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THESIS

HYDROPHOBIC BEHAVIORS AND FRICTION LOSSES OF ANACARDIC ACID BASED PHENOLIC RESINS

KUTSALIN KAVEERAT

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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Anacardic acid, by-product of the cashew nut processing industry, was synthesized with cresol and formaldehyde using magnesium hydroxide as alkali catalyst. Anacardic acid based resole-type phenolic resins, the newly developed polymer, can be used to reduce friction losses/ operating cost for material transfer in a variety of processes. The surface characteristics of anacardic acid based resole-type resins were studied via contact angle measurement. The three-liquid method was utilized to determine the Lifshitz-van der Waals components (γ^{LW}), electron-acceptor (γ^{+}) and electron-donor (γ^{-}) parameter of the prepared coatings. The lowest values of the γ^{LW} (24.44 mJ/m^2), γ^{-} (2.27 mJ/m^2) and the work of adhesion between water and resins (16.13 mJ/m^2) were observed for the case that anacardic acid was condensed with cresol and formaldehyde at the molar ratio of 1.55:0.38:3.5. Results suggested that anacardic acid based resole-type resin has lower resistance to water than phenol-formaldehyde resin. Furthermore, the formation of phenolic coatings was studied by Fourier transform infrared (FTIR) spectroscopic analysis and the melting point of phenolic coatings (184.14^{o}C) was determined by differential scanning calorimeter (DSC). FTIR spectrum of AnAc based-resole type resin shows the condensation of methylolated AnAc and the degree of *ortho*- and *para*- substitution. Stainless steel coated with this polymer provided a significant maximum reduction in pressure drop and Fanning friction factor (Reynolds number 4.36E+04 to 7.56E+04) around 14% (compared to the non-coated pipe) for the water flow in pipe (Reynolds number = 4.38E+04).

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Kutsalin Kaveerat
April 2010

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LIST OF ABBREVIATIONS

A = The pipe cross-sectional area, m^2

D = Diameter of pipe, cm

f = Fanning friction factor

L = Length of pipe, m

P = Pressure, bar

Q = The volumetric flow rate, m^3/s

Re = Reynolds number

V = Flow velocity, m/s

W_a = Work of adhesion, mJ/m^2

W_a^{LW} = Lifshitz-van der Waals components of adhesion, mJ/m^2

W_a^{LW} = Lewis acid-base components of adhesion, mJ/m^2

$W_{a,H_2O-resin}^{AB}$ = Lewis acid-base components of adhesion between water and resin, mJ/m^2

$W_{a,EG-resin}^{AB}$ = Lewis acid-base components of adhesion between ethylene glycol and resin, mJ/m^2

ΔP = Pressure drop, bar

μ = The dynamic viscosity of the fluid

ν = The kinematic viscosity, Pa·s

γ_S = The surface free energy of solid, mJ/m^2

γ_L = The surface free energy of liquid, mJ/m^2

γ_{SL} = The interfacial energy between the solid and liquid, mJ/m^2

γ^{LW} = Lifshitz-van der Waal component, mJ/m^2

γ^{AB} = Lewis acid-base components, mJ/m^2

γ^{+} = Electron-acceptor parameter, mJ/m^2

γ^{-} = Electron-donor parameter, mJ/m^2

θ = The contact angle, theta

HYDROPHOBIC BEHAVIORS AND FRICTION LOSSES OF ANACARDIC ACID BASED PHENOLIC RESINS

INTRODUCTION

Thailand ranks as the third most important cashew producing country in Asia, while India remains the main producer. A total production of cashew (Food and Agriculture Organization [FAO], 2005) is 24,000 tons and exported of raw nut and kernel was only 70 and 79 tons, respectively. Any future increases in production may have to find export markets. The fruit of cashew nut including and outer shell, inner shell and kernel, which accounts for approximately 25% by weight. Large amounts of the outer shell are released from the cashew nut decorticators each year. This materials have low values in its present form. Therefore, it is wise to extract as much of the cashew nut shell liquid (CNSL) prior to disposal. This will ultimately help reduce the environmental load for the residual portion of the shell.

A by-product from the cashew industry is anacardic acid (AnAc), a major constituent of cashew nut shell liquid (CNSL) that can form organic solvent-soluble metal derivatives (Nagabhushana *et al*., 1995). It is a source of unsaturated hydrocarbon phenol with carboxylic acid group, an excellent monomer for thermosetting polymer production. In the base-catalyzed process, formaldehyde reacts mainly with the free *ortho* and *para* positions of the phenolic group of CNSL (Tyman., 1973; Ramamurthy *et al*., 1977; Lubi *et al*., 2000). In the presence of alkaline catalyst with excess formaldehyde, the methylol phenols undergo condensation through either methylene or ether linkages.

Phenol-formaldehyde (PF) resin and its composites have been widely used for industrial products, e.g. adhesive, composite materials, coatings, etc. The surface properties of PF resin such as liquid proof behaviors are very important for industrial applications. Gotfryd (2003) studied the coating composition of PF resin and urethane prepolymers. The coatings exhibited good elasticity and a very good adhesion to metallic substrate. Moreover, the coatings showed an excellent chemical resistance to selected corrosive media.

Contact angle measurement is a widely used technique to determine the surface free energy of solids. The three-liquid method was used to determine the Lifshitz-van der Waals components (γ^{LW}), electron-acceptor (γ^{+}) and electron-donor (γ^{-}) parameter of the surface (Lifshitz., 1955; Van Oss *et al*., 1987). Lifshitz-van der Waals interactions include London's dispersive interactions, Keesom's dipole-dipole interactions and Debye's interactions (van der Waals., 1873; Keesom., 1915; Debye., 1920; London., 1930). Such intermolecular attractive interactions are always present at an interface . In addition, Lewis acid-base interactions (including hydrogen bonds) may also occur. The Lewis acid-base concept is based on two complementary definitions: a Lewis acid is an electron acceptor and a Lewis base is an electron donor (Good *et al*., 1992). Matsushita *et al*. (2006) studied the surface characteristics of phenol-formaldehyde resin with lignosulfonate and kraft lignin by using contact angle measurement and inverse gas chromatography (IGC). The results of both measurement suggested that the γ_S^{LW} , γ_S^{-} and the acid-base component of the work of adhesion between water and the prepared resin increased with the substitution of lignin for phenol due to the chemical component change.

Internal pipeline coatings can be used to reduce friction loss/operating cost for material transfer in a variety of processes. There has been interest on the possible use of polymers as film forming corrosion inhibitors and friction reductors. This research contribution concerns the synthesis of anacardic acid based resole-type phenolic resin with different molar ratios of formaldehyde, anacardic acid and cresol so as to improve hydrophobic behaviors and reduce friction in transfer of liquid in a straight pipe.

OBJECTIVES

1. To investigate the effects of anacardic acid, formaldehyde and cresol content on hydrophobic behavior of the synthesized polymers.
2. To study contact angles of water, surface free energy and work of adhesion of anacardic acid based resole-type resin.
3. To reduce pressure drop and Fanning friction factor of water flow in stainless steel pipe coated with anacardic acid based resole-type resin.

Scopes

Synthesized anacardic acid based resole-type resin by varying anacardic acid, formaldehyde and cresol content. Phenolic coatings were coated on stainless steel sheet 7 cm × 7 cm × 0.05 cm in order to evaluate contact angles of water, diiodomethane and ethylene glycol with anacardic acid based-resole type resin. The formation of phenolic coatings was determined by Fourier transform infrared spectroscopic analysis. Thermal properties of phenolic coatings were studied by differential scanning calorimeter. The pipe was coated with the polymer providing maximum contact angle. Fanning friction factors were calculated for water flow in pipe with different values of Reynolds number.

Benefits

The newly-developed polymer will be an important material for use in industry for reducing friction losses/ operating cost for aqueous solution flow in pipes. Moreover, the polymers can help promote the utilization of cashew nut shell.

LITERATURE REVIEW

1. Cashew nut shell liquid

The cashew tree, *Anacardium occidentale* Linn, belongs to the *Anacardiaceae* family of plants. The tree, a native plant of Brazil, is called by its Portuguese name *Caju* (the fruit) or *Cajueiro* (the tree). In the nineteenth century, the tree grows in the areas of Africa, Asia and Latin America. Cashew processing, using manual techniques, was started in India in the first half of the twentieth century. In 1901, Payaratsadanupadit was the first who brought it from adjacent areas of Malaysia to the southern part of Thailand. Cashew, a tropical crop, can be grown from about 25^{O} south of the equator to 25^{O} north. It grows best in the warm, moist and typically tropical climate (Ohler, 1979). The crop began to be considered as having economic importance to the country by 1984 following the government policy. Although cashew shares only a small portion of the national economy, it is increasingly becoming important to growers in the East, in terms of regional economy at present.

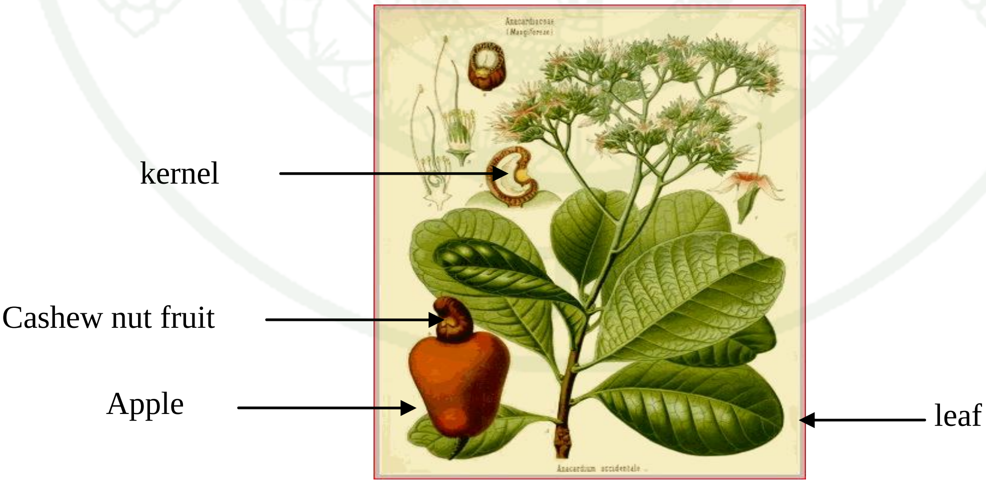


Figure 1 Cashew apple and cross-section of a cashew fruit.

Source: Hughes (1926)

The cashew nut tree consists of the cashew nut fruit, the apple, leaf and bark (Figure 1) and the fruit including an outer shell, inner shell and the kernel. The honeycomb structure, which contains cashew nut shell liquid, commercially known as CNSL. About 30–35% CNSL is present in the shells where the shells amount to approximately 67% of the nut (Patel *et al.,* 2006). Crude cashew nut shell liquid represents one of the major and cheapest sources of naturally occurring non-isoprenoid phenolic lipids such as 70% anacardic acid (1), 20% cardol (2), 5% cardanol (3) and very low content of 2-methylcardol (4) (Figure 2). However, technical CNSL consists of very low content of anacardic acid, 60-65% cardanol, 15-20% cardol and other polymer 10%. These natural products could serve as alternative source of phenolic compounds from petrochemical industry. On the other hand, CNSL has found important commercial usage as the phenolic raw material for the manufacture of certain resins and plastics having unusual electric and frictional properties. The resins from CNSL are used in laminating for papers, the manufacture of an anti-corrosive for metals, water proofing compounds and adhesives (Menon *et al.,* 1985).

