

## Hydroxylated Rendered Chicken Oil as Novel Processing Oil for Nitrile Rubber

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### Abstract

The most important aspect that encourages the research in fats/oils is their renewable nature. Among the renewable resources, vegetable oils constitute about 80% of global oils and fat production while the remaining 20% is of animal origin. Chicken waste from slaughter houses has become a major source of pollution in the state of Kerala. The effect is intense in tourist places like Wayanad, where the consumption of chicken by the visitors also comes in to picture. A dry rendering process of the slaughter waste can yield rendered chicken oil (RCO) with a high level of unsaturation. In the present work, hydroxylation of rendered chicken oil was carried out in a two step reaction; the first reaction is the epoxidation of the unsaturation which is followed by epoxy ring opening at high temperature to form the hydroxylated product. Rendered Chicken oil and its hydroxylated form have been evaluated as processing aid in nitrile rubber (NBR), while incorporating particulate fillers such as carbon black and silica. Their performance as processing aids has been compared with two already existing and established processing aid in elastomer processing, such as aromatic oil and naphthenic oil. The results of the study reveal that there is a considerable reduction (89 %) in the iodine value of rendered chicken oil with hydroxylation. This clearly indicates the reduction in the unsaturation of RCO due to the hydroxylation reaction at the double bond site. It can be seen that when the viscosity drops regularly with the shear rate in the case of RCO, an increase in viscosity with the shear rate has been obtained in the case of HRCO. The optimum cure time of the sample containing HRCO has been found to be higher than that of sample containing RCO. This means that hydroxyl groups in the processing oil retard the cure process. Better tensile strength values are observed for the NBR vulcanizate with HRCO as the processing aid. The higher values of tear strength for HRCO in the case of silica filled NBR vulcanizates indicate that the secondary interactions between hydroxy groups in HRCO and those in silica is reflected very well in the tear strength values. Greater hardness than all other mixes has been observed with HRCO as a processing aid. Similar behavior can be observed in the case of silica filled samples also. The research not only addresses the serious pollution issues due to the dumping of chicken waste from slaughter houses but also offers a novel processing aid for nitrile rubber.

### INTRODUCTION

Fats are a wide group of compounds that are generally soluble in organic solvents and generally insoluble in water. Chemically, fats are triglycerides: triesters of glycerol and any of several fatty acids. Fats may be either solid or liquid at room temperature, depending on their structure and composition. Although the words "oils", "fats", and "lipids" are all used to refer to fats, in reality, fat is a subset of lipid [1]. "Oils" is usually used to refer to fats that are liquids at normal room temperature, while "fats" is usually

used to refer to fats that are solids at normal room temperature. "Lipids" is used to refer to both liquid and solid fats, along with other related substances, usually in a medical or biochemical context, which are not soluble in water. The word "oil" is also used for any substance that does not mix with water and has a greasy feel, such as petroleum (crude oil), heating oil, and essential oils, regardless of its chemical structure [2].

A saturated fat is a fat that consists of triglycerides containing only saturated fatty acids. Saturated fatty acids have no double bonds between the individual carbon atoms of the fatty acid chain. That is, the chain of carbon atoms is fully "saturated" with hydrogen atoms. There are many kinds of naturally occurring saturated fatty acids, which differ mainly in number of carbon atoms, from 3 carbons (propionic acid) to 36 (hexatriacontanoic acid). Various fats contain different proportions of saturated and unsaturated fat. Examples of foods containing a high proportion of saturated fat include animal fat products such as cream, cheese, butter, ghee, suet, tallow, lard, and fatty meats [3]. Certain vegetable products have high saturated fat content, such as coconut oil, cottonseed oil, palm kernel oil and chocolate (primarily from its cocoa butter [4]). Many prepared foods are high in saturated fat content, such as pizza, dairy desserts, bacon and sausage [5].

An unsaturated fat is a fat or fatty acid in which there is at least one double bond within the fatty acid chain. A fatty acid chain is monosaturated if it contains one double bond, and polysaturated if it contains more than one double bond. Where double bonds are formed, hydrogen atoms are eliminated. Thus, a saturated fat has no double bonds, has the maximum number of hydrogens bonded to the carbons, and therefore is "saturated" with hydrogen atoms.

### **Poultry farming and rendered chicken oil**

Poultry farming is the raising of domesticated birds such as chickens, turkeys, ducks, and geese, for the purpose of farming meat or eggs for food. Poultry are grown in great numbers with chickens being the most numerous. More than 50 billion chickens are raised annually as a source of food, for both the meat and eggs [6]. Chickens raised for eggs are called layers while chickens raised for meat are called broilers [7]. In total, the UK alone consumes over 29 million eggs per day.

