

Synthesis and Characterization of Chlorinated Oils Based on Unmodified Castor Oil Polyol

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Abstract: Chlorinated oils based on unmodified castor oil polyol were prepared by phosphorus pentachloride (PCl₅) – chlorination. Six (6) number chlorinated oils were obtained using 10, 20, 30, 40, 50 and 60 wt% concentrations of the chlorinating agent respectively. The oils were characterized by physical and chemical methods, as well as by Fourier transform infra red (FTIR) and gas chromatography – mass spectrometry (GC - MS) techniques. These chloro-derivatives of castor oil (by substitution) were all non-drying oils. Results show that PCl₅-chlorination of castor oil polyol has led to reduced viscosity and specific gravity, reduced hydroxyl and saponification numbers, but increased acid and peroxide numbers relative to the base polyol. Chlorination has also enhanced oil polarity. The implications of these on oil property and application are discussed. GC-MS suggested chloro-derivatives obtained as a result of the PCl₅-chlorination included 9, 12 –octadecadienoyl chloride, linoleoyl chloride, linoleic acid chloride, n-caproyl chloride, caproic chloride and caproic acid chloride. The chlorinated oils were found unsuitable for polyurethane (PU) foam synthesis, but could be utilized in fire retardancy, insecticidal/pesticidal and plasticizing applications.

Index Terms: Chlorinated oils; castor oil; properties; applications.

INTRODUCTION

Chemical modification of plant oils is often carried out in order to introduce certain functionalities or chemical entities into the oil structure, thereby improving reactivity and imparting desirable physical and chemical characteristics in them. Modification of plant oils such as soybean, castor, palm, canola, sunflower and rapeseed oils has been a widely reported subject in literature.

Chemically, these oils consist of saturated and unsaturated fatty acids (FAs) tied in triacylglycerol (TAG) units. Chemical modification is important because in the chemical industry, most plant oils are used in form of their modified derivatives (Petrovic *et al.*,2000; Ogunniyi, 2006). Quite often, chemical modification transforms these oils into polymerizable monomers for polymer synthesis (Mutlu and Meier, 2010; Islam *et al.*, 2014). The advantages of these products derived from renewable (natural) green source materials include renewability and abundance, low cost, low emission properties, degradability and ecofriendliness.

Halogenation of plant oils has often led to products with enhanced fire retardancy, greater polarity and plasticizing ability, among other advantages (Yousef *et al.*, 2001). However, the halogenated products are less ecofriendly than their unmodified plant oil base polyols because of their potential toxicity. This makes them suitable candidates for insecticidal and pesticidal applications (Abdul Qadir *et al.*, 2011). Halogenation of plant oils may include chlorination, bromination or iodination, and this can be achieved either by addition or substitution procedures (Yousef *et al.*, 2001, Patel *et al.*, 2004).