Anacardic acid
(6-pentadecenyl salicylic acid)

Cardol
(5-pentadecenyl resorcinol)

Cardanol
(3-pentadecenyl phenol)

2-Methyl Cardol
(2-methyl, 5-pentadecenyl resorcinol)

Figure 2 Naturally occurring non-isoprenoid phenolic lipids from *Anacardium occidentale.*

Where n = 0, 2, 4 or 6

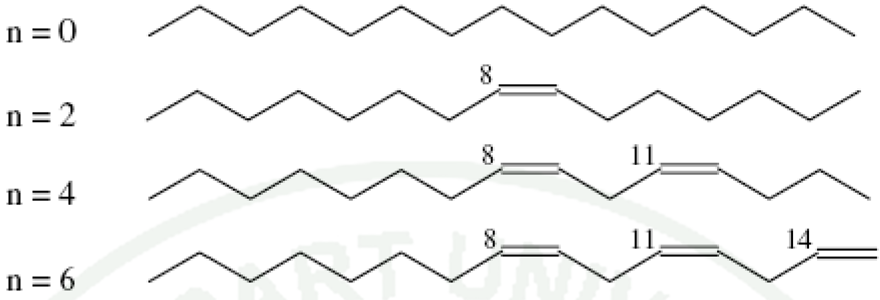
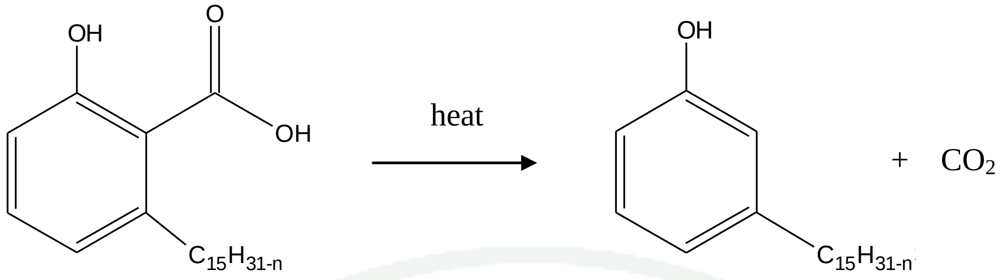


Figure 2 (Continued)

Source: Santos *et al.* (1999)

The raw nuts are passed through a bath of hot CNSL at 180-200 ^{O}C. The outer part of the shell bursts open and releases CNSL and about 50% of the oil is thus recovered. Improvements over this basic technique include initial surface wetting and dipping in water at 20-25 ^{O}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. Another 20% could be extracted by passing the spent shells through an expeller and the rest by a solvent extraction technique. The expelled oil can be upgraded by acid washing followed by centrifugation and heating.

Reactions of CNSL are of commercial importance, which several useful industrial products can be produced starting from this substance. Ohler (1979) reported that fresh CNSL contains anacardic acid of about 90% by weight, which is a derivative of salicylic acid and readily decarboxylates upon heating and converts to obtain anacardol or cardanol (Figure 3). This reaction can occur during the extraction of CNSL or the refining process. Distillation of the crude CNSL also leads to decarboxylation as the distillate is found to contain mainly cardanol.



Anacardic acid Cardanol

Figure 3 Decarboxylation of CNSL

Source: Tychopoulas *et al*. (1990)

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 polymers show flexibility, due to internal plasticization resulting from the presence of a long side-chain. CNSL can be polymerized by the aliphatic side-chain providing pronounced hydrophobicity for these resins. The unsaturation in the side-chain can be the basis for addition polymerization using free radicals or ionic initiators such as HCl, para-toluene sulfonic acid (PTSA). The kinetics and mechanism of the polymerization of CNSL show that CNSL undergoes oligomerization under acidic conditions through the side-chain unsaturation (Lubi *et al.*, 2000).

The Phenolic resin from CNSL are synthesized via condensation polymers by reacting with formaldehyde. These polymers are similar to the product of phenol and formaldehyde condensation.

For the resol-type polymers, the structure of the final product has been studied by Tyman (Tyman *et al.*, 1973) (Figure 4). In the presence of alkaline catalyst and with more formaldehyde, the methylol phenols condense either through methylene linkages or through ether linkages. In the latter case, subsequent loss of formaldehyde may occur with methylene link formation.

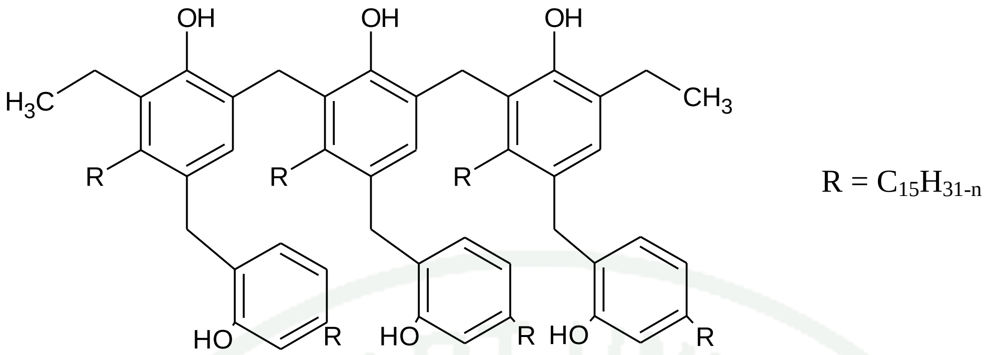


Figure 4 Resole resin made from cardanol

Source: Lubi *et al*. (2000)

In the case of the novolac-type polymers, the structure of the final product has been studied by Tyman (Tyman *et al.,* 1973) (Figure 5). In the presence of acid catalyst and with less formaldehyde, the resin has no reactive methylol groups and therefore is incapable of condensing with other molecules on heating in the absence of hardening agents. To complete resinification more formaldehyde is added, resulting in cross-linking.

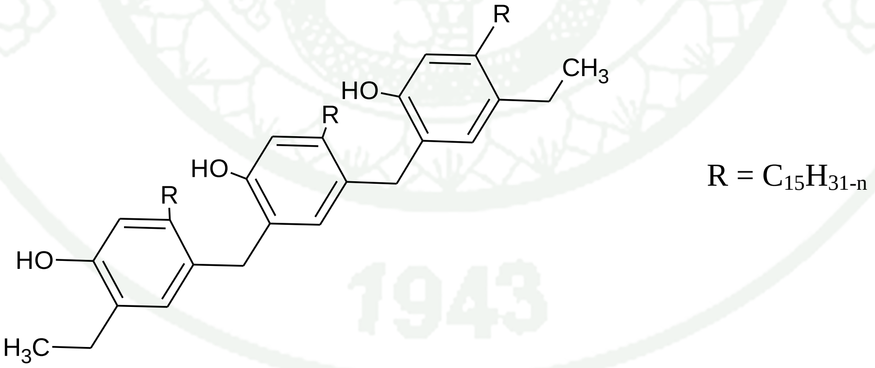


Figure 5 Novolac resin made from cardanol

Source: Lubi *et al*. (2000)

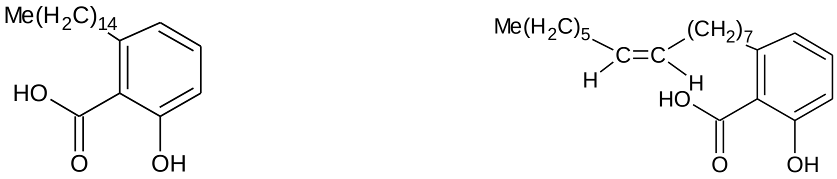
Mwaikambo and Ansell (2001) investigated the cure characteristics of alkali-catalyzed CNSL-formaldehyde resin. For the reaction catalyzed by sodium hydroxide

(NaOH) and hexamethylenetetramine (HMTA), the change in the glass transition temperature shown by DSC, can be related to the extent of cure of the resins. It was found that the alkaline catalyzed content increases with increasing curing temperature. FTIR results revealed that the phenolic hydroxyl groups have reacted with formaldehyde due to the reduced intensity of the phenolic peak.

Devi and Srivastava (2006) studied the kinetics of novolac resins with two different mole ratios of cardanol and formaldehyde by using aliphatic tricarboxylic acid as catalyst. For the reaction catalyzed by citric acid, second-order kinetics has been reported and the rate constant for various reaction condition, the energy of activation (E), change in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been calculated. The positive values of change in entropy and free energy indicated that the reaction is spontaneous, irreversible and produces disordered complex compounds.

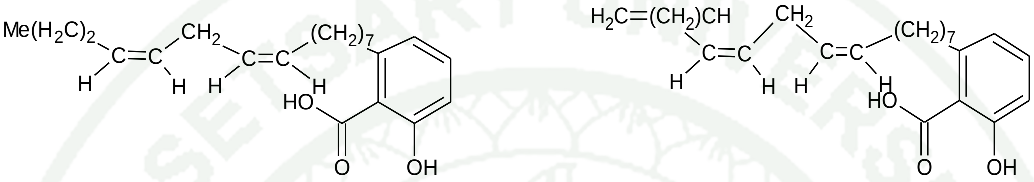
2. Anacardic acid

Anacardic acid (AnAc), a major constituent of CNSL, is the product of hydrogenation of the naturally occurring unsaturated anacardic acids, namely, the 6 [8’(Z), 11’(Z), 14’-pentadecatrienyl] salicylic acid (C15:3), 6[8’(Z), 11’(Z) pentadecadienyl] salicylic acid (C15:2), and 6[8’(Z)-pentadecenyl] salicylic acid (C15:1) (Figure 6). Moreover, AnAc readily decarboxylates upon heating and converts to obtain cardanol. However, AnAc plays a role in the protection of the kernel and affects the fecundity of the insect population living on the tree, which are accumulated in the shell during the early part of the growth of the cashew nut. They also inhibit the activity of several other interesting enzymes such as tyrosinase (Kubo *et al.,* 1994), lipoxygenase (Shobha, *et al.,* 1994), and cyclooxygenases or prostaglandin endoperoxidase synthase (Grazzini *et al.*, 1991). Anacardic acid, with its phenolic and carboxylic acid groups, can be an excellent monomer for thermosetting polymer production. The synthesis of polymers from renewable resources or CNSL is already in use in the manufacture of special phenolic resins for coating, lamination and as friction material (Bhunia *et al.*, 1998).



6-pentadecylsalicylic acid

6-[8(*Z*)-pentadecenyl]salicylic acid



6-[8(*Z*),-11(*Z*)-pentadecadienyl] salicylic acid

6-[8(*Z*),11(*Z*),-14-pentadecatrienyl] salicylic acid

Figure 6 Chemical structures of a mixture of four 6-alkylsalicylic acids

Source: Satoh *et al.* (2001)

Lubi and Thachil (2000) reported that anacardic acid can react with tris(2-hydroxyl ethyl)isocyanurate to form products which can be used as improved binders for friction materials. The preparation of resins for brake linings reportedly involves an acid catalyst side-chain polymerization followed by conventional formaldehyde condensation. Resins friction composition can be obtained with desired properties when synthesized in the presence of aryl borates.

Paul and Yeddanapally (1954) identified the components of anacardic acid as 1-hydroxy-2-carboxy-3-pentadecyl benzene, 1-hydroxy-2-carboxy-3-(8'-pentadecenyl)benzene, 1-hydroxy-2-carboxy-3-(8',11'-pentadecadienyl)benzene and 1-hydroxy-2-carboxy-3-(8',11',14'-pentadecatrienyl)benzene. The constituents of anacardic acid determined by various techniques are shown in Table 1.

Table 1 Composition of the constituents of anacardic acid as determined by various techniques (values are in wt%)

Constituents of anacardic acid	Technique employed					
	Low temperature crystallization	TLC-UV	TLC-gravity	TLC-GLC	HPLC	TLC-mass spectrometry
Saturated	4.00	-	-	4.00	4.30	3.65
Monoene	15.00	38.70	38.40	38.3	33.4	38.19
Diene	44.00	16.30	17.30	17.30	19.90	16.50
Triene	37.00	45.10	44.10	40.40	42.4	41.62

Source: Gedam and Sampathkumaran (1986)

According to an Indian patent, Rye (1946) purified CNSL by adding calcium hydroxide, which dissolved in isopropyl alcohol to the anacardic acid as calcium anacardate. HCl was treated with pure dried calcium salt of anacardic acid to realease free anacardic acid ene mixture (n=0, 2, 4, 6) but the purity of product was not supported by any modern chromatographic or spectral data.

Nagabhushana and Ravindranath (1995) used column chromatography in order to investigate the means for isolation of anacardic acid from CNSL, which was loaded onto a silica gel bed, prepared in ethyl acetate-hexane (25:75) and 0.5% triethylaminel. HPLC was used to confirm identity of the compounds. It was found that the product consisted of 70 grams of anacardic acids and 27 grams of cardols from 100 grams of CNSL.

