihydroquinoline. In high temperature applications, polynuclear phenols generally are preferred over monophenols because of their lower sublimation rates.
3. **Metal salts of dithioacids** act as hydroperoxide decomposers and propagation inhibitors and are used in conjunction with other antioxidants, particularly phenols for rubber, petroleum products and plastics.

4. **Bound antioxidants** are copolymerized into the elastomer chain. The main advantage of such a system is low antioxidant extractability in applications where the elastomer is in contact with solvents capable of extracting conventional antioxidants.

According to their mode of action antioxidants are classified as primary or chain breaking and secondary or preventive antioxidants

1. **Chain breaking antioxidants** interfere with the chain propagation steps of polymer degradation. These antioxidants terminate the chain by
   i. **Free radical traps** which interact with chain propagating RO₂ radicals to form inactive products. Quinones and conjugated molecules can function as free radical traps.
   ii. **Electron donors** give electron to peroxy radical thus stabilizing the system
   iii. **Hydrogen donors** are the most commonly used chain terminating antioxidants. Inhibitors of aromatic amine type interfere with oxidative chain propagation by competing with the polymer for peroxy radicals.

2. **Preventive antioxidants**
   i. **Light absorbers**: Ageing induced by light can be prevented by using photostabilizers like hydrobenzophenone derivatives, benzotriazole derivatives, metal complexes of different metals etc.
   ii. **Metal deactivators**: These are strong metal ion complexing agents that inhibit catalyzed initiation. eg. Ethylene diamine tetra acetic acid.
   iii. **Peroxyde decomposers**: These reduce hydroperoxides to alcohols without substantial formation of free radicals. eg. zinc dialkyl dithiophosphates.

Most conventional antioxidants trap the peroxy radicals or decompose the hydroperoxide. Amines and phenols are radical traps for peroxy and alkoxy radicals. Phosphites are peroxide decomposing antioxidants.
b. Antiozonants

Atmospheric ozone degrades polydiene rubbers by reacting directly with polymer main unsaturation. The most effective compound for ozone protection under static and dynamic stress are nitrogen substituted p-phenylenediamines. They increase the critical energy necessary to form ozone cracks. Therefore crack formation will start at higher extension and crack growth rate will be reduced.

c. Ageing protection against hydrolysis

Elastomers containing hydrolysable groups in the rubber matrix or in the side chain can be degraded by moisture. Ageing protectors for such rubbers should react with steam and moisture faster than rubber eg. carboimides

d. Ageing protectors against crazing

Ageing protectors used against crazing are alkylated phenols. The quantities used lie between 0.5 – 2 phr.

e. Ageing protectors against frosting

The best protection against frosting is obtained by proper choice of fillers and vulcanization accelerators. To some extent p, p’ diaminediphenyl methane acts against frosting.

f. Ageing protectors against fatigue

The most effective fatigue protectors are aryl/alkyl-substituted p-phenylenediamines

g. Ageing protectors against rubber poison

The protection of rubber vulcanizates against Cu and Mn depends on a complex formation of the damaging ion. Ethylene diamine tetraacetic acid can act as copper protector.

h. Ageing protectors against heat ageing

For the selection of ageing protectors for heat resistant vulcanizates their volatility is important. The volatility depends strongly on the molecular structure. The least volatile protective agent yields the highest high temperature resistance.
1.4 POLYMER WOOD COMPOSITES FROM CNSL.

Composite wood products may be produced using wood fibers, flakes, chips or shavings or veneers. During the manufacturing process these materials are often combined with different glues, resins, water repellents and preservatives to produce sheet boards. Addition of CNSL increases the heat resistance of phenolic molding compositions (183). Major composite wood products include (1) particleboard (from wood flakes, shavings or splinters) (2) fiberboard (from fibers of wood) (3) plywood (from one or more veneers) (184).