Broiler chicken has become the cheapest source of animal protein in Kerala. It is estimated that about 5.3 Lakh birds are slaughtered daily in the state [8]. This results in the production of 350 tonnes of broiler chicken waste per day. The annual Production of broiler waste is to the tune of 15 crore kg. The disposal of this much waste is a daunting task. In India, these wastes are collected by agents from the chicken stall at the rate of Rs.4 per kg and are now disposed off in un-inhabited areas and in water bodies. This leads to ground and surface water pollution, obnoxious odour and health hazards due to breeding of microorganisms, parasites and house flies. This poses a serious threat to the environment and becomes a health hazards to human beings.

Among the different bio-secure and sanitary disposal methods, rendering is an excellent way to recycle a troublesome waste material in to a good feed ingredient [9]. The end products are carcass meal and rendered chicken oil. Carcass meal can be used as feed ingredient and fertilizer [9]. But the rendered chicken oil (RCO) which has high free fatty acid content does not have much commercial value at present.

There are also exotic oils composed of fatty acids with other type of functionalities such as hydroxyl, epoxy and other groups. The presence of many types of fatty acids indicates that at the molecular level, these oils are composed of many different types of triglycerides with diverse levels of saturation. Newly developed genetic engineering techniques [10] are likely to make unique contribution to the expansion of raw materials available to the chemical industry such as increasing the content of individual fatty acids or dramatically changing the oil quality by introduction of new fatty acids. Triglycerides contain several reactive positions that can act as starting points in different reactions. These include ester groups, c=c bonds and alpha-position of ester groups.

It is also worth mentioning here that the chemical modification of the unsaturation (double bonds) in these renewable resources are a good choice for investigations leading to the production of environmental friendly but advanced performance materials. Among these chemical modifications, epoxidation [11] has a prominent place because of the simplicity in the process, better economics and the combination of useful properties in the final product. Also as the epoxy groups can be easily converted to a large number of other functional groups, the epoxidised oils can be a potential resource for a large number of other industrially important raw materials. More interestingly, the high temperature heating of the ERCO can result in a ring opening reaction leading to the formation of hydroxylated rendered chicken oil (HRCO).

The chemical modification of oil-based fatty compound has recently made important advances. Chemical modification of fatty compounds is an important route to obtaining useful products from renewable feed stock. Industrial chemistry has focused on the carboxylic functionality of fatty acids [12]. The basic oleo chemicals are free fatty acids, methyl ester, fatty alcohols and fatty amines, with glycerol as bi-product, although synthesis methods have been recently applied [13] extensively to fatty compounds for the selective functionalisation of the alkyl chain. Moreover enzymatic and microbial transformation [14] constitutes another vast branch of chemistry that still needs to be explored. Therefore, there is potential to develop new, efficient and environmentally friendly reaction pathways for new products or to find new application for one that already exist.

The unsaturation present in animal fat can be chemically modified to a value added product by a complicated reaction called epoxidation [15]. Epoxidation of fatty acids is a reaction of a c-c double bond with active oxygen, which results in the addition of an oxygen atom, converting the original double bond in to a three membered epoxide (oxirane) ring [11]. It is also worth mentioning here that the chemical modification of the unsaturation (double bonds) in these renewable resources are a good research choice for the production of environmental friendly but advanced performance materials which may sacrifice the economy but can certainly satisfy the society.

One of the important reactions that can be used to improve these fats and oils performance is epoxidation. Epoxidation processes are becoming popular due to its role as a starting material to many other reactions. An epoxide is cyclic ether with three ring atoms. This ring approximately defines an equilateral triangle which makes it highly strained. The strained ring makes epoxides more reactive than other ethers. Fatty epoxides are used directly as plasticizer that is compatible with Poly (vinyl chloride) [PVC] and as stabilizers for poly (vinyl chloride) [PVC] resins to improve flexibility, elasticity and toughness and to impart stability of polymer towards heat and UV

radiation. The high reactivity of oxirane ring enable epoxides to act as raw material for a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds olefinic compounds and polymers like polyesters, polyurethanes , and epoxy resins [16-19]. The oils were epoxidised successfully by performic acid generated ‘in situ’ by reacting formic acid (methanoic acid) with hydrogen peroxide. The reaction time was optimized and the possibility of controlling the level of epoxidation was attempted by limiting the reagents; hydrogen peroxide and methanoic acid [11].