Paramashivappa *et al.* (2001) isolated anacardic acid as calcium anacardate from 100 g of CNSL. The pure dried calcium salt of anacardic acid was treated with HCl to release free anacardic acid ene mixture and acid-free CNSL was extracted with hexane/ethyl acetate (98:2) to separate the mono phenolic component, cardol.

Consequently, ammonia solution was extracted with ethyl acetate/hexane (80:20) to obtain cardol (Figures 7,8).

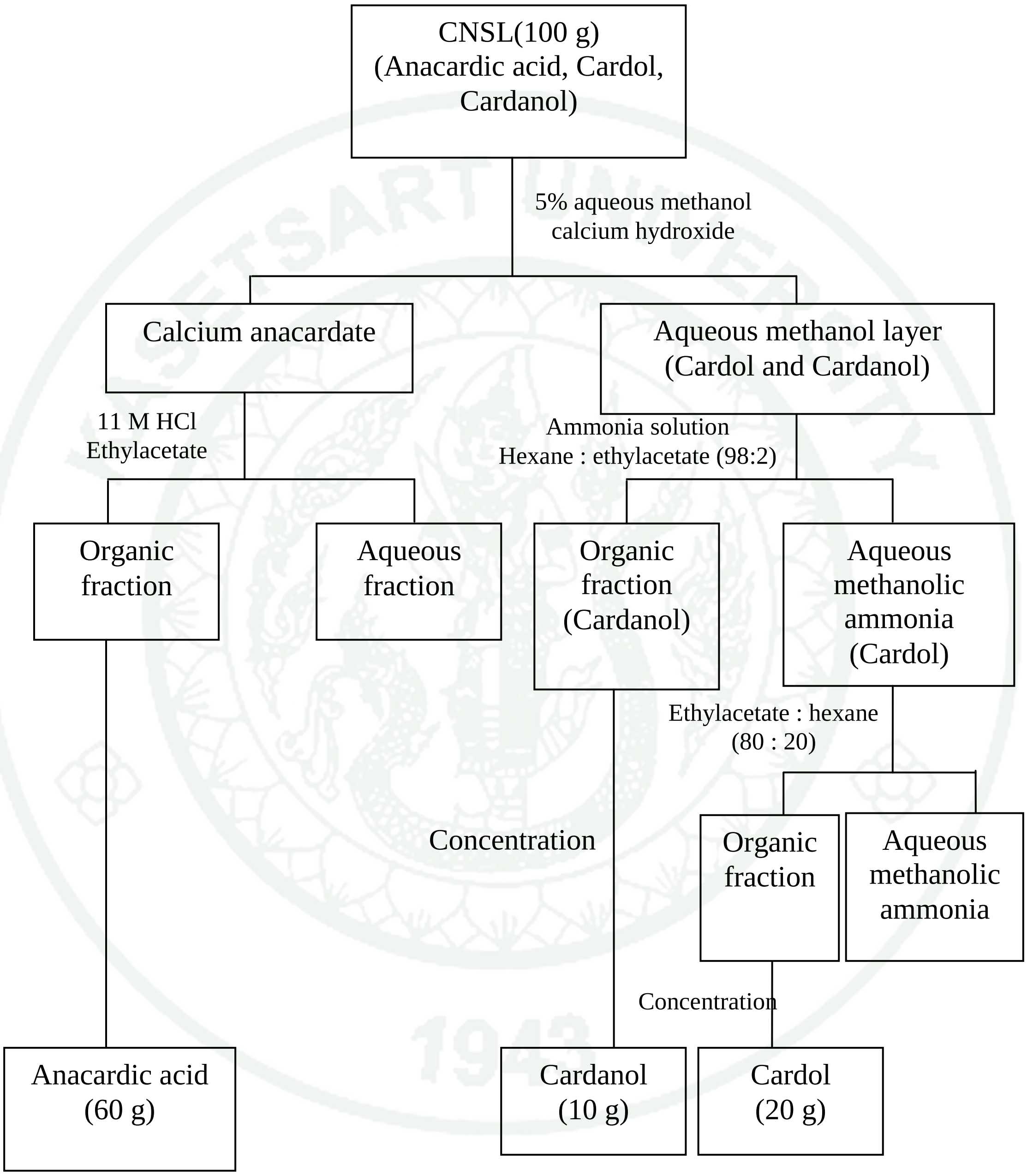


Figure 7 Flow diagram for separation of anacardic acid, cardol and cardanol from CNSL

Source: Paramashivappa *et al.* (2001)

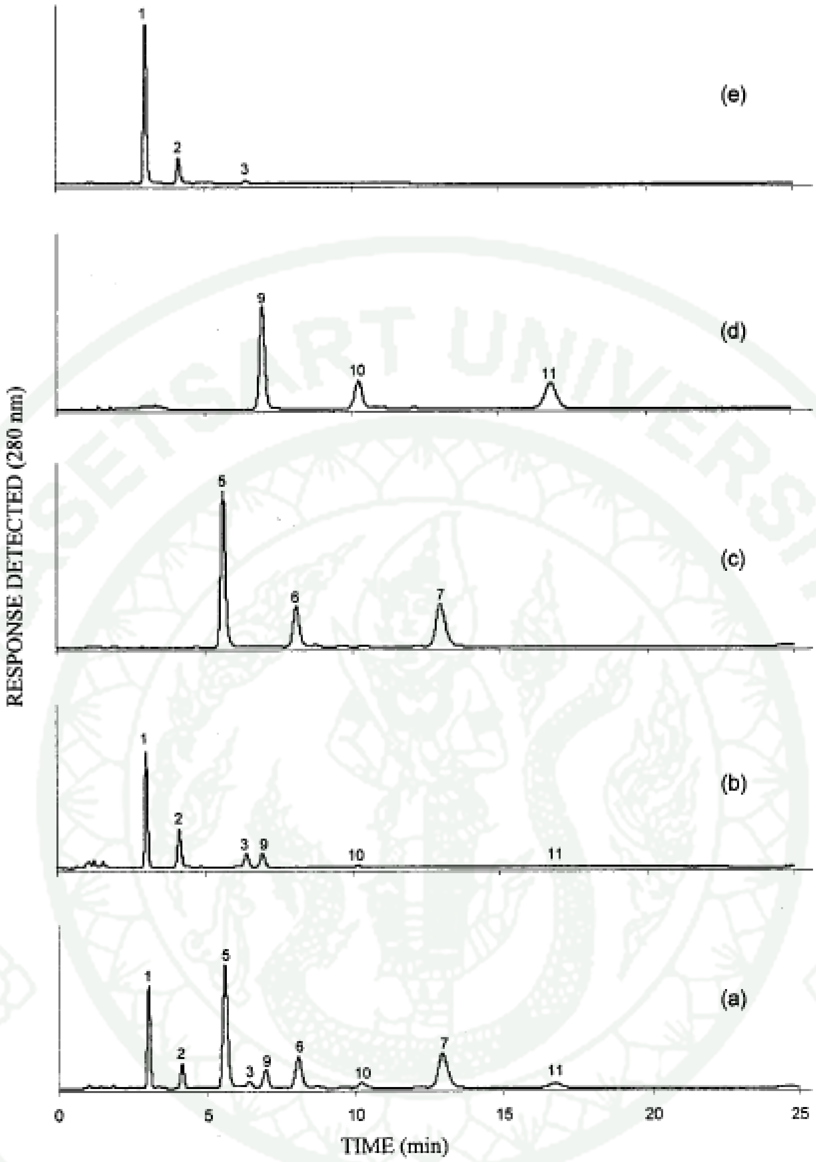


Figure 8 HPLC profiles of (a) CNSL, (b) anacardic acid free CNSL, (c) anacardic acid, (d) cardanol, (e) cardol; using Supelcosil, LC-18 and acetonitrile/ water/acetic acid (80:20:1) as mobile phase at 280 nm

Source: Paramashivappa *et al.* (2001)

Where numbers 1-3 represent cardols
numbers 5-7 represent anacardic acid
numbers 9-11 represent cardanol

Philip *et al.* (2008) synthesized a molecularly imprinted polymer using anacardic acid monomer derived from cashew nut shell. From anacardic acid (AnAc) monomer, anacardanyl acrylate (AnAcr) and anacardanyl methacrylate (AnMcr) monomers were synthesized and their chemical structures were characterized by Fourier transform IR. At a polymer concentration of 2 mg/mL, AnAcr and AnMcr based imprinted polymers were able to bind over 50% of trace propranolol (initial concentration of 1.2 nM). Under the same condition propranolol uptake by the two nonimprinted control polymers was less than 20%. Moreover, cross reactivity studies of these polymers showed that the (*S*)-imprinted sites have higher cross-reactivity toward (*R*,*S*)-metoprolol than (*R*)-propranolol and (*R*)-timolol (Figure 9).

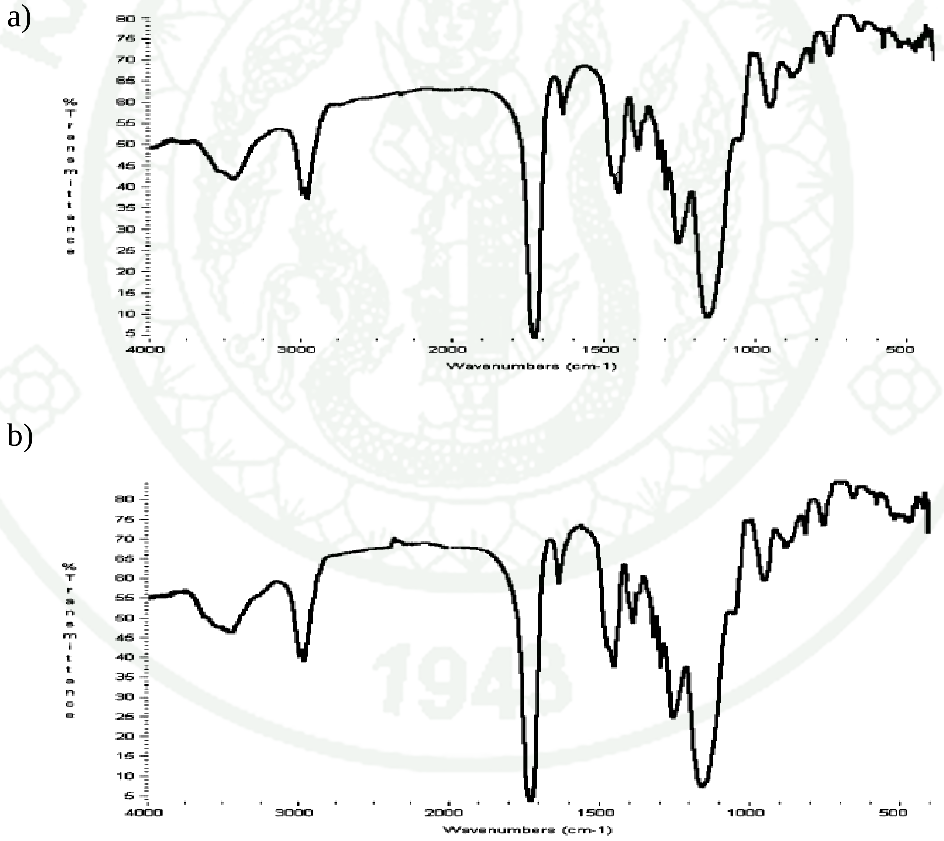


Figure 9 FTIR spectra of (a) molecular imprinted and (b) nonimprinted poly(AnAc-co-EGDMA)

Source: Philip *et al.* (2008)

3. Phenolic resins

Phenol-formaldehyde resins or phenolic resins are among the oldest known and highest volume thermosetting materials produced in the United States (Gibson, 2001). As phenolic resins are the oldest thermosetting polymers the influence of many synthesis parameters has been studied for different phenol constituents by lot of authors using several analytical techniques. The most common phenolic prepolymers are derived from reacting phenol with formaldehyde or with formaldehyde derivatives. Resins are polymers made by repeatedly linking discrete molecules (monomers) together to form chains or networks. Phenolic resins are oligomers (polymers with a few repeating units) synthesized by repeatedly linking phenolic (hydroxy-aromatic) monomers with aldehyde chemicals. The majority of products are combinations of phenol (hydroxybenzene, C_6H_6O) and formaldehyde (methanal, CH_2O), though specialized applications may require use of substituted phenols (e.g., cresols, resorcinol, cashew nutshell liquid distillate), or other aldehydes (e.g., furfural). This reaction occurs most rapidly under extremely acidic or basic conditions. The selection of suitable reaction parameter results in optimum molecular weight distribution and residual monomer content necessary for maximum efficiency. The wide range of reaction conditions and monomers available to the resin producer allows for the production of a variety of resins specifically designed for use in individual applications.