Acid catalyzed CNSL - formaldehyde resins cured with CuCl₂ have been used as adhesives in the manufacture of particleboard (185). Alkali catalyzed CNSL- formaldehyde resins have been recommended as bonding materials for the preparation of particleboard (186). Composite panel showing excellent ablation characteristics were developed from CNSL (187). Properties of particleboards from hemp fibre and CNSL (188) and coffee husk and CNSL (189) have been reported. Particleboard were prepared from rice husk by mixing them with resin prepared by the condensation of CNSL with formmalehyde and an alkaline catalyst (190). Medium density fiberboards have been moulded comprising coir fibre, CNSL and formaldehyde (191, 192). Jute reinforced composite laminate have been manufactured by soaking jute in a CNSL- modified formaldehyde phenol copolymer and pressing together several layers of the soaked jute (193). Fire resistant coconut pith sheets for use as building materials have been prepared by mixing coconut pith and adhesives prepared by copolymerising CNSL with orthophosphoric acid and neutralizing the polymer before mixing it with formaldehyde and HMTA (194). Mechanical and thermal properties of boards made with kenaf fibers and CNSL have been investigated (195). Central Building Research Institute (CBRI), Roorke, India has developed medium density composite doors containing coir fiber, CNSL and paraformaldehyde (196). A novel resin has been developed by the Centre for Advanced and Renewable Materials, Bangor, Wales based on CNSL primarily for use in particleboard (197).
1.4.1 Particleboard

Wood waste of the wood working industry induced the idea of particleboards. The story of the growth of the particleboard industry may be found in the review article by Klauditz (198). Particleboards are made from almost any form of wood residue except bark.

a. Wood fillers - different forms

1. **Cut flakes** - These are prepared by slicing wood into flat thin particles in which the grain direction of wood lies in the plane of the particle. With this type of particles high length to thickness ratio can be developed. Such particles orient very well in the plane of the board, so that maximum bending strength and dimensional stability can be achieved.

2. **Planar shavings** - Planar shavings tend to have undesirably high bulk because of their curled nature, and to reduce their bulk, the shavings may be passed through a mechanical reduction treatment to split them and eliminate curl. Compared to flakes, shavings have a lower net length to thickness ratio. Planar shaving boards tend to develop higher strength in the direction perpendicular to the plane of the board. A detailed study of the use of planar shavings in particleboard has been made by Heebink et al. (199).

3. **Splinter** - Splinter is produced from solid wood residue by human milling. Splinter is produced without any cutting action. Instead the wood is broken down by a hammering or smashing action. This breakdown process tends to produce comparatively blunt particles in which length to thickness ratio of the particles is still less favorable than is obtained from pure planar shavings. The actual shape of the particle depends on the species used and moisture content (200).

4. **Sawdust** - Sawdust represents a still lower grade of wood residue. The work by Klauditz and Buro (201) explores the use of sawdust in particleboard as a mixture with high quality flakes.

5. **Bark and sander dust** - These materials are wood residues of the lowest value. Bark does not have the oriented fiber structure of wood and therefore has low strength. Sander dust appears as a residue from a plywood operation, and in greater quantities from a particleboard mill.
b. Ingredients of particleboard

1. Adhesives

i. Thermoset binders— Commonly used thermoset adhesives include phenol formaldehyde, urea formaldehyde and melamine formaldehyde.

a) **Phenol formaldehyde** – PF is available as powdered resin and as liquid resin. Liquid resin is a water dilutable aqueous resin containing small amounts of caustic soda. Powdered phenolic resin has one particular process advantage in boards made from flakes. These long flakes do not fluidize readily. Powdered resin mechanically mixed with the flakes tends to distribute uniformly over the particles. The performance of the synthetic resins as particleboard binders has been studied by Carroll (202). The efficiency of these resins depends on the proportion of the resin binder and the moisture content of the wood. Excess moisture content tends to plasticize the resin and can also retard the cure of the resin. CNSL based resin can be used in the present context as the adhesive.

b) **Urea formaldehyde** – The major virtues of UF resin are low cost, rapid cure, process convenience and clear colour. The resin is commonly supplied in the form of an aqueous resin solution containing 60-65% solids and with viscosity in the range of 200-500 cp. It is also available in powdered form which can be reconstituted to an aqueous solution, a form that is more suitable for shipment to isolated board plants.

Two main objections to UF resin now used are its tendency to release formaldehyde fumes when the finished board is exposed to heat and humidity and the lack of complete durability of the resin especially towards moisture (203). If the durability of the particleboard is inadequate for an intended application UF resin may be modified by addition of resorcinol-formaldehyde or MF resin.

c) **Melamine formaldehyde** – MF resins are used primarily for decorative laminates, paper treating and paper coating. They are more expensive than PF resins. MF resins may be blended with UF resins for certain applications.
ii. Proteinaceous and thermoplastic binders

Other binders used in particleboard manufacture are proteinaceous adhesives and thermoplastic adhesives. Proteinaceous adhesives have high inherent viscosity which is unsuited for spray application and their water resistance is generally poor. eg. Soybean glue, caseine glue.