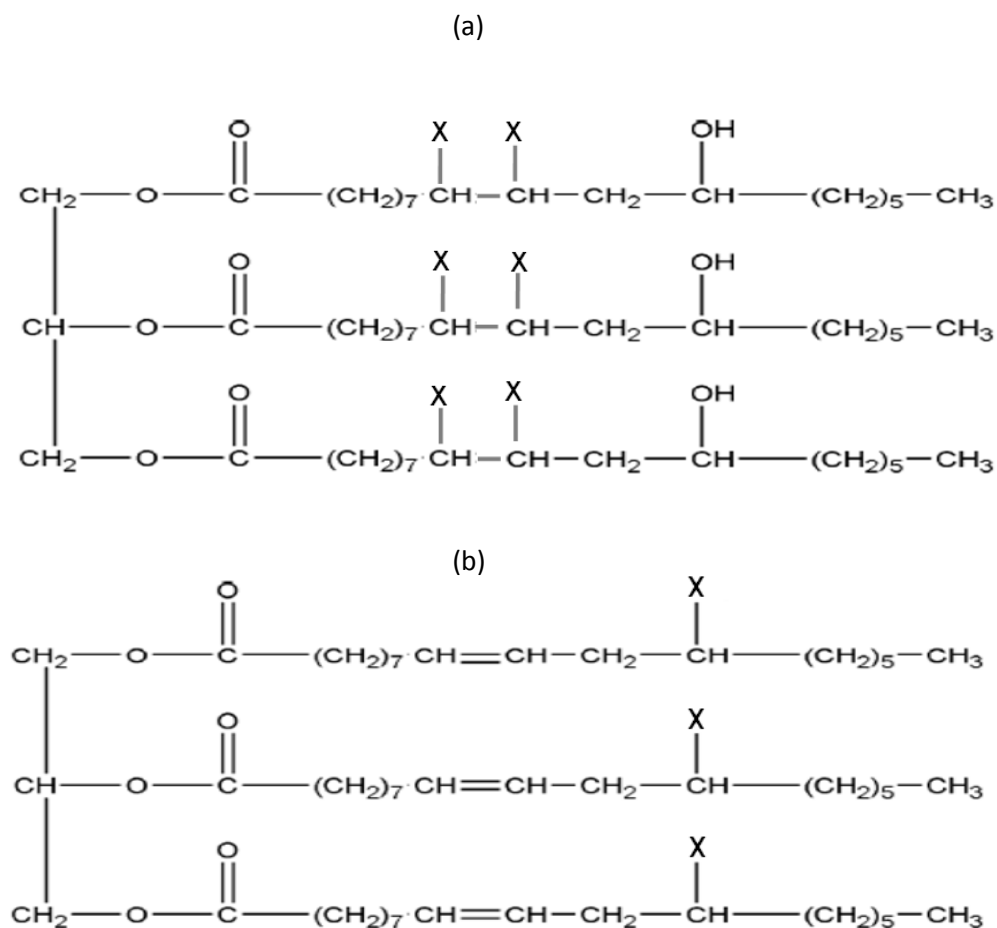


Fig. 1: Halogenated castor oil: (a) by addition; (b) by substitution.

Castor oil is non-edible plant oil obtained from the seeds of the castor plant (*Ricinus communis* Linn). Pure unmodified castor oil contains up to 80 – 90% ricinoleic acid (RA). Chemically, castor oil consists of TAG molecules, each containing three esters of ricinoleic acid or “ricinoleates” (in place of three hydroxyl groups) on a glycerol backbone. The properties of castor oil are therefore largely influenced by this major constituent fatty acid – RA. Castor oil is the only source of an 18-carbon hydroxylated FA with one double bond in each of the FA chains (Conceicao *et al.*, 2007; Chakrabarti and Rafiq, 2008). Other plant oils have to be hydroxylated usually via epoxidation, followed by oxirane ring opening, or by hydroformylation/ozonolysis and subsequent hydrogenation, or by microbial conversion (Petrovic *et al.*, 2000; Zhang, 2008; Tayde *et al.*, 2011; Dworakowska *et al.*, 2012; Saremi *et al.*, 2012). Halogenation of castor oil by addition and by substitution is possible because of the double bond unsaturation at C9, the hydroxyl group on C12 of the RA, and the ester linkages in the castor oil TAGs – three main reaction sites in the oil structure. Thus like other plant oils, castor oil has to be chemically modified for its optimal exploitation and usage.

The objective of this work was to synthesize chlorinated oils from unmodified castor oil polyol using PCl_5 as chlorinating agent, and to characterize the products having in view their potential uses both as end products, and as intermediates in the synthesis of a variety of other castor oil-based products.

MATERIALS AND METHODS

Materials

Castor oil was sourced locally by mechanical (cold-press) extraction from the seeds of castor plant (*Ricinus communis* Linn) at ambient temperature. The virgin oil (obtained as clear, viscous pale yellow liquid) was further purified by filtration through sintered glass (fine mesh screen). This was to eliminate any dust, gum or other particulates present. The chlorinating agent (PCl_5), petroleum ether (40-60⁰ C), diethyl ether and all other reagents were analytical grade reagents supplied by BDH chemicals Ltd, Poole, England, and were used without further purification.

Methods

PCl_5 Chlorination

Method employed by Yousef *et al.* (2001) was adopted with slight modification. 32g of castor oil was dissolved in petroleum ether (40-60⁰C) in 500cm³ distilling flask. 10wt% equivalent of PCl_5 was calculated, measured and added, and the mixture refluxed for 1 ½ hours. The reaction was monitored periodically after every 20 minutes by taking a small portion of the reaction mixture and determining its hydroxyl number. This procedure was repeated using 20, 30, 40, 50 and 60 wt% PCl_5 in the mixture. After each treatment, resultant product was water-washed, dried over anhydrous Na_2SO_4 , and the solvent evaporated under vacuum. The oils obtained were dark and oil colour became darker with increasing concentration of the chlorinating agent (PCl_5).

Decolourization/Bleaching

Ground, purified local clay activated by 2M HCl was used as adsorbent (Akpan *et al.*, 2006). The process involved a hot (90⁰C) adsorbent/oil mixture in a beaker in which the adsorbent constituted 15% of the oil by weight. The mixture was vigorously stirred for 30 minutes, and heating continued to allow the temperature rise to 110⁰C for another 30 minutes. Content was then filtered hot in an oven at 70⁰C.

Characterization of the chloro-derivatives

The unmodified castor oil polyol (control) and its chloro-derivatives were characterized in terms of their physical and chemical properties.

Physical Analysis

Relative viscosity

The relative viscosity of oil (in chloroform) was determined at 30⁰c from viscometric measurements using an Ubbelohde dilution type viscometer with an efflux time of about 120 seconds for the solvent.

Specific gravity

Specific gravity of oil was determined in accordance with AOAC (1990) procedure.

pH

pH of 2.30g dispersion of oil in 15cm³ hot water was determined (after cooling to 30⁰C in a water bath) with the acid of a glass electrode pH meter (HANNA – 209-209R).