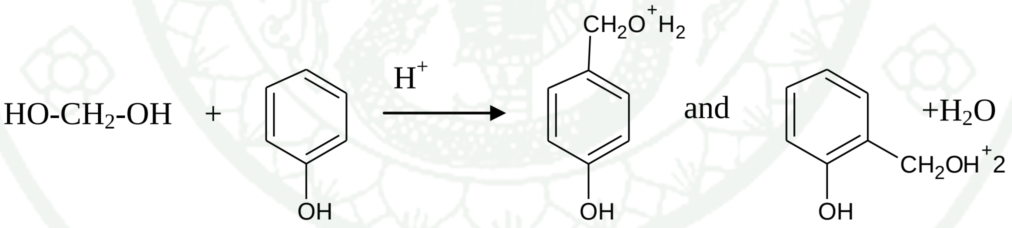
According to an USPTO patent application (2008) the phenolic resins can be produced by reacting a molar excess of phenol with formaldehyde in the presence of an acid catalyst, such as sulfuric acid, hydrochloric acid or oxalic acid (usually in an amount of 0.2 to 2% by weight based on the weight of phenol). However, phenolic resins can also be prepared under alkaline conditions using an excess of formaldehyde over phenol (1:1 to 3:1) at typical temperatures of 60-80^{O}C. The basic catalysts commonly used are NaOH, Na_2CO_3, $Mg(OH)_2$, K_2CO_3, $Ba(OH)_2$, NH_3, RNH_2 and R_2NH (Gibson, 2001).

The general chemistry of the polymerization of phenol with formaldehyde, the most common molecules used, to provide a general background of resin manufacture. In aqueous solution, formaldehyde exists in equilibrium with methylene glycol.

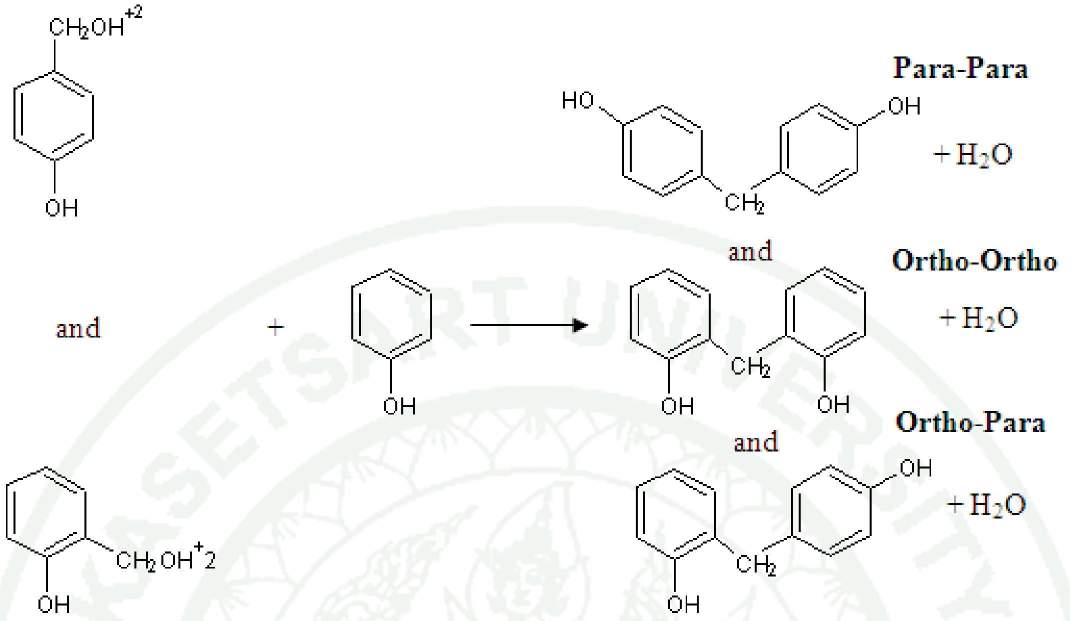
Phenol Formaldehyde Methylene Glycol

The pH of the reactions and the stoichiometric ratio of the monomers give rise to two classes of phenolic prepolymers known as novolacs and resoles.

An acidic catalyst and a molar excess of phenol to formaldehyde are conditions used to make novolac resins. The following simplified chemistry illustrates the wide range of polymers possible. The initial reaction is between methylene glycol and phenol.



The reaction continues with additional phenol, and splitting off of water.



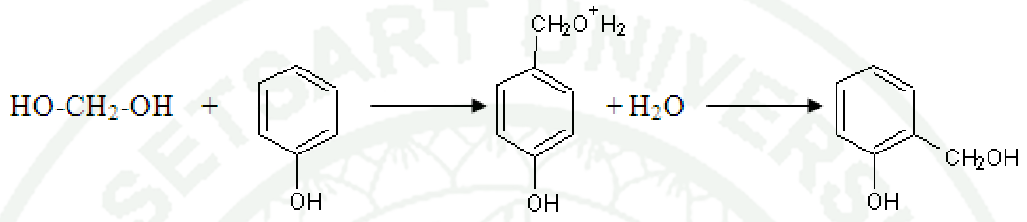
The reaction creates a methylene bridge at either the ortho position or the para position of the phenolic aromatic rings. The para position is approximately twice as reactive as the ortho position, but there are twice as many ortho sites (two per phenol molecule) so the fractions of ortho-ortho, para-para and ortho-para bridges are approximately equal.

The final novolac resin is unable to react further without the addition of a cross-linking agent. The resins having the curing agent incorporated cure or “thermoset” to the desired degree when processed by the customer.

Novolac resins are amorphous (not crystalline) thermoplastics. As they are most typically used, they are solid at room temperature and will soften and flow between 150^{O} and 220^{O}F (65^{O}C – 105^{O}C). The number average molecular weight (M_n) of a standard phenol novolac resin is between 250 and 900. As the molecular weight of phenol is 94 grams per mole, a M_n of 500 corresponds to a resin where the average polymer size in the entire distribution of polymers is five linked phenol rings. Novolac resins are soluble in many polar organic solvents (e.g., alcohols, acetone), but not in water.

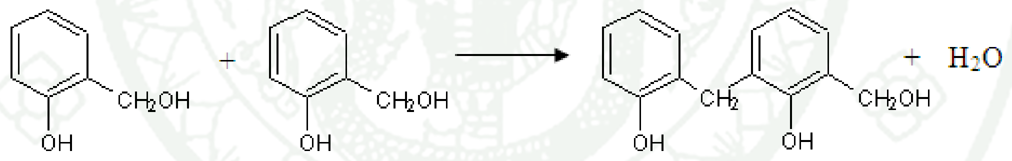
A basic (alkaline) catalyst and, usually but not necessarily, a molar excess of formaldehyde is used to make resol resins. The following two stages describe a simplified view of the reaction

First, phenol reacts with methylene glycol to form methylol phenol

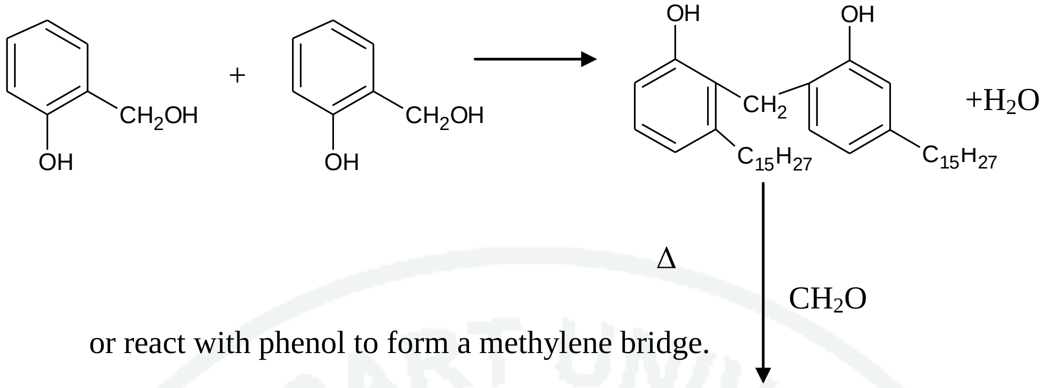


Methylene Glycol Phenol Methylolphenol

Methylol phenol can react with itself to form a longer chain methylol phenolic compound



or form dibenzyl ether



or react with phenol to form a methylene bridge.

The most important point in resol resin chemistry is that, when an excess of formaldehyde is used, a sufficient number of methylol and dibenzyl ether groups remain reactive to complete the polymerization and cure the resin without incorporation of a cure agent. For this reason, the industry commonly refers to resol resins as “single-stage” or “one-step” type products. Resol resin manufacture includes polymerizing to the desired extent, distilling off excess water or tempering the polymerization reaction by rapid cooling. Because resol resins continue the polymerization reaction at even ambient temperatures, albeit at much slower rates than during manufacturing, they demonstrate limited shelf lives dependent on the resin character, storage conditions and application.

The typical number average molecular weight (M_n) of a straight phenol resol resin is between 200 and 450. Plastics Engineering Company supplies resol resins as liquids or in solvents with viscosities from 50 to 50,000 cp, or as solids in the form of lumps, granules, or fine powders. Organic solvents and the amount of water or phenol monomer left in the resin control the viscosity of the liquid resin products. Resol resins are usually water-soluble to a certain degree.

Phenolic resins have an excellent affinity for graphitic and other forms of carbon. Manufacturers often use the resin simply as a binder and adhesive for their carbon materials. At high temperature, phenolic resins form a char of amorphous carbon. This means phenolic bonded carbon materials can be heat-treated to yield an all carbon structure. Because of these unique properties, phenolic resins find application in the manufacture of electrodes, carbon-carbon composites, carbon seals, and washers.

Zhang *et al.* (2008) studied the properties of phenolic resin expanded graphite composites via in situ condensation polymerization of the monomers in the presence of foliated graphite. The composite containing graphite grains exhibited an improved electrical conductivity percolation threshold with 3.2 wt% graphite content in polymer matrix. Inverse gas chromatography (IGC) measurement detected some functional groups such as –OH and –COOH, which can promote the monomer and chain segments of phenolic resin into the interspace of graphite.

Lubi and Thachil (2000) reported that mixing of CNSL-HCHO resin dissolved in solvents with Portland cement gives a cement that sets within 6 hours at room temperature and has good resistance to water, oil, and heat. CNSL reacted with alkali materials such as cement, alumina, barium hydroxide, sodium carbonate etc. can be used as coatings for wall of cement, wood, fabric which are impervious to water.

Devi and Srivastava (2006) revealed that novolac resins with two different mole ratios between cardanol and formaldehyde for the condensation reaction in presence of tricarboxylic acid catalysts at different temperatures (100-130^{O}C), which proceeded with second-order rate kinetics (Figure 10). First reaction, the addition of formaldehyde onto the free *ortho* and *para* of cardanol. Next, methylol cardanol can react with itself to form a longer chain methylol cardanol compound.

