# CASHEW NUT SHELL LIQUID AND ITS DERIVATIVES
# IN
# POLY (VINYL CHLORIDE) FORMULATIONS

BY

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Submitted
In fulfilment of the requirements of
the degree of
**DOCTOR OF PHILOSOPHY**

**Centre for Materials Science & Technology**
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**April, 1988**

DEDICATED TO MY PARENTS

# CERTIFICATE

This is to certify that the thesis entitled "Cashew nut shell liquid and its derivatives in poly (vinyl chloride) formulations", being submitted by Swapan Kumar Dhara to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. Swapan Kr. Dhara has worked under our guidance and supervision and has fulfilled the requirement for submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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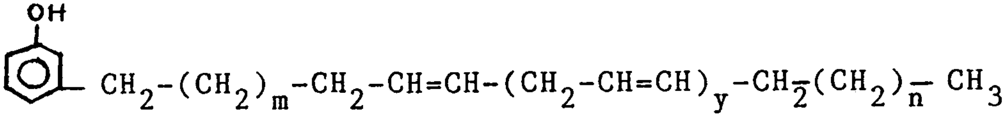
# ABSTRACT

The diminishing amounts of petroleum and coal-based feed stocks has led to rapid progress in isolation, synthesis and characterization of a multitude of renewable resources. In the present studies, the objective was to extend potential application areas of cashew nut shell liquid (CNSL) which is a byproduct of cashew industry. Because of its phenolic nature and presence of a long alkyl side chain it can perform the dual function of a stabilizer as well as a plasticizer. In terms of tonnage consumption, poly (vinyl chloride) is one of the most important plastic material available today. Success of PVC in any field is dependent on careful attention to compound formulation. Therefore it was considered of interest to investigate the potential application of CNSL in PVC formulations.

Cashew nut shell liquid is a dark coloured viscous liquid. Major components of CNSL were separated by fractional distillation under reduced pressure as well as under atmospheric conditions. Reduced pressure distillation gave two fractions which were collected at 205°C and 215-220°C. The residual viscous tar was neglected. The low boiling fraction was identified as a mixture of saturated or monoenyl cardanol as well as some cardol on the basis of mass spectroscopy. The higher boiling fraction-2 which was yellow in colour was found to be cardanol. Presence of one -OH group was indicated by acetylation

studies as well as $^1$H- NMR. Attempts were made to identify the structure of the side chain which was containing 15 carbon atoms. For this purpose $^1$H- NMR and mass spectroscopic techniques along with elemental analysis and IR studies were carried out. Following general structure could be assigned to this fraction on the basis of $^1$H-NMR studies.



$$\text{C}_6\text{H}_4(\text{OH})-CH_2-(CH_2)_m-CH_2-CH{=}CH-(CH_2-CH{=}CH)_y-CH_2-(CH_2)_n-CH_3$$

when $y = 1$ then $m + n = 6$

$y = 2$ then $m + n = 3$

Distillation of CNSL under atmospheric conditions also gave two fractions at 298°C and 315-320°C along with a tar residue. These fractions were of darker colour and indicated presence of oxidised structures.

Acetylation and benzoylation of fraction-2 was done by acetic anhydride/pyridine and benzoyl chloride respectively. The structure of these derivatives was confirmed by elemental analysis, FT-IR, $^1$H-NMR techniques. These acetylated derivatives were also coloured.

Solution degradation of PVC was carried out in nitrogen atmosphere using ethyl benzoate, CNSL fraction-2 and CNSL acetate and CNSL benzoate as solvent. Degradation of PVC was carried out at 180°, 200° and 220°C for 120 min. in nitrogen atmosphere in all the above mentioned solvents. Crosslinking reaction during PVC degradation was restricted in CNSL or CNSL derivatives.

The rate of dehydrochlorination was slow initially in fraction-2, CNSL acetate and CNSL benzoate and gradually increased. The induction period for dehydrochlorination was evaluated by extrapolating the steady state portion of the acid evolved vs. time plot. Induction period was found to be 35-55 min in CNSL, 16-39 min in CNSL acetate and 7-30 min in CNSL benzoate. Induction period depended on the polymer concentration and the temperature of dehydrochlorination. Induction period decreased with the increase in temperature from 180°-220°C and polymer concentration. In ethyl benzoate the induction period was lowest.