Chemical Analysis

Hydroxyl (ASTMD 1957-86), acid (ISO 660:1996), saponification (ISO 3657:2002), iodine (ISO 3961:1996) and peroxide (AOCS, 2009) numbers of oil were determined using indicated standard methods and procedures.

All physico-chemical determinations were performed in triplicate, and an average evaluated in each case.

FTIR and GC-MS analyses

FTIR and GC-MS analytical techniques were used as complementary methods (after chemical methods) for the characterization of structural functionalities in the chlorinated oils. FTIR spectrum of oil was recorded with a Shimadzu 8400S FTIR spectrophotometer over the range 4500 – 350 cm⁻¹ using 10 scans at a resolution of 4cm⁻¹.

GC-MS chromatograms of separated fatty acid methyl esters (FAMES) and other oil components were recorded on a GC-MS QP2010 plus Shimadzu (Japan) instrument, comprising an AOC-20i liquid auto-sampler and a GC equipped with fused silica capillary column (30x0.25mm ID x 1 µm df) coated with 5 phenyl-, 95% dimethyl siloxane polymer. This was interfaced to a mass spectrometer at an interface temperature of 250⁰C. Peak identification was done by comparing peak retention times with reference standards for the individual FAMES.

PU conversion procedure

Obtained chlorinated oils were reacted with excess toluene diisocyanate (TDI) in presence of stannous octoate (gelation catalyst), dimethylaminoethanol (DMAE) (amine catalyst), methylene chloride (physical blowing agent) and silicone oil (surfactant) as per PU foam formulation below (Yusuf *et al.*, 2016).

Table 1: Foam Formulation – NCO/OH ratio (1/1)

Component	Actual weight	Pph (polyol)
Neat/chlorinated CO polyol	50.00	100.00
TDI	49.20	98.20
Methylene chloride	1.50	3.00
Stannous octoate	0.25	0.50
DMAE	0.225	0.45
Silicone oil	0.25	2.50
Water	1.00	2.00

Pph = parts per hundred (polyol)

RESULTS AND DISCUSSION

Physico-chemical properties of the chlorinated oils

Determined physico-chemical properties for the unmodified castor oil polyol (control) have been discussed in an earlier presentation (Yusuf *et al.*, 2015).

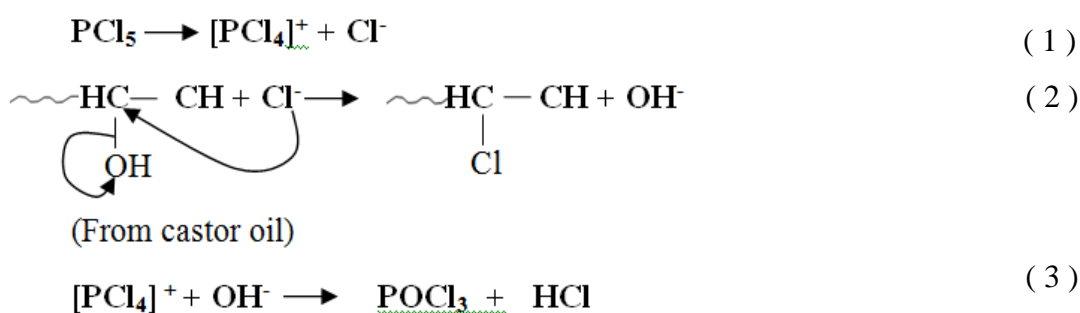
Table 2: Physical characteristics of the chlorinated oils

Property	Wt% PCl ₅						
	0	10	20	30	40	50	60
Specific gravity	0.959	0.950	0.940	0.934	0.925	0.900	0.868
pH	6.16	6.04	5.90	5.85	5.70	5.60	5.50
Relative viscosity	1.86	1.82	1.74	1.62	1.55	1.44	1.21

Table 2 depicts changes in specific gravity, pH and relative viscosity of castor oil polyol with increasing PCl₅ – chlorination up to 60wt% of modifier.

Variation of hydroxyl number (HN) with modifier concentration

In Fig. 2, the higher the PCl₅ content in oil, the more rapid the decline in hydroxyl number. It is observed that both hydroxyl number (Fig. 2) and relative viscosity (Table 2) decreased monotonically as concentration of the chlorinating agent (PCl₅) was increased up to 60wt%. This is mainly because PCl₅ - Chlorination of castor oil is known to proceed by nucleophilic substitution in which hydroxyl groups on C12 of ricinoleic acid chains are replaced with chlorine (Naughton, 1974) (Scheme 1). This translates to diminishing hydroxyl functionality in oil as concentration of PCl₅ increased. However, viscosity, as well as specific gravity of castor oil would increase if chlorinated by addition across its double bonds (Yousef *et al.*, 2001, Ali *et al.*, 2005). Diminishing hydroxyl functionality also resulted in specific gravity decline (Table 2) because of decreasing ability to form hydrogen bonds in the oil structure. Changes in saponification number (SN) of oil (Fig. 2) are related to changes in the average molecular weight of FAs in the oil. According to Ali *et al.* (2005), oil SN and oil molecular weight are inversely related. For the PCl₅ – chlorinated oils, decreasing SN values correspond to increases in oil molecular weight.