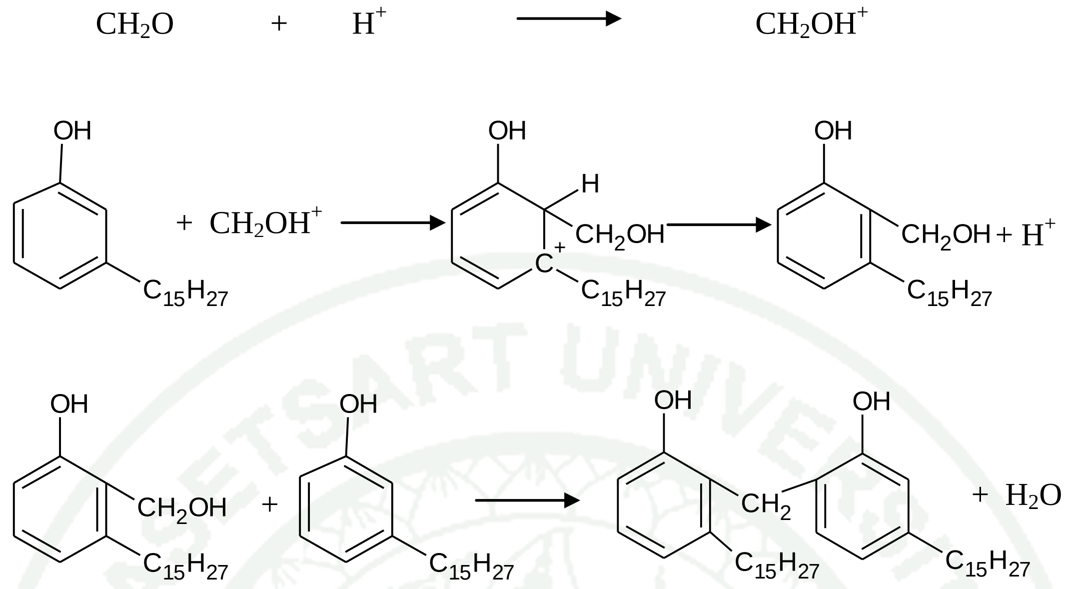


Figure 10 Reaction mechanism for the synthesis of cardanol-based novolac resin

Source: Devi and Srivastava (2006)

Phenolic resins are invariably used as binder in friction materials due to low cost along with a good combination of mechanical properties such as high hardness, compressive strength, moderate thermal resistance, creep resistance and very good wetting capability with most of the ingredients. The main advantages of phenolic resins, both novolacs and resoles, and their networks are excellent flame retardance and low cost. (Gurunath *et al.*, 2007). Phenolic resins or their modified versions are invariably used as adhesives, coatings, in various electric, structural, aerospace applications and binder materials for friction composites which can help improve compressibility, thermal stability, damping capacity, and mechanical strength (Hong *et al.*, 2009).

4. Pipe flow theory

The term pipe is defined herein as a closed conduit, usually of circular cross section. It can be made of any appropriate material such as steel or plastic. The term pipeline refers to a long line of connected segments of pipe, with pumps, valves, control devices and other equipment or facilities needed for operating the system.

The concept of energy is important in pipe flow. In pipe flow there have three energy components due to motion (kinetic energy), elevation (gravitational potential energy) and pressure.

The energy can be transformed from one form to the other, or it can be used to perform work. The total energy at any point in piped system is given by Bernoulli's equation.

Total Energy = Kinetic Energy + Potential Energy + Pressure Energy

$$H = \frac{v^2}{2g} + z + \frac{P}{\rho g} \qquad (1)$$

Where H = Total energy

v = Flow velocity

P = Pressure

z = Elevation above some fixed level

g = Acceleration due to gravity (9.81 m/s^2)

ρ = Density of water (1 g/cm^3)

Pressure is measured relative to atmospheric pressure, that is, atmospheric pressure is assumed to be zero. A positive pressure indicates a pressure greater than atmospheric while a negative pressure denotes a pressure less than atmospheric.

Pressure is important for pipe selection. There are conditions that can cause dramatic increases in the fluid pressure. Pipes must be able to withstand these high instantaneous pressures that the fluid exerts on it.

Based on the Law of Conservation of Energy, the state of flow can be determined at any point in a pipe system.

$$H = \frac{v_2^{\,2}}{2g} + z_2 + \frac{P_2}{\rho g} = \frac{v_1^{\,2}}{2g} + z_1 + \frac{P_1}{\rho g} \qquad (2)$$

Pressure is normally expressed in terms of force per unit area (e.g. pounds per square inch, *psi*). However, pressure may also be expressed in terms of a height or head of water.

4.1 Factors that influence the friction loss in a pipe

4.1.1 The roughness of the inside of the pipe. For new pipes, roughness is dependent on the pipe material and the method of fabrication. As pipes get older they deteriorate and the roughness increases. The roughness value used in design calculation is usually the roughness at the end-of-life of the pipe. In pipes, roughness is represented by a roughness coefficient (C). The rougher the pipe, the bigger is the roughness coefficient.

4.1.2 The length of the pipe. Friction loss is directly proportional to the length of pipe.

4.1.3 The velocity of flow. The greater the velocity, the greater the drag forces and consequently, the greater the friction loss.

4.1.4 The diameter of the pipe. Pipes with smaller area of contact between the water and the pipe walls will have less friction loss. As with open channels, the parameter that is used to get a handle on the contact area is the hydraulic radius. This is defined as the cross-sectional area divided by the wetted perimeter. Pipe flow is almost always in circular pipes. Thus the hydraulic radius in pipe flow is always half the radius of the pipe. Bigger pipes have greater hydraulic radii than smaller pipes and thus would have smaller friction losses.

Pressure drop occurs along the length of the pipe due to wall friction when there is a flow of fluid in pipe. The Fanning friction factor can be determined by using the Fanning's equation.

$$f = \frac{\Delta PD}{2\rho LV^2} \tag{3}$$

Where: ΔP = pressure drop

f = friction factor

L = length of pipe

V = velocity of fluid through pipe

D = diameter of pipe

ρ = density

The velocity of fluid is Q/A where Q is volumetric flow rate and A is pipe area. The Moody diagram gives the friction factor of a pipe. The factor can be determined by its Reynolds number and the relative roughness of the pipe.

The rougher the pipe the more turbulent the flow is through that pipe. The relative roughness of a pipe is given by

$$r = \frac{\varepsilon}{D} \tag{4}$$

Where r = relative roughness

ε = absolute roughness

D = diameter of pipe

To determine the frictional factor, find the relative roughness value for the pipe on the right. Then locate the pipes Reynolds number on the bottom. Follow the relative roughness curve to where it crosses the determined Reynolds number. Now at that point project a straight line to the left, the number determined on the left is the frictional factor.

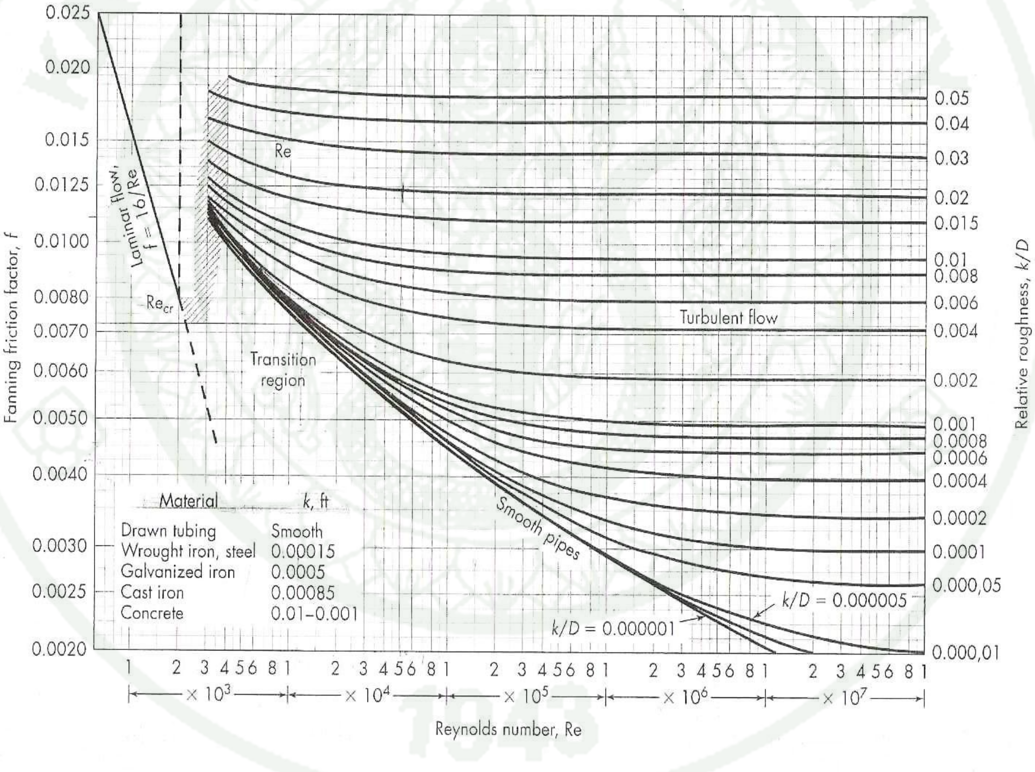


Figure 11 Fanning friction factor plot for circular pipes

Source: McCabe (2005)

The flow in a pipe may be either laminar or turbulent, depending on the Reynolds number which can be defined for a number of different situations where a fluid is in relative motion to a surface. For flow in a pipe or tube, the Reynolds number is generally defined as

$$\mathrm{Re} = \frac{\rho VD}{\mu} = \frac{VD}{\nu} = \frac{QD}{\nu A} \qquad (5)$$

Where

V = velocity of fluid through pipe
μ = the dynamic viscosity of the fluid
ν = the kinematic viscosity
ρ = the density of the fluid
Q = the volumetric flow rate
A = the pipe cross-sectional area

The Reynolds number is an important parameter in the equations that describe whether flow conditions lead to laminar or turbulent flow.

Laminar flow occurs when a fluid flows in parallel layers, with no disruption between the layers. For Reynolds number of less than 2,300, friction factor can be related to Reynolds number via the following equation

$$f = \frac{16}{\mathrm{Re}} \qquad (6)$$

Laminar flow is a flow regime characterized by low velocity, low momentum convection, and high momentum diffusion.

Reynolds number above about 4,000 (a Reynolds number between 2,100 and 4,000 is known as transitional flow). Friction factor depends on Reynolds number and relative roughness; the ratio between absolute roughness and diameter of the pipe. Moreover, the relative roughness also depends on the type of materials.

Song and Zhang (2006) investigated the tribological and hydrophobic behaviors of phenolic coating reinforced with PFW, PTFE and FEP by spray-coating technique. The worn surfaces and the transfer films formed on the surface of the steel ring were investigated using a scanning electron microscope. The results showed that the friction coefficient of the phenolic coating was reduced and the wear life and contact angle were enhanced by adding the fluoropolymers. The FTIR analysis indicated that some active groups were generated during the curing of the PFW-filled phenolic composite coating.

Park *et al.* (2006) employed the friction and wear characteristics of carbon fiber phenolic compositesunder dry sliding and oil-lubrication conditions. Nano-size particles were mixed in the surface layers of the composite specimens to improve their wear characteristics.

Kim and Jang (2000) showed that the modified novolac resin had better friction stability than those with the unmodified novolac resin, and the phenolic resin mixed with 10 vol% of aramid pulp substantially improved the friction stability regardless of the resin type.

Kim *et al.* (2008) studied the tribological properties of phenolic resin, potassium titanate whiskers, and cashew nut shell liquid (CNSL) cured by aldehide using a pad-on-disk type friction tester. The friction properties were evaluated using a non-asbestos organic type formulation. Results showed that the phenolic resin increased the coefficient of friction while it revealed high noise propensity during sliding. the noise occurrence was reduced by increasing the CNSL in the friction material. Wear resistance of the friction material was enhanced by additional phenolic resin, whereas potassium titanate and CNSL deteriorated wear resistance.

Safri and Bouhadef (2008) studied the pressure drop, pipe friction factor and drag reduction by varying concentration of carboxymethyl cellulose (CMC) and polyethylene oxide in the transport of silt and studied the effect pipe diameter. It was demonstrated that 15% reduction of pressure drop was achieved.