Ring-opening of epoxidised vegetable oils is an established method of introducing Polymerisable groups into glycerides. Several triglycerides-based polyols suitable for polyurethane synthesis were synthesized by reacting epoxidised vegetable oils with different chemical reagents. The conversion of epoxy groups to secondary hydroxyl groups was accomplished by (a). Reacting with hydrochloric or hydrobromic acid, resulting in halogenated polyols (b) an acid-catalysed ring opening reaction with methanol, yielding a methoxylated polyol or with water, forming vicinal hydroxyl groups [20].

Epoxidation of soybean oil as potential source of high temperature lubricants was done by A.Adhvaryu et.al. [21]. Epoxidation and hydroxylation of vegetable oil were done by Padmasiri K.Gamage et.al. [22]. Epoxidation of karanja oil was done by Prerna Singh Chauhan et al., [22] and that of linseed oil were done by G. Ligadas et.al. [23]. Epoxidation of Palm Kernel oil Fatty acids were done by Michael Ni Fong Fong et.al. [24]. As the epoxy group shows extend of tendency for ring opening in acid medium, studies [25] also focused on the conversion of the epoxy groups to hydroxyl groups [26] and the resulting change in properties.

The present work deals with the hydroxylation of epoxidised rendered chicken oil and the use of hydroxylated rendered chicken oil (HRCO) as processing aid in nitrile rubber (NBR) in the presence of particulate fillers such as carbon black and silica. The curing behavior and mechanical properties of the particulate filled NBR samples containing HRCO as processing aid is compared with sample containing traditional processing oils such as aromatic and naphthenic oils. Primarily, the work addresses one of the serious environmental pollution due to the dumping of chicken waste from slaughter houses. The economic value of the rendered chicken oil can be increased by converting rendered chicken oil into hydroxylated rendered chicken oil, which can show excellent promise as inexpensive, renewable material for industrial applications. Secondly, the work can lead to the production of chemically modified oils which are biodegradable. Also, the work can lead to the production of nitrile rubber products based on silica and carbon black where hydroxylated rendered chicken oil can be used as a processing aid. Compared to other traditional processing aids, such as naphthenic oil and paraffinic oil, rendered chicken oil and its hydroxylated forms are more economic and biodegradable.

## EXPERIMENTAL ASPECTS

### Materials Used

The materials used in the present work and their sources were the following; Rendered Chicken Oil, RCO (obtained from Kerala Veterinary and Animal Sciences University (KVASU), Pookode, Wayanad, Kerala. Aromatic oil and naphthenic oil were obtained from Hindustan Petroleum Corporation Ltd., Mumbai. Formic acid (85%), sodium thiosulphate (99%), chloroform (99%), potassium dichromate, diethyl ether were all obtained from Merck Specialties Pvt. Ltd., Mumbai. Hydrogen Peroxides (32%),

Wij's solution (0.1M Iodine monochloride (ICl) in acetic acid), starch indicator, hydrochloric acid (35%), sodium hydroxide and phenolphthalein were all obtained from Nice Chemicals Pvt. Ltd., Kochi, Kerala. Potassium iodide(99%) was obtained from Thermo Fisher Scientific India Pvt. Ltd., Mumbai. Vulcanizing agents such as sulphur, MBTS (Mercaptobenzthiazyl disulphide), activators (zinc oxide, stearic acid, nitrile rubber (NBR), antioxidant TDQ, fillers (silica and carbon black) etc. were all procured from local rubber chemical suppliers.

### **Methods adopted**

#### **1. Hydroxylation of RCO**

The procedure used was as follows. At first, rendered chicken oil (RCO) and formic acid were poured to a steel container and mechanically stirred and the temperature was controlled. Then, the container was fixed by metal clamp in a water bath with water temperature of 50 °C (with an accuracy of 2 °C and speed of 550 RPM. In order to start the epoxidation, hydrogen peroxide solution (30%) was gradually charged into the mixture during the first 5 hours of reaction, mole ratio of carbon double bonds to hydrogen peroxide (C=C:H2O2) were used :1:1.7. After the charging of H<sub>2</sub>O<sub>2</sub> was completed, the reaction was continued by mixing and controlling the temperature at 50 °C for a further 5 hours .After that, the mixture was cooled down and neutralised by water. Diethyl ether was used to enhance the separation of the oil product from water phase. The final product was dried out by heating less than 50 °C. The replication was performed concurrently. The double bonds are one of the active sites that can react with functional groups. Epoxy groups react with double bonds in an epoxidation reaction to form Epoxidised rendered chicken oil (ERCO). Subsequent hydroxylation reaction was carried out by raising the temperature to 80 °C after the epoxidation and keeping the reaction mixture at this temperature for another 14 hours. At the end of the reaction, the product was treated as described above in the case of epoxidation.