Scheme 1: Chlorination of castor oil by substitution using PCl₅ as chlorinating agent.

Variation of other physico-chemical properties

Iodine number (IN)

Iodine number was constant up to about 20wt% PCl₅ concentration, but surprisingly decreased slightly thereafter (Fig. 2). Decrease in iodine number is unexpected as PCl₅ chlorination of castor oil proceeds via substitution. However, there is possibility of random free radical addition at the oil double bond involving HCl molecule generated as by-product via Scheme 1.

This could happen at high concentrations of the chlorinating agent (PCl_5) and at very high temperatures that can promote the thermal dissociation or homolytic cleavage of the HCl molecule. Iodine number is a measure of the unsaturation level in oil. All the chlorinated oils (Fig. 2) had $\text{IN} < 100$, suggesting that they were essentially non-drying oils.

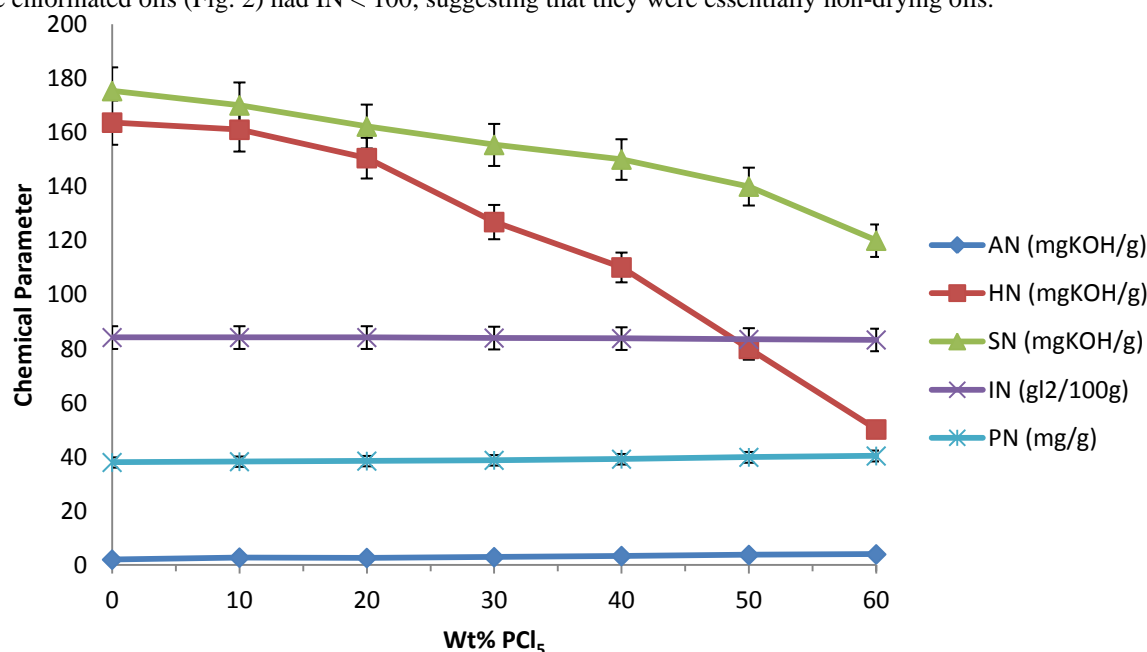


Fig. 2: Variation of chemical parameters with wt% PCl_5 concentration in oil.

Peroxide number (PN)

Fig. 2 shows gradual rise of peroxide number with increasing concentration of the chlorinating agent. Peroxide number is related to the susceptibility of the double bonds in the oil to oxidation. Higher peroxide numbers are indications of low oxidative stability, that is, oil being more susceptible to oxidative rancidity. Higher peroxide numbers with increasing PCl_5 concentration are as a result of the replacement of hydroxyl groups in the oil structure which provide protection to the double bond unsaturation in the oil (ICOA, 2013). Increasing PN of the chlorinated oils relative to that of castor oil suggests shorter shelf life or reduced keeping quality for the former.