5. Hydrophobic behaviors

5.1 Contact angle measurement

Surface energy quantifies the disruption of intermolecular bonds that occur when a surface is created. Many characterization techniques, such as x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), inverse gas chromatography (IGC) and contact angle measurements, can be used to study the Lifshitz-van der Waals and acid-base properties of polymer surfaces (Chehimi *et al*., 1992; Watts *et al*., 1992; Watts *et al.,* 1993). The contact angle measurement is a relatively simple technique for which results can be obtained rapidly (Yekta *et al.,* 1992; Good, 1992). In this work, the three-liquid method was employed in order to determine the parameters of surface free energy via contact angle measurement. Young’s equation defines the balances of forces caused by a wet drop on a dry surface as shown in equation 7

$$\gamma_S = \gamma_L COS\,\theta + \gamma_{SL} \tag{7}$$

Where γ_S, γ_L and γ_{SL} are the surface free energy of the solid, the surface tension of the liquid and the interfacial energy between the solid and liquid, respectively. θ is the contact angle between the solid and the liquid.

Fowkes (1983) demonstrated that the surface free energy of a solid or liquid may be separated into a Lifshitz-van der Waals component γ^{LW} and a Lewis acid-base component γ^{AB} as shown in equation 8

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{8}$$

The Lewis acid is a chemical substance that can accept a pair of electrons from the Lewis base, that acts as an electron-pair donor. In addition, Lewis acid-base interactions indicate polar interactions of the hydrogen-bonding type. The Lewis acid-base component may be expressed as

$$\gamma^{AB} = 2(\gamma^{+}\gamma^{-})^{1/2} \tag{9}$$

Where γ^{+} and γ^{-} represent the surface free energy of electron-acceptor and electron-donor parameters, respectively.

The interfacial surface free energy is the sum of free energy of all molecules present in the interface between solid and liquid phases. Van Oss *et al.* (1998) suggested that the interfacial energy may be calculated using the following equation.

$$\gamma_{SL} = \gamma_S + \gamma_L - 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^{+}\gamma_L^{-})^{1/2} + (\gamma_S^{-}\gamma_L^{+})^{1/2}] \tag{10}$$

Coupling equation 10 with Young's equation 7 leads to

$$\gamma_L(1 + cos\theta) = 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^{+}\gamma_L^{-})^{1/2} + (\gamma_S^{-}\gamma_L^{+})^{1/2}] \tag{11}$$

Thus, it is possible to determine the γ_S^{LW}, γ_S^{+} and γ_S^{-} components of the surface free energy of the solid from the contact angle measurement using three-liquid method. In this study, water, diiodomethane and ethylene glycol were used as reference. The γ_L^{LW}, γ_L^{+} and γ_L^{-} components of these liquids are shown in Table 2.

Table 2 Surface free energy and its components of liquid employed

	γ_L	γ_L^{LW}	γ_L^{+}	γ_L^{-}
Water	72.8	21.8	25.5	25.5
Diiodomethane	50.8	50.8	0	0
Ethylene glycol	48.0	29.0	1.92	47.0

Where the unit are the mJ/m^2 (Matsushita, 2005)

5.2 Work of adhesion

The work of adhesion refers to the required work in order to separate the interface between liquid and solid phase of surface and can be written as

$$W_a = W_a^{LW} + W_a^{AB} \tag{12}$$

where W_a^{LW} and W_a^{AB} are Lifshitz-van der Waals and Lewis acid-base components of adhesion, respectively (Fowkes, 1983). The work of adhesion between solid and liquid can be expressed as

$$W_a^{LW} = 2\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} \tag{13}$$

$$W_a^{AB} = 2[(\gamma_s^{+}\gamma_L^{-})^{1/2} + (\gamma_s^{-}\gamma_L^{+})^{1/2}] \tag{14}$$

W_a , W_a^{LW} and W_a^{AB} are determined from the calculated values of γ_S^{LW} , γ_S^{+} and γ_S^{-}.

Matsushita *et al.* (2005) studied the surface characteristics of phenol-formaldehyde resin with lignosulfonate and kraft lignin by using contact angle measurement and inverse gas chromatography (IGC). In the contact angle measurement, it was found that the γ_S^{LW} and γ_S^{-} of the prepared resin increased with the substitution of lignin for phenol. This may be due to the chemical component change. The acid-base component of the work of adhesion between water and the resins increased with the amount of lignosulfonate substituted. In IGC, the same γ_S^{LW} trends were obtained from the contact angle measurement. This agreed well with the fact that phenol-formaldehyde-lignosulfonate resin has lower resistance to water than phenol-formaldehyde resin.

Gulec *et al.* (2005) determined hydrophilicity, hydrophobicity and surface free energy glass of polyethylene (PE) and stainless steel (SS 316) by using contact angle measurements. Phenol and 1,1,1,3,3,3-hexaflouroisopropylacrylate (HFIPA) were used to produce hydrophobic materials with low surface energy, and hydroxyethyl-methacrylate (HEMA), ethylenediamine (EDA), polyethyleneglycolethylethermeth-acrylate (PEGEEMA) and polyethyleneglycolmethacrylate (PEGMA) were used to produce hydrophilic materials with higher surface energy. Polyethylene was the most hydrophobic material among the materials used in this study related to its air contact angle and γ_{SL} values. γ_{SL} value was found 38.91 mJ/m^2 for polyethylene. Glass was determined as the most hydrophilic material (γ_{SL} = 1.11 mJ/m^2) among the used surfaces, and its surface energy was (γ_S = 58.95 mJ/m^2).

Mykhaylyk *et al.* (2002) determined surface energy of ethylene-*co*-1-butene copolymers by using contact angle measurement. Results from three methods of calculation are reported one-liquid (Good–Girifalco and Neumann), two-liquid (harmonic mean and geometric mean) and three-liquid (Lifshitz–van derWaals acid–base) methods. The mean results of the three-liquid acid–base method are judged to be the most reliable and informative, leading to surface energies of 30.8 mJ/m^2 for poly(ethylene-*co*-1-butene) copolymer composed of 92 mol% ethylene and 30.2 mJ/m^2 for copolymer composed of 88 mol% ethylene.

MATERIALS AND METHODS

This section described the experimental procedure for laboratory-scale and details of all component include materials, reagents, synthesis and coating method for anacardic acid based phenolic resins.

Materials

1. Erlenmeyer flask
2. Stand and clamps
3. Beaker
4. Glass funnel
5. Separatory funnel
6. Condenser
7. Thermometer
8. Hotplate stirrer (model MSH-20D Wisestir and HTS-1003)
9. Stirrer (Kika Labortechnik)
10. High Performance Liquid Chromatography (HPLC; Thermo Sprectra System Isocratic Pump)
11. HPLC columns LC-18 Phenomenex ® (size 150 × 4.60mm i.d., 5 µm particle size)
12. Hot air oven (Memmert)
13. Digital weigh scales (model Adventurer ARC120)
14. Cross Beater mill (model Retsch muhle)
15. Stainless steel sheet (10 cm × 10 cm × 0.5 cm)
16. Stainless steel pipe (diameter 1 inch)
17. Vacumm pump (model FY-1C MIZU)
18. Contact Angle measuring equipment (KRUSS, DSA10 MK2)
19. Fourier transform infrared spectroscopy (PERKIN ELMER)
20. Differential scanning calorimeter (PERKIN ELMER DSC7)

Chemicals

1. Cashew nut shell
2. Deionize water (DI)
3. Acetic acid 100% supplied by Merck Germany
4. Ethanol 99.9% supplied by Merck Germany
5. Acetonitrile (HPLC grade) supplied by Burdick& Jackson
6. Methanol supplied by Burdick& Jackson
7. Calcium hydroxide supplied by Ajax chemical
8. Anhydrous sodium sulfate supplied by Ajax chemical
9. Hydrochloric acid 37% supplied by Merck Germany
10. Ethyl acetate supplied by Ajax chemical
11. Formaldehyde 37% supplied by Merck Germany
12. Phenol 99% supplied by Panreac England
13. Magnesium hydroxide supplied by Ajax chemical
14. P- cresol 99% supplied by Acros organics
15. M-cresol 99.9% supplied by Carlo erba
16. Acetone 100% supplied by Merck Germany
17. Cyclohexanone 99.9% supplied by Ajax chemical

Methods

1. Preparation of cashew nut shell

1.1 Rinsing the cashew nut shell with water

1.2 Drying in an oven at 60°C for 3 hours

1.3 Grinding the cashew nut shell to small particles by using a cross-beater mill

2. Solvent extraction

2.1 Weighing the cashew nut shell 125 g into the beaker

2.2 Putting 95 percent of ethanol solvent 1 liter

2.3 Extracting by using stirrer at 30°C for 1 hour

2.4 Filtrating the solution by using vacuum pump

2.5 Collecting the resultant solution for analyzing and using in the next step

3. Preparation of Calcium anacardate from CNSL

3.1 Adding calcium hydroxide 31.25 g in the portions under stirring

3.2 Stirring the mixture at 50°C for 3 hours

3.3 Filtering and washing thoroughly with ethanol 100 ml

3.4 Drying the calcium anacardate at 45-50°C for 2 hours

4. Separation of Anacardic acid from calcium anacardate

4.1 Suspending calcium anacardate 62.5 g in distilled water 250 ml and 37% HCl 68.125 ml and stirring for 1 hour

4.2 Extracting the resultant solution with ethyl acetate (2 × 175 ml)

4.3 Drying the organic layer with anhydrous sodium sulfate and distilling under reduced pressure to obtain the mixture of anacardic acid (monoene, diene, and triene)

4.4 Collecting and analyzing the sample by using High performance liquid chromatography (HPLC)

5. Preparation of anacardic acid based resole-type resin

5.1 Mixing phenol (0-0.52 moles), anacardic acid (0.5-2.0 moles), cresol (0-0.38 moles of an equimolar mixture between 3-hydroxy-1-methyl benzene and 4-hydroxy-1-methyl benzene) and formaldehyde (0.5-5.5 moles)

5.2 Stirring monomer solution on stirrer 30 minutes in the 500-ml reactor at room temperature

5.3 Adding 1 percent by weight of magnesium hydroxide powder of anacardic acid as catalyst and the pH of the solution was adjusted to 6

5.4 Mixing with stirrer at 85°C for 1.5 hours and proceeding at 96°C for 1.5 hours

5.5 Dehydrating at 60°C under an oven for 1.5 hours

6. Coating Preparation

6.1 Rinsing surface of steel 304 sheet 10 cm × 10 cm × 0.5 mm with acetone and polishing with 220-grade water abrasive paper

6.2 Dissolving anacardic acid based resins in the mixed ethanol / acetone / cyclohexanone in a volume fraction of 4:2:1

6.3 Coating anacardic acid based resins from step 2 by calculating volume of coating precursors in order to control thickness of the cure coatings 60-70 µm

6.4 Curing the samples in three step; 2 hours at 60°C/ 2 hours at 120°C and 2 hours at 180°C

6.5 Testing with contact angle measuring equipment in order to obtain the average value of the contact angles measured for at least five different positions on each phenolic coatings

6.6 Calculating surface free energy and work of adhesion of phenolic coatings

7. Pressure drop in pipes

7.1 Injecting phenolic coatings into stainless steel pipes in diameter 1 inch pipes are pre-heated to 80°C

7.2 Rotating stainless steel pipes around its longitudinal center axis with motors

7.3 Curing the phenolic coatings in three step; 2 hours at 60°C/ 2 hours at 120°C and 2 hours at 180°C

7.2 Testing pressure drop by pumping water into pipes and controlling flow rate by using flow meter

7.3 Controlling the flow rate by adjusting the valve position

7.4 Collecting pressure at the inlet and outlet pressure in order to calculate pressure drop and Fanning frictional factor

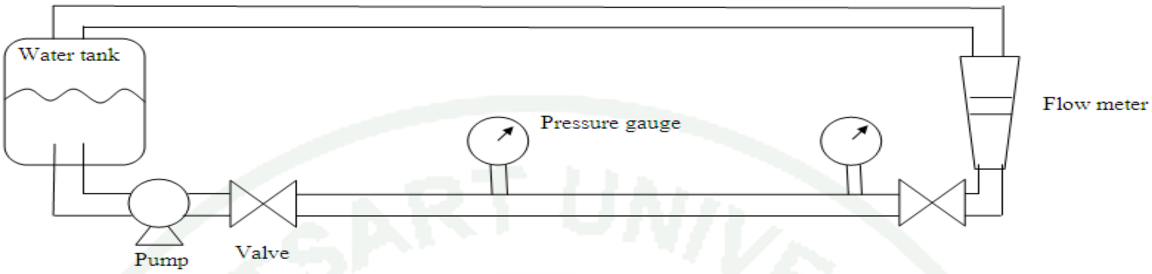


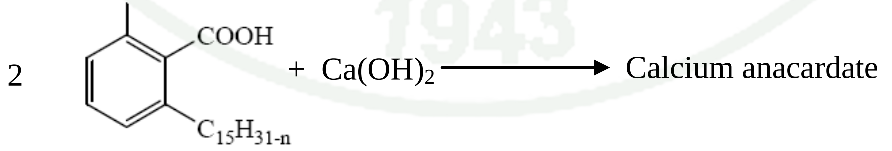
Figure 12 Schematic diagram of the experimental system

RESULTS AND DISCUSSION

In this study, the experiments were divided into 4 parts which consisted of the preparation of anacardic acid, the effects of anacardic acid, formaldehyde and cresol content on hydrophobic behaviors of anacardic acid based resole-type resin, the study on thermal and chemical properties of anacardic acid based resole-type resin followed by the pressure drop and Fanning friction factor for the smooth and coated pipe.