Inorganic binders used are portland cement, magnesite cement and gypsum. The finished product is low in bending strength, high in compressive strength and is resistant to fire and insect attack.

2. Additives

Particleboard retains many of the properties of wood from which it is made. For most applications, the properties of these boards are adequate. For special applications, the properties of the boards may be modified by the addition of chemical agents to provide additional properties such as water repellence, fire resistance and resistance to decay or insect attack.

i. Paraffin wax – Paraffin wax imparts water repellency to board (204). The amount of wax used is 1-1.5% referred to dried wood. A higher percentage reduces binder wetting and adhesive strength (205).

ii. Fungicides and insecticides – For a few applications of particleboard, wood does not have sufficient resistance to attack by fungi and insects. Resistance to fungi can be improved by the addition of pentachlorophenol in amounts not more than 1-2% of the wood (206). Tri butyl tin oxide or fluorine compounds in quantities up to 1.5% are also used (207).

iii. Flame retardants – The requirements of flame retardance can be met by adding flame retardant materials. Ammonium hydrogen phosphate and ammonium polyphosphate are preferred. They may be used in combination with halogen compounds. The addition of inorganic substance like vermiculate or perlite has been recommended but board strength is reduced.
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c. Properties and uses of particleboard

Table 1.7 shows the requirements for different grades of particleboard as specified by American National Standards for particleboard ANSI A208.1 (NPA 1993)(208).

<table>
<thead>
<tr>
<th>Grade</th>
<th>Internal bond (MPa)</th>
<th>MOR (MPa)</th>
<th>MOE (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>0.9</td>
<td>16.5</td>
<td>2400</td>
</tr>
<tr>
<td>H-2</td>
<td>0.9</td>
<td>20.5</td>
<td>2400</td>
</tr>
<tr>
<td>H-3</td>
<td>1</td>
<td>23.5</td>
<td>2750</td>
</tr>
<tr>
<td>M-1</td>
<td>0.4</td>
<td>11</td>
<td>1725</td>
</tr>
<tr>
<td>M-S</td>
<td>0.4</td>
<td>12.5</td>
<td>1900</td>
</tr>
<tr>
<td>M-2</td>
<td>0.45</td>
<td>14.5</td>
<td>2225</td>
</tr>
<tr>
<td>M-3</td>
<td>0.55</td>
<td>16.5</td>
<td>2750</td>
</tr>
<tr>
<td>LD-1</td>
<td>0.1</td>
<td>3</td>
<td>550</td>
</tr>
<tr>
<td>LD-2</td>
<td>0.15</td>
<td>5</td>
<td>1025</td>
</tr>
</tbody>
</table>

H= density > 800 kg/m³, M=density 640 to 800 kg/m³, LD= density <640 kg/m³
M-S refers to medium density; special grade added to standard grades M-1, M-2 and M-3. Grade M-S falls between M-1 and M-2 in physical properties.

Table 1.8 shows the requirements for different grades of particleboard as per IS 3087-1985
Table 1.8
Physical and mechanical properties of flat pressed single layer particleboard (IS 3087-1985)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>500-900 Kg/m^3</td>
</tr>
<tr>
<td>Moisture content</td>
<td>5-15%</td>
</tr>
<tr>
<td>Water absorption (24h soaking)</td>
<td>50%</td>
</tr>
<tr>
<td>MOR</td>
<td>11 N/mm²</td>
</tr>
<tr>
<td>Tensile strength (perpendicular to surface)</td>
<td>0.8 N/mm²</td>
</tr>
</tbody>
</table>

Particleboard is used for furniture cores and as underlayment.

1.4.2 Plywood

In general, plywood is a material made of at least three layers of wood, mostly veneers, with application of adhesives, pressure and heat (209). Plywood is generally classified into interior and exterior grades.