pH

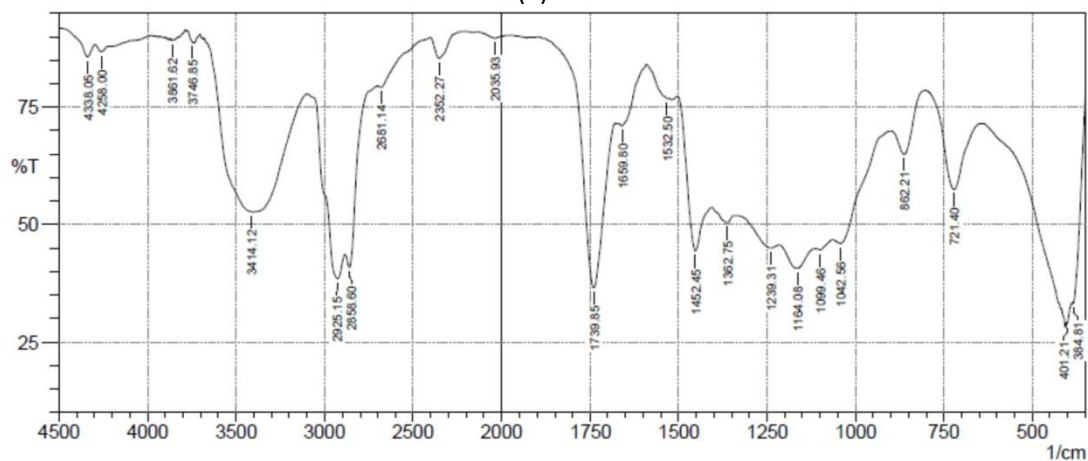
Reduced pH (Table 1) and increased acid number (AN) on chlorination (Fig. 2) were the result of higher free fatty acid (FFA) concentration, likely due to the breaking of ester bonds from the oil's TAG ester linkages (Ramzya *et al.*, 2014).

FTIR and GC – MS

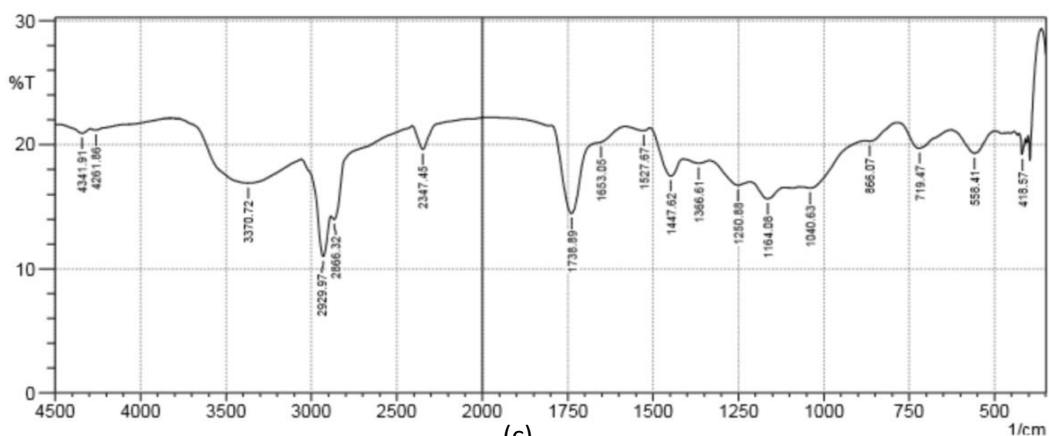
FTIR

Figs. 3 (a-d) represent the FTIR spectra for castor oil polyol (control), and chlorinated oils containing 20, 40 and 60wt% PCl_5 . Carbon-chlorine (C-Cl) absorption peak (due to C-Cl stretching) featuring between $600\text{-}500\text{cm}^{-1}$ and hydroxyl absorption featuring as broad band between $3600\text{-}3300\text{cm}^{-1}$ were the main absorption peaks of interest. The appearance of absorption peaks within the frequency range $582\text{-}500\text{cm}^{-1}$ in the FTIR spectra of the chlorinated oils (Figs. 3b –d) is a confirmation of castor oil chlorination. The chlorinated oils were thus characterized by simultaneously monitoring the growth of C-Cl absorption ($582\text{-}500\text{cm}^{-1}$) and the diminishing hydroxyl presence ($3453\text{-}3291\text{cm}^{-1}$) with increase in concentration of chlorinating agent (PCl_5).

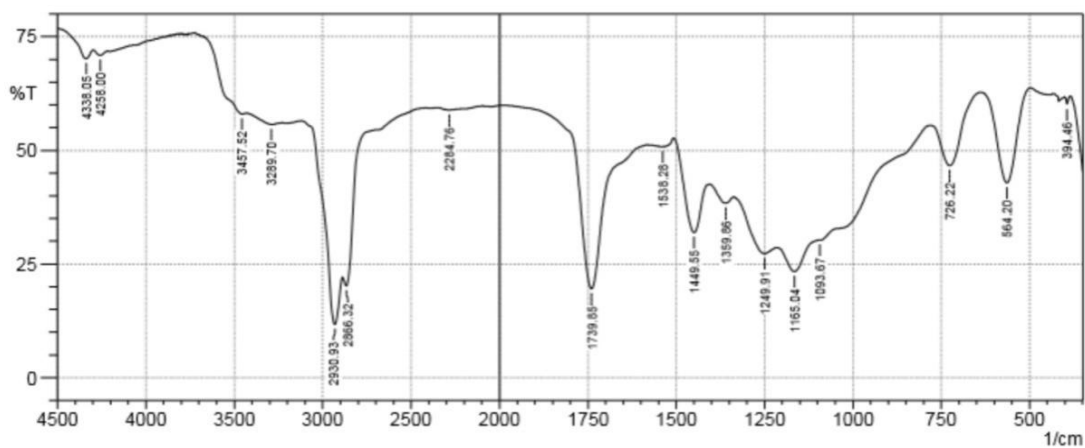
(a)