1. Anacardic acid preparation

Isolation of anacardic acid was performed as per Paramashivappa *et al.* (2001) with a few operational modifications. The cashew nut shell (CNS) was rinsed with water in order to remove adulterated things and then was dried in an oven at $60^{O}C$ for 3 hours. The obtained CNS was put in a cross-beater mill where the shell structure was broken down to clumps of oily and sticky tiny solid particles. This presumably would help to substantially reduce the equilibration time during solvent extraction. When 125 g of crushed CNS was dissolved in 1 liter of 95 percent ethanol and vigorously stirred at $30^{O}C$ for 1 hour, the color of the solution became dark brown**.** The resultant solution as received was vacuum-filtrated and reacted with $Ca(OH)_2$ at $50^{O}C$ as the reaction proceeded for 3 hours under the acid-base reaction as shown in equation 15.



(15)

Accordingly, the obtained cake of fine particles (calcium anacardate) was filtered, thoroughly washed out with ethanol, and dried in an oven at $50^{O}C$ for two hours in order to remove any solvent retained within the cake. Concentrated hydrochloric acid (37%) was used to remove calcium in the form of calcium chloride ($CaCl_2$) while protons combined with the anacardate ions. Liquid-liquid extraction with ethyl acetate was applied in order to separate the anacardic acid from a homogeneous solution which consisted of both anacardic acid and $CaCl_2$. Being soluble in water, calcium chloride stayed in the aqueous phase and anacardic acid moved into the organic phase appeared as brown oil floating on top of the aqueous phase. A separating funnel was used to take apart the two phases. The upper organic phase was dried over anhydrous sodium sulfate in order to get rid of water dissolved in ethyl acetate. The solvent was concentrated using a rotary evaporator at 40^{O}C, which gave anacardic acid. The sample of anacardic acid was taken for analysis using high-performance liquid chromatography (HPLC). The structure of anacardic acid consisted of 4 structures of striking similarity as shown in Figure 13.

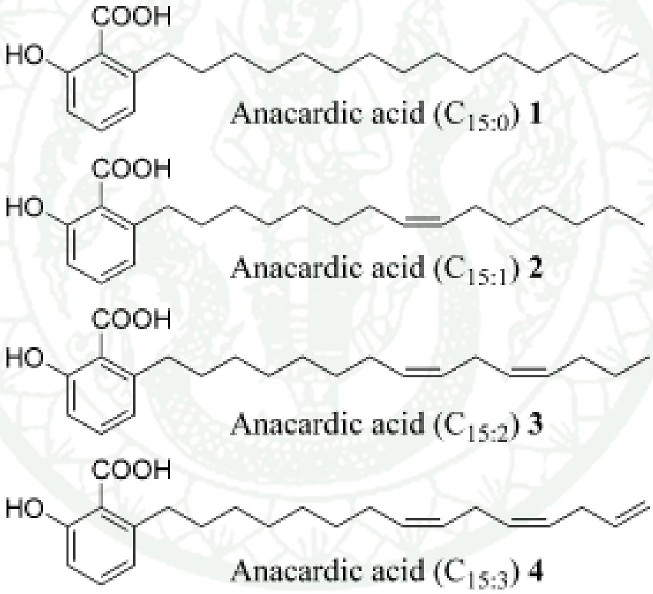


Figure 13 Structure of anacardic acid

Where number 1 is saturated form of anacardic acid (MW= 348 gram mole)

number 2 is monoene form of anacardic acid (MW= 346 gram mole)

number 3 is diene form of anacardic acid (MW= 344 gram mole)

number 4 is triene form of anacardic acid (MW= 342 gram mole)

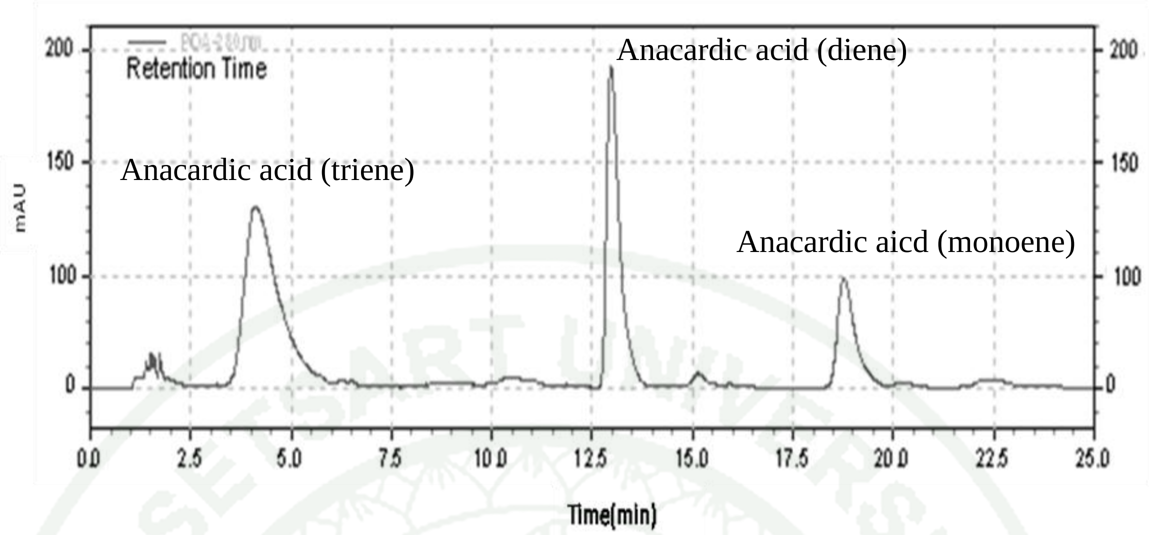


Figure 14 Chromatogram of anacardic acid

Name	**Retention time (min)**
Anacardic acid (triene)	4.033
Anacardic acid (diene)	13.272
Anacardic acid (monoene)	19.208

A chromatogram of anacardic acid is shown in Figure 14. There are three distinct peaks at 4.033, 13.272 and 19.208 minutes corresponding to triene-, diene-, and monoene anacardic acid respectively. It is evident that other constituents of cashew nut shell were not appreciably present in the sample. Therefore, this acid was used to synthesize anacardic acid resole-type phenolic resin.

2. Hydrophobic behaviors of anacardic acid resole-type phenolic resin

The hydrophobic behaviors are the property that water on non-polar surfaces exhibits high contact angle. The contact angle is the angle at which a liquid/vapor interface meets the solid surface. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The wettability of materials is determined by contact angle measurements, which is defined as wettable (highly hydrophilic 0°≤θ≤45°), less strongly hydrophobic (45°≤θ≤90°) and not wettable (highly hydrophobic 90°≤θ≤ 180°). The static contact angles of water on the surfaces of phenolic coatings were measured with contact angle measuring equipment using sessile drop method. The sessile drop technique is a method used for the characterization of surface free energy by placing droplet of liquid on the surfaces. The contact angle of the droplet and the known surface free energy of the liquid are the parameters which can be used to calculate the surface free energy of the solid sample. Hydrophilicity is indicated by small contact angle and high surface free energy. Contact angle measurement was performed in order to obtain the average value of the contact angles measured for at least five different positions on each phenolic coating.

2.1 The effect of anacardic acid to phenol ratio

The initial anacardic acid molar ratio is one of the factors that influences most the formation of phenolic resole resins. First study, we focused on the effect of anacardic acid to phenol ratio in order to determine the parameters of surface free energy of phenolic coatings by contact angle measurement. The three-liquid method described previously was used.

The calculated results of γ_S^{LW}, γ_S^{+} and γ_S^{-} components of phenolic coatings are shown in Table 3. It can be seen that the contact angle slightly increases with increasing AnAc content (No.2-5), where the reverse trend was observed for both γ_S^{LW} and γ_S^{-}. The hydrophobic property of coating was enhanced due to alkylphenols leading to strongly hydrophobic phenolic resins which are compatible with oils, natural resins and rubbers. Such alkylphenolic resins can be used as modifying and crosslinking agents for oil varnishes, as coatings/ printing inks, and as antioxidants/ stabilizers. The stainless steel sheet coated with PC (No.5) provided a significant reduction in contact angle as much as 24.39% (compared to the non-coated sheet, No.1). These results suggest that the phenolic coatings from AnAc are strongly hydrophobic.

Table 3 Surface characteristics of the prepared resins obtained by contact angle Measurement

Sample	Contact angle (Theta)			Surface free energy (mJ/m^2)			
	Water	Diiodo-methane	Ethylene Glycol	γ_S	γ_S^{LW}	γ_S^{+}	γ_S^{-}
1. Control	73.96(1.24)	52.16(0.6)	57.72(1.09)	33.72	33.06	0.01	14.42
2. Synthesized phenolic resin (PRS)	89.66(0.41)	54.76(0.4)	65.72(4.58)	32.11	31.58	0.02	3.67
3. Phenol : AnAc 1:2 (PC1:2)	87.26(0.27)	61.6(3.36)	71.18(0.5)	27.96	27.65	0.003	7.54
4. Phenol : AnAc 1:4 (PC1:4)	89.28(0.24)	56.6(1.9)	71.28(0.81)	31.48	30.53	0.04	5.71
5. 1.55 mol AnAc (PC)	92.00(0.6)	59.72(0.26)	72.08(0.84)	28.93	28.74	0.002	4.19

1. Control: non-coated stainless steel sheet
2. Phenolic resin synthesized with the molar ratio of phenol (P) : formaldehyde (F) : cresol (C) = 1.55 : 4.5 : 0.38 (PRS)
3. Phenolic resin synthesized with the molar ratio of P : anacardic acid (AnAc) : F : C = 0.52 : 1.03 : 4.5 : 0.38 (PC1:2)
4. Phenolic resin synthesized with the molar ratio of P : AnAc : F : C = 0.31 : 1.24 : 4.5 : 0.38 (PC1:4)
5. Phenolic resin synthesized with the molar ratio of AnAc : F : C = 1.55 : 4.5 : 0.38 (PC)

Values in parentheses are the standard deviation for the data set of five.

We investigated the wettability between the prepared phenolic coatings and liquid (water and ethylene glycol) by calculating the work of adhesion using the γ_S^{LW}, γ_S^+ and γ_S^- components as shown in Table 4. The work of adhesion between water and resin ($W_{a,H_2O-re\sin}^{AB}$) decreases with increasing AnAc content. Stainless steel sheet coated with PC provided a significant reduction in $W_{a,H_2O-re\sin}^{AB}$ as much as 29.32% (compared to the non-coated sheet). Ethylene glycol has 2 hydroxyl groups, which can accept hydrogen ions from the prepared coatings; therefore, it can be considered predominantly Lewis basic. The W_a^{AB} between ethylene glycol and the resin ($W_{a,EG-re\sin}^{AB}$) increases with substitutions of AnAc suggesting that the phenolic coatings from AnAc and ethylene glycol are strongly bound via intermolecular forces. These results can be attributed to an increase in the acidic character of the resin surface.