#### **2. Fourier Transform Infrared Spectroscopy**

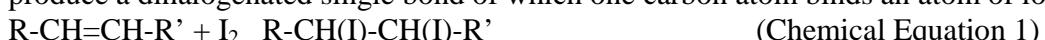
ATR-Fourier Transform Infrared Spectroscopy of samples were taken in ATR-FTIR Spectrometer [Shimadzu, Japan, Model IR Affinity], at St. Thomas College Thrissur, Kerala,

#### **3. Determination of iodine value of oils**

Determination of iodine value of various types of oils and fats was determined by Wij's method. Iodine value or number is the number of grams of iodine consumed by 100 gram of fat. Higher iodine value indicates higher degree of unsaturation.

#### **PRINCIPLE**

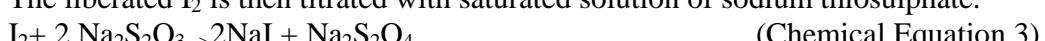
Fatty acids reacts with a halogen (iodine) resulting in the addition of halogen at the c=c bond site. In this reaction, iodine monochloride reacts with the unsaturated bonds to produce a dihalogenated single bond of which one carbon atom binds an atom of iodine.



Both alkene and organo iodine product are colourless. After the completion of addition reaction, excess ICl reacts with potassium iodide [KI] liberating iodine.



The liberated I<sub>2</sub> is then titrated with saturated solution of sodium thiosulphate.



Saturated fatty acids will not exhibit the iodination reaction shown above.

Starch is used as the indicator of the reaction so that the liberated iodine will react with starch to give purple coloured product and thus the end point can be observed. This is due to the formation of Starch – Iodine complex. Sodium thiosulphate solution used in the process is standardized at first using  $K_2Cr_2O_7$  solution.

Experimental procedure employed was as follows.

1g of oil is weighed accurately by difference methods and transferred into iodine flask. 10ml of chloroform is added and warmed slightly. It is then cooled for 10 minutes. 25ml of Wij's solution is added and is shaken vigorously and is then allow the flask to stand for half an hour in dark place. Then 10ml of KI solution is added and is titrated against already standardized  $Na_2S_2O_3$  solution (0.1) until the appearance of yellow colour. 1ml starch indicator is added and again titration is added and again titration is continued till the blue colour disappears. The disappearance of blue colour indicates end point (V2). A blank titration is conducted.

$$\text{Iodine value} = ((V_1 - V_2) * N_1 * \text{equivalent weight of iodine} * 100) / (W * 1000)$$

(Chemical Equation 4)

Where  $V_1$  = Volume of thiosulphate required by the blank

$N_1$  = Normality of thiosulphate required by the sample.

$W$  = Weight of sample

#### 4. Determination of viscosity of oils

Viscosity of oils were determined using Brook Field viscometer, Manual No.M/97-164-F1102, Condition: Normal, at National Institute of Technology (NIT), Calicut, Kerala

#### 5. Mixing of RCO and HRCO with Nitrile Rubber

Mixing of RCO and HRCO with Nitrile Rubber as carried out using a two roll mill which was set for a ratio of roll surface frictional speed of about 1.25:1. Two roll mills are used to mix as homogenize polymer materials. After weighing proper amounts of ingredients the compounding is done on a lab size two roll mill (15×300mm). First NBR is fed in to the nip and it is masticated. After getting a smooth band sulfur is added and then ingredients are added one by one and properly dispersed by cutting and blending. Finally curing ingredients are added. After proper dispersion the compound is sheeted out as 2.5–3.0 mm thickness and grain direction is marked.

The different formulations used for the mixing in the present work are shown in **Table 1**.

**Table 1 Formulations used**

Ingredient	Mix Number								
	1	2	3	4	5	6	7	8	9
NBR	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5
St. Acid	2	2	2	2	2	2	2	2	2
MBT	1	1	1	1	1	1	1	1	1
TDQ	1	1	1	1	1	1	1	1	1
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CB	0	6	6	6	6	0	0	0	0
Silica	0	0	0	0	0	6	6	6	6

Ar Oil	0	6	0	0	0	6	0	0	0
Naph Oil	0	0	6	0	0	0	6	0	0
RCO	0	0	0	6	0	0	0	6	0
HRCO	0	0	0	0	6	0	0	0	6

St. Acid – Stearic Acid, TDQ – polymerized trimethyl dihydroquinoline,

CB – Carbon black, Ar Oil – Aromatic oil, Naph Oil – Naphthenic oil

S – Sulphur

#### **6. Determination of Optimum cure time of the mixed rubber compounds**

The rheometer used in the present work is GOTTFERT ELASTOGRAPH. It is an intelligent rotor, less rotator thrust cure meter with an externally fast acting temperature controlling and homogeneous temperature distribution in the reaction chamber. A rubber compound is subjected to torsion stress by means of oscillatory motion of the lower half of the heated chamber. The torque and the control temperature are recorded and evaluated as a function of time. Optimum cure time was taken as the time needed for the formation of 90 % of the crosslinks, as evidenced by the time taken for the minimum torque value to increase by 90% of the maximum torque.