(b)



(c)



(d)

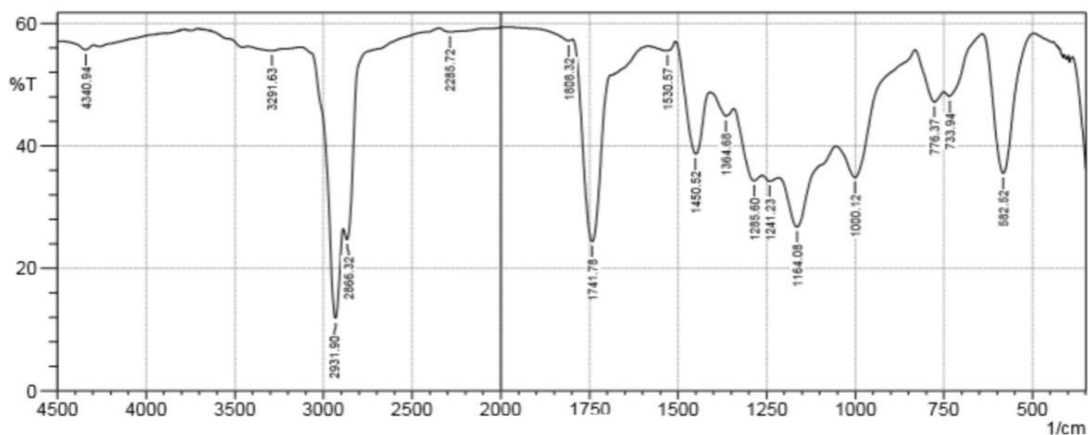
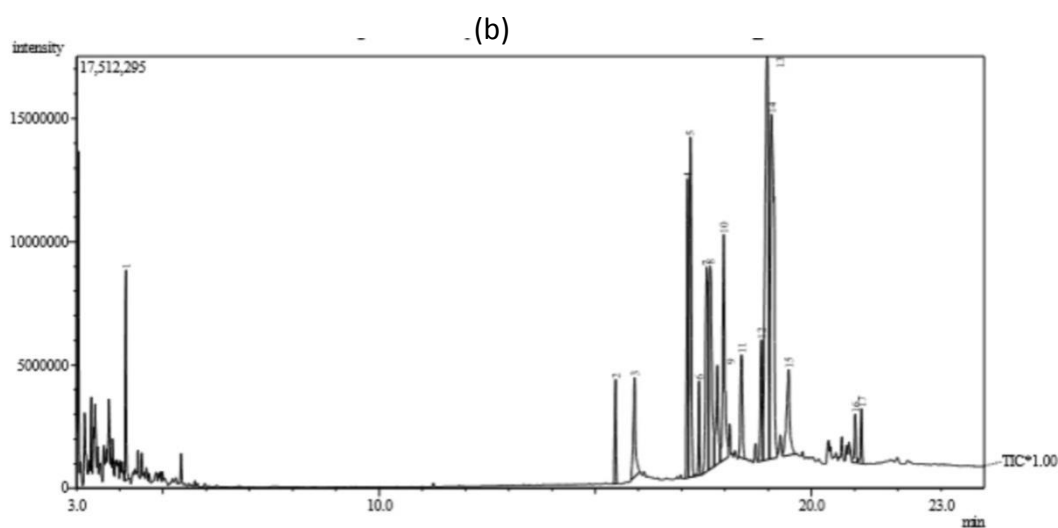
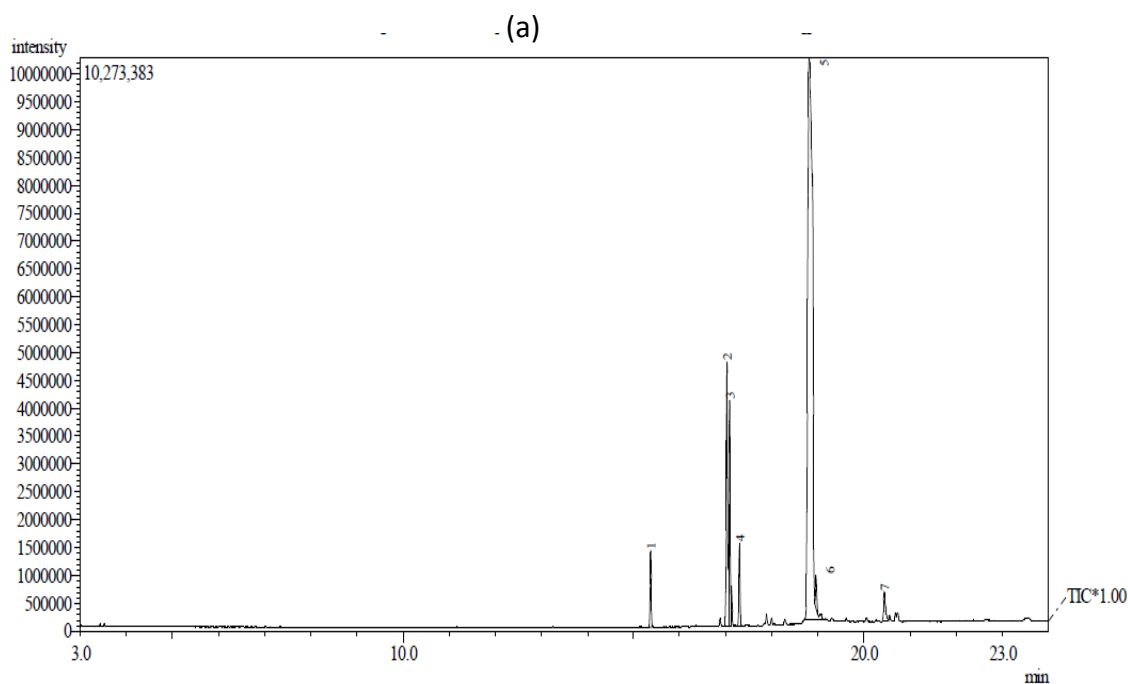