The order of dehydrochlorination depended on temperature and solvent and varied from 0.33 to 1.42 in CNSL fraction-2, 0.69 to 0.91 in CNSL acetate and 0.15 to 1.7 in CNSL benzoate in the temperature range of 180°C-220°C.

Apparent activation energy of dehydrochlorination of PVC was higher in CNSL fraction-2 (180 ± 4 KJ/mole) and almost similar in CNSL acetate and CNSL benzoate (117 ± 4 KJ/mole).

Polyenes containing 6 or less number of double bonds were found to be predominant in PVC degraded in ethyl benzoate. Fewer polyenes were observed having double bonds greater than ten in degraded PVC. The optical density of degraded solution containing CNSL fraction-2 and its acylated derivative was higher. But this was primarily due to change in colour of CNSL fraction on heating. The polyene sequence distribution in PVC samples degraded in presence of these derivatives for longer duration (i.e. more than 30 min), therefore, could not be estimated in these samples.

Tg of PVC was found to be 85°C and on addition of 10% CNSL acetate and CNSL benzoate Tg was found to be 82° and 83°C respectively. Specific heat (Cp) was found to be 0.229 J/g. deg with PVC. With 10% addition of CNSL fraction-2, CNSL acetate and CNSL benzoate, specific heat was found to be 0.374, 0.260 and 0.278 J/g. deg respectively. The plasticization efficiency was very low.

TG traces were also recorded in nitrogen atmosphere (flow rate 60 mL/min) at a heating rate of 10°C/min in the temperature range of 50°-500°C. From the TG traces, initial deomposition temperature (IDT) and final decomposition temperature were determined by extrapolation. The temperature of maximum rate of weight loss ($T_{max}$) was also determined from differential thermogravimentric traces. Addition of 10% CNSL to PVC resulted in a reduction in IDT, $T_{max}$ and $T_f$ by about 15°C. However no significant decrease in these characteristic temperatures was observed in the presence of CNSL acetate and CNSL benzoate.

TG of formulated PVC compounds containing 5, 10 and 15 phr of CNSL and CNSL acetate was carried out in nitrogen atmosphere. IDT of PVC formulations was 15°C lower when compared with PVC. However, all formulations showed similar IDT, $T_{max-1}$ and $T_{f-1}$. Char yield at 400°C was lower in PVC formulations than in PVC alone showing thereby the loss of some additives from PVC in this temperature range. These results indicated that substitution of chlorinated paraffin wax by CNSL fraction-2, and CNSL acetate does not alter the thermal stability.

Fusion time was found similar when CNSL based formulations were compared with chlorinated paraffin wax based formulation. CNSL acetate based formulations showed lower fusion time at higher phr level when compared with equivalent formulations based on CNSL fraction-2. Torque values were found to decrease with an increase in CNSL and CNSL acetate, in these formulations. Significant improvement in stability was observed when 10-15% CNSL fraction-2 and CNSL acetate were used. CNSL acetate based formulations showed improved stability in comparison with CNSL fraction-2 based formulations. Apparent viscosities were found to decrease with an increase in CNSL fraction-2 and CNSL acetate.

In comparision to formulation containing chlorinated paraffin wax, an increase in elongation at break and decrease in tensile strength was observed in presence of CNSL fraction-2 and CNSL acetate.

CNSL acetate based formulations showed higher volume resistivity when compared with equivalent CNSL fraction-2 based formulations.

Heat ageing of CNSL fraction-2 and CNSL acetate based formulations showed insignificant loss of volatiles at ageing temperature.

Loss of mass was also insignificant but oxygen index decreased with the increase in CNSL fraction-2 and CNSL acetate.

Based on these studies a mechanism has been suggested to account for the role of CNSL and its acylated derivatives on PVC degradation.

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