#### **7. Moulding of rubber compounds**

Moulding process is carried out using the electrically heated hydraulic press at 160°C for optimum cure time determined from the rheographs earlier. Using the control panel, the temperature of the electrically heated platens was maintained at the required value. The mould was placed in between the platens. The maximum pressure applied on the mould can be regulated by the use of pressure switch.

#### **8. Determination of Tensile properties of NBR Vulcanizates**

The INSTRON 4411 was used for measuring the tensile and tear properties of the vulcanizates. Dumbbell shaped test pieces were used for the testing of tensile properties. The type 1 dumbbell of ISO 37 with a 6 mm wide center portion and preferably cut from 2mm thick sheet was used for measurement of tensile properties. Dog bone type samples (90 ° angle) were used for tear testing. The standard rate of grip separation is 500+50 mm/min. (ISO 5893). The testing is carried out 27±2 °C. The elongation at break of dumbbell was also measured using the same INSTRON 4411 using a contact extensometer.

#### **Expression of results**

The quality directly measured in a tear test is the force on the test piece during testing. ISO 34 takes the minimum force realized in the case of crescent and angle methods having obtained the force. The tear strength is given as,

$$TS = F \div D \quad (\text{Equation 1})$$

where, TS = tear strength in kilo Newton per meter of the thickness.

F = the force, D = the thickness

#### **9. Determination of hardness of NBR vulcanizates**

Hardness is defined as a material's resistance to permanent indentation. The shore Durometer uses indenters in the form of truncated cones of specified geometry acting under the force of a calibrated spring with defined relation between force and shore hardness. Shore A instrument operates with a substantially constant spring pressure, varying by 56gf in an 822 gf mean force.

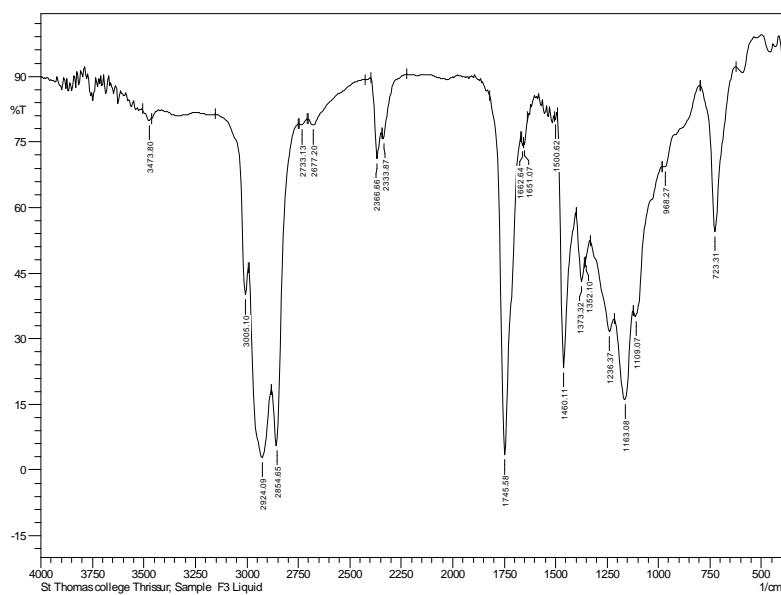
#### **10. Determination of relative density of NBR Vulcanizates**

The relative density was measured using electron densimeter MD – 200S. It adopts Archimedes principle and the determination of density value is based on the density of water 1g/cm<sup>3</sup>. MD – 200S can measure density of solid and liquid materials by density resolution 0.001g/cm<sup>3</sup> except powders and highly viscous liquids. Scale capacity is 0.01 – 200g.