Fig. 3: FTIR spectra for the chlorinated oils: (a) pure castor oil; (b) 20wt% PCl_5 ; (c) 40wt% PCl_5 ; (d) 60wt% PCl_5 .

GC-MS

GC-MS chromatograms for the products (Figs 4a-d) show signals for the castor oil polyol and the chlorinated products at various peaks, and corresponding to different retention times.

The chlorinated products identified by mass spectral library matching against reference standards were 9,12-octadecadienoyl chloride, linoleoyl chloride, lineoleoyl chloride, linoleic acid chloride, hexanoyl chloride, n-hexanoyl chloride, caproyl chloride, n-caproyl chloride, caproic chloride and caproic acid chloride.



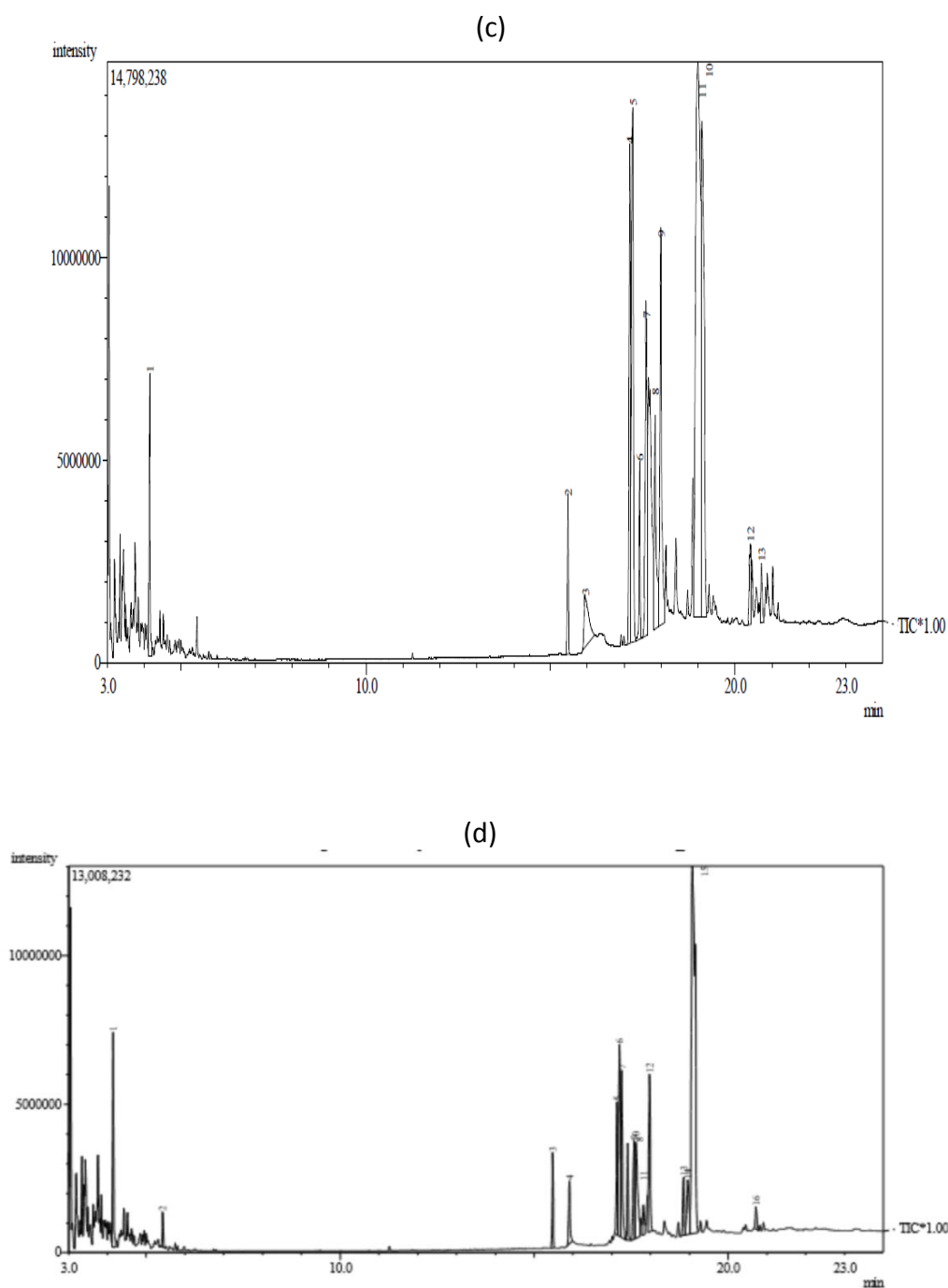
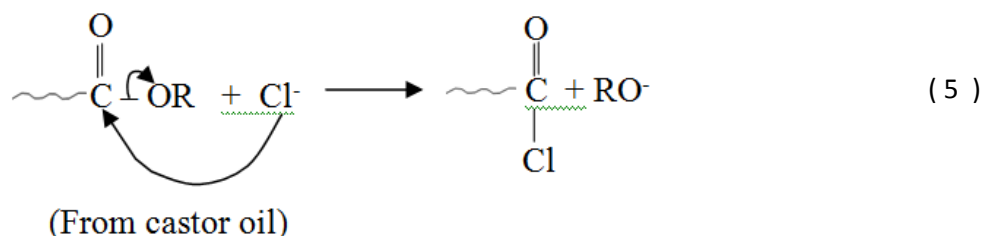


Fig. 4: GC-MS chromatograms for the chlorinated oils: (a) castor oil; (b) 20wt% PCl_5 ; (c) 40wt% PCl_5 ; (d) 60wt% PCl_5

Number of peaks, peak intensity and peak area in respect of the chlorinated products all generally increased with increase in the concentration of the chlorinating agent in polyol, with the polyol containing 60wt% PCl_5 recording six such peaks, having peak areas of 4.91, 8.89, 4.58, 2.30, 3.37 and 37.28 respectively. The presence of small quantity of acid chlorides (linoleic and

caproic acid chlorides) in the chlorinated oils was unexpected, though this might suggest the possibility of chloride ions from PCl_5 dissociation (Scheme 1) reacting (at random) with castor oil TAGs at ester linkages (Scheme 2).



Scheme 2: Probable mechanism for PCl_5 -chlorination of castor oil TAG at ester linkages.