Exterior type plywood will retain its glue bond when repeatedly wetted and dried or otherwise subjected to weather and is intended for permanent exposure. Within each type there are a number of panel grades based on the quality of veneers and the panel construction.

a. Ingredients of plywood

Non modified resols catalyzed by NaOH are used for weather resistant plywood. In order to adjust wetting and avoid excessive penetration and to obtain a uniform joint thickness, diluents and fillers are almost always used. Rye or wheat flour can be used for interior grades and non-swelling fillers like coconut shell flour for exterior grades. Apart from cost reduction the brittleness of the adhesive joint is reduced by these additives.

b. Properties and uses of plywood

Plywood has high strength-to-weight ratio and strength-to-thickness ratios. It has excellent dimensional stability along its length and across its width and minimal
edge swelling. Plywoods are used as roof sheathing, subflooring and numerous applications in panelling and furniture apart from countless industrial applications.

1.4.3 Fiberboard

Fiberboard includes hardboard, medium density fiberboard and insulation board. Because wood is fibrous by nature, fiberboard exploits the inherent strength of wood to a greater extent than does particleboard. To make fibers, bonds between the wood fibers must be broken by attrition milling. This can be accelerated by water soaking, steam heating or chemical treatments. A number of classifications of fiberboards can be given according to the appearance, method of production, kind of application and specific gravity (210)

a. Ingredients of fiberboard

Only wood of inferior quality and industrial wood is used for the production of fibers. The bark is not completely removed because its presence up to 15% does not affect the properties of fiberboard substantially. Sawdust can also be added up to 30%. In general, fiberboards can be produced without bonding agents, using only the bonding ability of the fiber. In order to improve mechanical properties and to reduce water absorption and swelling, phenolic resins are used as bonding agents. Urea resins are also used. Urea resins are used for boards which are not subjected to high humidity.

Dry resin content for boards is 1-3% calculated on dry fiber weight. The PF resin is precipitated out of a diluted aqueous solution by acidic chemicals like diluted sulphuric acid or aluminium sulphate and fixed to the fiber. Hydrophobic agents like wax and paraffin reduce water absorption and swelling. The amount of wax is normally within the range of 1% based on the weight of the dry fiber. Furthermore, flame retardants, fungicides and insecticides, release agents and other improving materials like drying oils can be added.

b. Properties and uses of fiberboard

The most familiar application is acoustical tile. In building construction, insulation board panels find use as boards for poured-in-place concrete, rigid roof insulation for built up roofs, and low cost single backing.

Medium density panels have found acceptance as siding. Sound transmission from one room to another is reduced through the use of insulation board products.
Medium density board is used in place of solid wood in many furniture applications (211).

Hardboard is widely used in building construction for paneling, siding, decking and in manufactured products such as garage doors. In automobiles it has been used for door panels, for a package shelf, and for interior roof linings.

1.5. CNSL BASED PHENOLIC RESIN

By virtue of its phenolic nature CNSL can be condensed with formaldehyde to give PF type resins. Phenolic resin discussed in the earlier section can be prepared starting from CNSL by similar methods. Reactions of CNSL are discussed in Section 1.1.5 and preparation of CNSL based resins in Section 2.3. The long chains in CNSL impart flexibility due to internal plasticizing, resulting in the formation of soft resins at elevated temperature unlike phenol- formaldehyde resins which are hard (212).

1.6 SCOPE AND OBJECTIVES OF THE WORK

CNSL can be polymerized in a variety of ways: addition polymerisation through the side chain double bonds, condensation polymerisation through the phenolic ring, oxidation polymerisation etc. Several modifications are possible due to its special structural features. CNSL is cheap, renewable and underutilized. It can replace phenol in many applications. Greater utilization of CNSL as a monomer for industrial polymer products can be an attractive proposal in view of its low cost, abundant availability and chemically reactive nature. By using CNSL in place of phenol, phenol derived from petrochemicals can be conserved and a cheap agro-byproduct can be utilized.

The overall objective of the study is to develop new applications for CNSL in the polymer field.

Specific objectives of the work can be stated as follows

1. To synthesize CNSL-phenol-hexa resin and study the effect of varying parameters phenol: formaldehyde and CNSL: phenol ratios on the properties of the synthesized resin.
2. To study the adhesive properties of blends of neoprene and CNSL based resin for bonding metal-to-metal, metal-to-rubber and rubber-to-rubber.

3. To study the effect of synthesized CNSL based resin as age resistant for the elastomers NBR, SBR, CR, IIR, EPDM and NR.

4. To develop particleboard from wood waste and CNSL based resin.
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