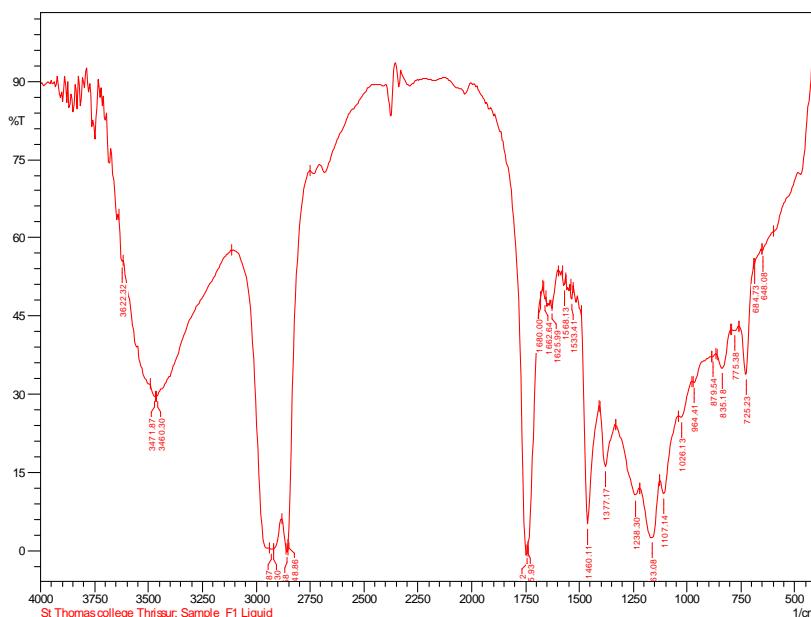
## RESULTS AND DISCUSSIONS

### 1. Attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra of RCO and HRCO are presented in **Figure 1A and B** and the peak assignments to various functional groups are given in **Table 2A and B**.



**Figure 1A. FTIR of RCO**



**Figure 1B. FTIR of HRCO**

The peak due to unsaturated C=C in RCO is visible at 3005 cm<sup>-1</sup>.

**Table 2A. Peaks assignment for RCO**

Sl. No.	Frequency, cm <sup>-1</sup>	Assignment
1	3417	Hydrogen bonded OH peak
2	3005	C=C double bond stretch frequency of unsaturation
3	2924	Asym.C-H stretch frequency of CH <sub>2</sub> ,CH <sub>3</sub>
4	2854	C-H stretch frequency of alkene
5	1745	C=O stretch frequency of ester
6	1460	C-H bending frequency of unsaturated alkene
7	1373	Methyl deformation band (sym.bending of CH <sub>3</sub> )
8	1236	Anti sym. Stretch frequency of ester
9	1163	C-O stretch frequency of ester
10	1109	C-O stretch frequency of O-CH <sub>2</sub>
11	963	C=C str
12	723	C-C bending frequency of saturated carbon

**Table 2B. Peaks assignments for HRCO**

Sl.No.	Frequency, cm <sup>-1</sup>	Assignment
1	3417	Broad peak due to OH stretch
2	2930	Asym.C-H stretch frequency of CH <sub>2</sub> ,CH <sub>3</sub>
3	2858	C-H stretch frequency of alkene
4	1750	C=O stretch frequency of ester
5	1460	C-H bending frequency of unsaturated alkene
6	1373	Methyl deformation band (sym.bending of CH <sub>3</sub> )
7	1238	Anti sym. Stretch frequency of ester
8	1150	C-O stretch frequency of ester
9	1026	C-O stretch frequency of O-CH <sub>2</sub>
10	835	Epoxy group
11	725	C-C bending frequency of saturated carbon

It is interesting to compare **Table 2A and 2B** to note that in the case of epoxidised RCO , the peaks at 3005 cm<sup>-1</sup> is absent due to the conversion of the unsaturation to epoxy group. It is also interesting to note that even after further reaction (hydroxylation) for more hours after epoxidation reaction, there are epoxy groups still remaining in HRCO (**Table 2B**). Also, peak at 3005 cm<sup>-1</sup> due to unsaturation is absent in **Figure 1B** due to its conversion to hydroxyl group via epoxy groups.

## 2. Determination of iodine value of different oils

The results of the determination of iodine value of RCO and HRCO are presented in **Table 3**.

**Table 3. Iodine Values of oils**

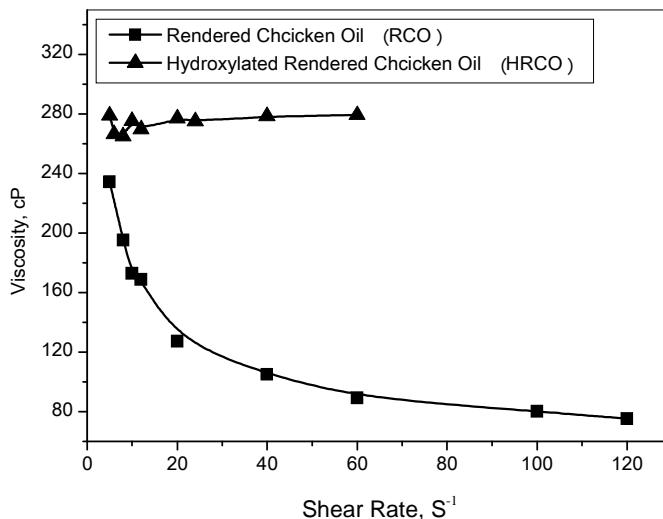
Oil	Iodine Values
Rendered Chicken Oil (RCO)	55.7137
Hydroxylated Rendered Chicken Oil (HRCO)	6.1041