Presence of acid chlorides is also supported by the appearance of weak IR absorption peaks at $1810 - 1750\text{cm}^{-1}$ (Fig. 3d) and $1000 - 910\text{cm}^{-1}$ (Fig. 3b). However, chlorination at the hydroxyl groups in the oil's TAG molecules was the major feature, and was predominant.

PU Foam from Chlorinated Castor Oil Polyols

Attempted PU foam synthesis from PCl_5 -chlorinated oils derived from unmodified castor oil polyol only yielded foams from oils containing 10 and 20wt% of the chlorinating agent. However, foam synthesis was characterized by delayed creaming and poor foam rise, while the obtained foams were brittle, and of low densities and low mechanical strengths. At higher concentrations of the chlorinating agent, there was marked reduction in hydroxyl number of the base polyol, i.e., decreasing functionality of the castor oil polyol. This resulted in much lower conversion rate to PU. These oils are thus unsuitable for PU foam synthesis. Nonetheless, there are reports that quality PU foams have been obtained from chlorinated and brominated polyols generated from epoxidized and ring-opened soybean oil (Petrovic *et al.*, 2000), though the halogenated polyols are generally less thermally stable than their non-halogenated counterparts (Petrovic, 2008).

CONCLUSION

Chlorinated oils of varying physico-chemical characteristics have been prepared from unmodified castor oil polyol, using PCl_5 as the chlorinating agent (by substitution). These oils were found unsuitable for PU development. However, they could be used in fire retardancy and pesticidal applications, in addition to their suitability for use as plasticizers in nitrile rubber formulations (Yousef *et al.*, 2001).

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