Iodine value of RCO is 55.7137. But the value for hydroxylated sample (HRCO) is 6.1041. It can be seen that there is considerable reduction (89 %) in iodine value of rendered chicken oil with hydroxylation reaction. The reduction in iodine value clearly reconfirms the reduction in the unsaturation of RCO.

### 3. Viscosity measurement of different oils (Brookfield viscometer)

Viscosity measurement values are presented in **Figure 2**.

It can be seen that when the viscosity drops with the shear rate in the case of RCO, a different behavior of the increase in viscosity with the shear rate is obtained in the case of HRCO. This indicates the probable interactions between the hydroxy groups in HRCO during the application of the shear. This also confirms the change in the chemical structure of the oil with hydroxylation.

**Figure 2. Viscosity verses shear rate for RCO and HRCO**

### 4. Rheometric optimum cure time of the NBR compounds

In the use of rendered Chicken Oil (RCO) and hydroxylated rendered chicken oil (HRCO) as processing aid for NBR, in the presence of particulate fillers such as Carbon black and Silica, different formulations used were earlier shown in **Table 1**. The optimum cure time of the NBR compounds are shown in **Table 4**.

**Table 4. Optimum cure time of NBR compounds**

Mix No	Description of Composition	Optimum Cure time ( $t_{90}$ ), min
1	NBR Compound without processing oils and particulate fillers	17.65
2	NBR Compound with aromatic oil and Carbon Black Filler	11.55

3	NBR Compound with naphthenic oil and Carbon Black Filler	18.06
4	NBR Compound with RCO and Carbon Black Filler	15.52
5	NBR Compound with HRCO and Carbon Black Filler	19.94
6	NBR Compound with aromatic oil and Silica Filler	18.06
7	NBR Compound with naphthenic oil and Silica Filler	15.56
8	NBR Compound with RCO and Silica Filler	17.90
9	NBR Compound with HRCO and Silica Filler	21.73

Sample 1 is the control compound without any filler and processing oil. Samples 2-5 contains carbon black filler and samples 6-9 contains silica black filler. The Optimum Cure time value of the sample containing aromatic oil is less than that of naphthenic oil. The Optimum Cure time of the sample containing HRCO is higher than that of sample containing RCO which means that hydroxyl groups in the processing oil retard the cure in the presence of carbon black filler. Similar cure retarding behavior of the epoxy groups in HRCO can be seen in the results of the samples containing silica filler also. The retardation in the cure and the consequent increase in optimum cure time will reduce the production rate of the articles made using the NBR compound.

##### 5. Tensile and tear properties of NBR Vulcanizates

The tensile and tear properties of the NBR Vulcanizates are presented in **Table 5**. It can be seen that the gum vulcanizate has a tensile strength of 3.09 MPa. In the presence of carbon black filler, the value increases considerably. The traditional processing oils such as aromatic oil and naphthenic oils present higher tensile strength values in the presence of carbon black filler while the values of RCO and HRCO are inferior to this. However, better tensile strength values are observed for the NBR vulcanizate with HRCO as the processing aid than the sample with RCO as the processing aid. The same behaviour can be observed in the case of silica filled samples also. This means that the polar interactions between –CN groups in NBR and hydroxy groups in HRCO is operative to a certain extent. But as expected, the interaction between hydroxy groups in HRCO and –OH groups in silica is not reflected in the tensile strength values and therefore, the tensile strength values of sample 9 (NBR sample containing silica and HRCO) is lower than that of sample 5 (NBR sample containing carbon black and HRCO). This means that the reinforcement effect of carbon black is much more effective than the possible polar interaction between hydroxy groups in HRCO and –OH groups in silica.

Usually, when the reinforcement of the filler in NBR occurs, tensile strength increases and this will be reflected in a reduction in the elongation at break. But when a processing oil plasticize the sample, then there will be an increase in the elongation at break. This can be seen in all cases of samples from 2-9 (**Table 5**). In the present cases, RCO present

higher values of elongation at break than conventional processing oils while that of HRCO is lower in the case of black filled samples. But the value for HRCO is higher than that for conventional processing oils in the case of silica filled samples.

The secant modulus values (M-100) (Modulus at 100 % elongation) (**Table 5**) of all the particulate filled NBR vulcanize samples are higher than that of gum NBR vulcanize. As expected, the values are generally higher for carbon black filled samples. The values for RCO and HRCO are higher than that of conventional processing oils such as aromatic oil and naphthenic oil when the filler is carbon black. When the filler is silica, the secant modulus values for RCO and HRCO are lower than that of conventional processing oils.

**Table 5. Mechanical Properties of NBR Vulcanizates**

Mix No	Description of Composition	Tensile Strength MPa	Elongation at break, %	Secant Modulus MPa	Tear Strength N/mm	Hardness Shore A	Density g/cc
1	NBR Compound without processing oils and particulate fillers	03.09	152	0.39	19.38	56	0.997
2	NBR Compound with aromatic oil and Carbon Black Filler	17.00	164	5.69	50.47	81	1.160
3	NBR Compound with naphthenic oil and Carbon Black Filler	15.78	180	8.32	46.14	83	1.215
4	NBR Compound with RCO and Carbon Black Filler	13.65	260	6.64	51.67	81	1.208
5	NBR Compound with HRCO and Carbon Black Filler	15.58	103	13.66	42.89	84	1.158
6	NBR Compound with aromatic oil and Silica Filler	13.52	487	3.99	75.15	84	1.212
7	NBR Compound with naphthenic oil and Silica Filler	17.46	428	5.37	68.87	87	1.232
8	NBR Compound with RCO and Silica Filler	09.45	612	3.52	57.45	83	1.182
9	NBR Compound with HRCO and Silica Filler	11.90	500	4.25	67.08	87	1.234

As far as tear strength is concerned (**Table 5**), there is good improvement in the value for particulate filled NBR vulcanizates. Here, the values are much better for the silica filled NBR vulcanizates. This is true for conventional processing oil as well as RCO and HRCO. The higher values of tear strength for HRCO in the case of silica filled NBR vulcanizates indicate that the interaction between hydroxy groups in HRCO and -OH groups in silica is reflected very well in tear strength values even though it was not reflected in the tensile strength values earlier.

## 6. Hardness

The hardness of NBR vulcanizates, tested using Shore A DUROMETER, are tabulated in shore A units and presented in **Table 5**. From the above results (**Table 5**) it can be seen that both silica filled and carbon black filled nitrile rubber vulcanizates have higher hardness values. Using HRCO as processing aid (Mix no:5 and 9) gives greater hardness than all other mixes. NBR vulcanizates containing HRCO have greater values than those with RCO. The interaction between hydroxy groups in HRCO and –OH groups in silica is reflected in hardness values also.

## 7 Density of NBR Vulcanizates

The density for NBR samples, measured using Densimeter, are given in **Table 5**. From the above results it can be seen that the density of the mixes slightly increases in all NBR samples with particulate fillers such as carbon black and silica. Notable effects of the presence of RCO, presence of epoxy groups in RCO are absent.

## CONCLUSIONS

The present work deals with the hydroxylation of the unsaturation in Rendered Chicken Oil (RCO) through an epoxidation process. The extend of hydroxylation of rendered chicken oil and the consequent decrease in the level of unsaturation was assessed by the decrease in the iodine number and by using Fourier Transform Spectroscopy. The success of hydroxylation was confirmed by the presence of the broad peak at  $3417\text{ cm}^{-1}$  and also by the disappearance of the peak at  $3005\text{ cm}^{-1}$ . Also, there was drastic reduction (89 %) in iodine value of rendered chicken oil with hydroxylation, which indicated a reduction in the unsaturation of RCO with hydroxylation. It could be seen that when the viscosity drops with the shear rate in the case of RCO, an increase in viscosity with the shear rate was obtained in the case of HRCO. The optimum cure time of the sample containing hydroxylated rendered chicken oil (HRCO) was higher than that of sample containing RCO which meant that hydroxyl groups in the processing oil retard the cure. Better tensile strength values were observed for the NBR vulcanizate with HRCO as the processing aid than the sample with RCO as the processing aid. The same behaviour was observed in the case of silica filled samples also. The higher values of tear strength for HRCO in the case of silica filled nitrile rubber (NBR) vulcanizates indicated that the interaction between hydroxy groups in HRCO and –OH groups in silica was reflected very well in tear strength values even though it was not reflected in the tensile strength values. Using HRCO as processing aid gave greater hardness than all other mixes.

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