Table 4 Lewis acid-base components of work of adhesion between prepared resin

	W_a^{AB}				
	Control	PRS	PC 1:2	PC 1:4	PC
Water	39.22	26.60	27.99	27.9	27.72
Ethylene glycol	11.71	10.47	10.60	10.78	11.68

2.2 The effect of formaldehyde content

According to previous results, the use of phenol in the formulation of the polymeric film weakened the hydrophobic properties of the surface. Therefore, subsequent surface preparations of AnAc based-rosole type resin were performed without phenol. The effect of formaldehyde content on the hydrophobic behaviours of the coatings is shown in Figure 15 (for the fixed amounts of 1.55 moles AnAc and 0.38 moles cresol). It is apparent that increasing formaldehyde content (less than 3.5 moles) causes the contact angle of the coatings to increase while γ_S^{LW} and γ_S^- decrease. Further increasing formaldehyde content beyond 3.5 moles, the contact angle decreases and γ_S^{LW} slightly increases while γ_S^- is unaffected. There are two proposed mechanisms in the literatures that involve ether and methylene bridges in the polymeric film (Knop and Pilato, 1985; Knof *et al.*,1988; Manfredi *et al.*, 1999). The addition of formaldehyde onto the free *ortho* and *para* phenolic sites results in the formation of 2,4-dihydroxymetylanacardic acid (2,4-DHMAnAc) or 2,6-dihydroxymetylanacardic acid (2,6-DHMAnAc) (Figure 16). When the formaldehyde content is low (less than the optimum content), some active *ortho* or *para* sites of each benzene ring in the polymeric film can interact with water. More hydroxymethyl groups appear on the phenolic ring with increasing formaldehyde content. These functional groups can interact with water via hydrogen bonding. The optimum content of formaldehyde (the maximum hydrophobicity) was found at 3.5 mol formaldehyde, 1.55 mol AnAc and 0.38 mol cresol (PCF 3.5).

The work of adhesion is carefully considered in order to support previous results on hydrophobic behaviors of the prepared coatings. Figure 17 shows the work of adhesion of water and ethylene glycol. The $W_{a,H_2O-re\sin}^{AB}$ decreases with increasing formaldehyde content (less than 3.5 mol). The $W_{a,H_2O-re\sin}^{AB}$ is virtually unaffected for formaldehyde content over 3.5 mol and the optimum content of formaldehyde was found at 3.5 mol. This is due to the limited free active *ortho* and *para* sites of the polymeric film causing excess hydroxymethyl groups in the polymer network (weakly-interacting with water). A similar trend was observed for the work of adhesion between ethylene glycol and resin, $W_{a,EG-re\sin}^{AB}$. These results show a decrease in the acidic character of the resin surface due to hydroxymethyl groups on the benzene ring of the polymeric film that act as an electron-pair donor.

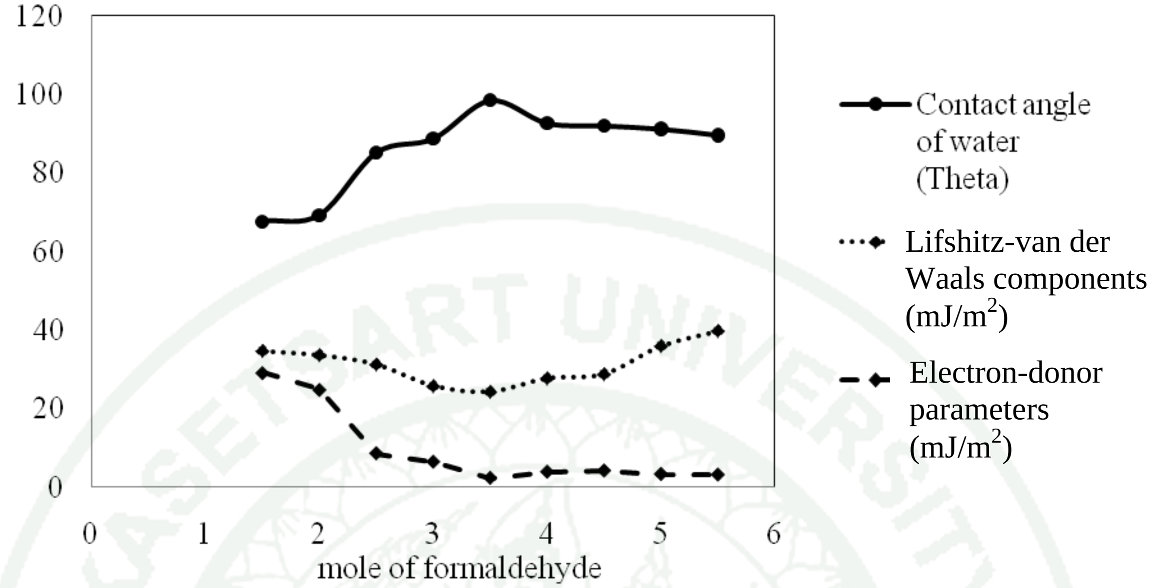


Figure 15 Effect of the formaldehyde content on the contact angle, Lifshitz-van der Waals and electron-donor components of the phenolic coatings

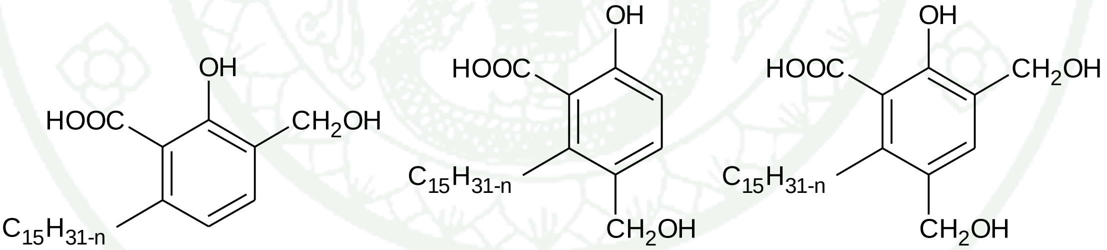


Figure 16 Structure of 2-hydroxymetylanacardic acid (2-HMAnAc), 2,4-dihydroxymetylanacardic acid (2,4-DHMAnAc) and 2,6-dihydroxymetylanacardic acid (2,6-DHMP)

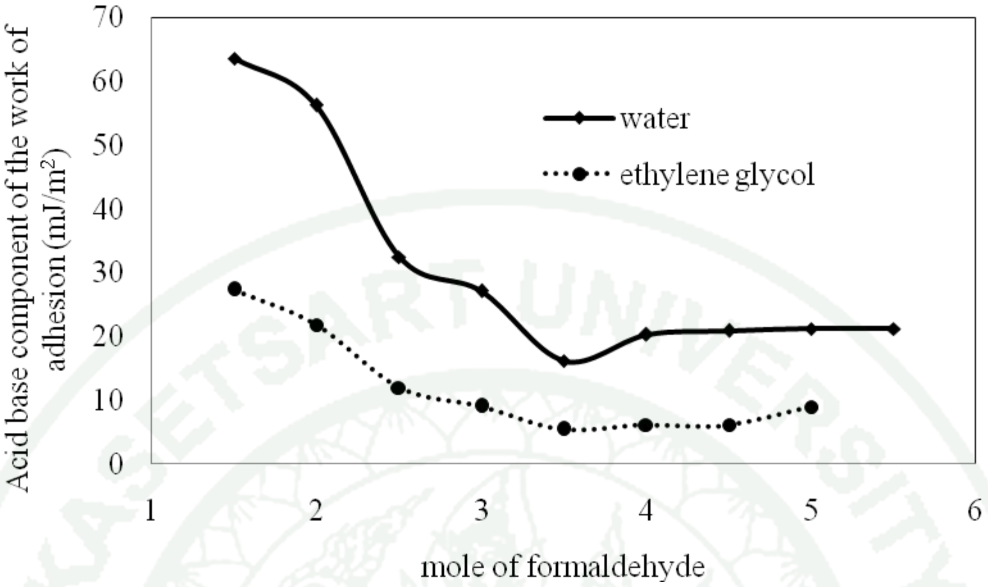


Figure 17 Effect of the formaldehyde content on the acid-base components of the work of adhesion of water and ethylene glycol of the phenolic coatings

2.3 The effect of cresol content

The effect of the cresol content in the coatings on hydrophobic behaviours is shown in Figure 18. The contact angle of the coatings shows a significant increase with increasing cresol content while the opposite trend was observed for both γ_S^{LW} and γ_S^-. In other words, the cresol-free formaldehyde-AnAc resin is more strongly hydrophilic compared to cresol-formaldehyde-AnAc resin (with 0.38 moles of cresol). It is probable that the water interaction around hydroxyl groups in close proximity to hydrocarbon methyl substituents in the phenolic network is hindered by steric effect. Similar observations were reported for o-cresol novolac-epoxy network (Gibson *et al.*, 2002; Ogata *et al.*, 1993)

The effect of the cresol content on the work of adhesion of water and ethylene glycol is shown in Figure 19. Both $W^{AB}_{a,H_2O-resin}$ and $W^{AB}_{a,EG-resin}$ decrease upon the addition of cresol indicating a decrease in the acidic character of the resin surface due to the hydrocarbon methyl and hydroxyl group on the benzene ring of cresol-formaldehyde-AnAc resin that act as an electron-pair donor.

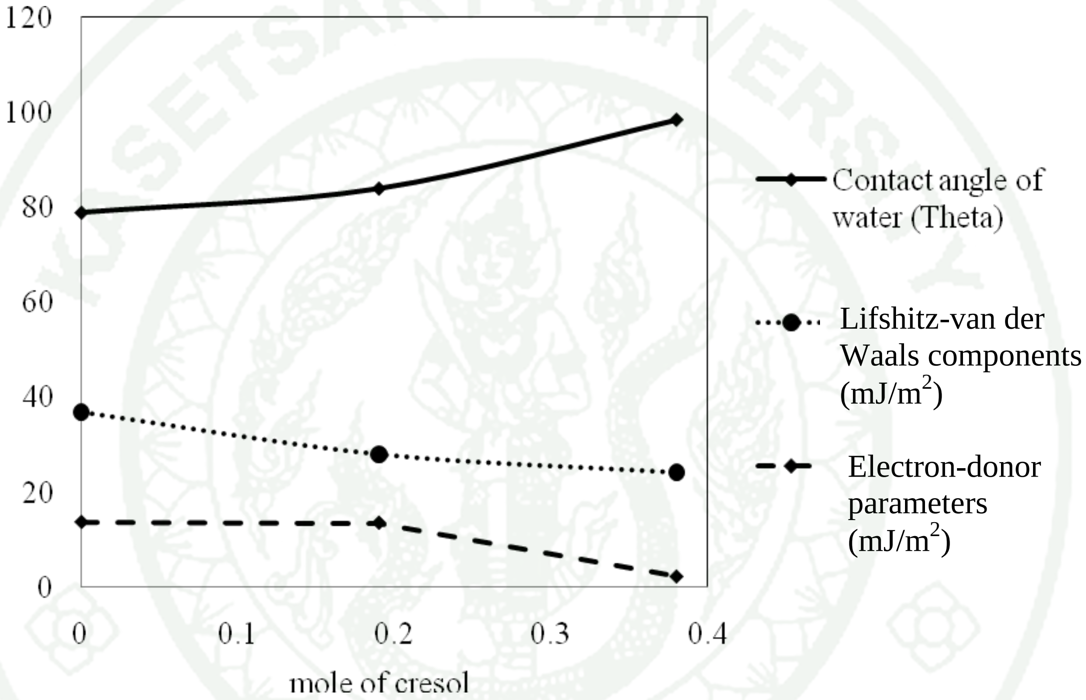


Figure 18 Effect of the cresol content on the contact angle, Lifshitz-van der Waals and electron-donor components of the phenolic coatings

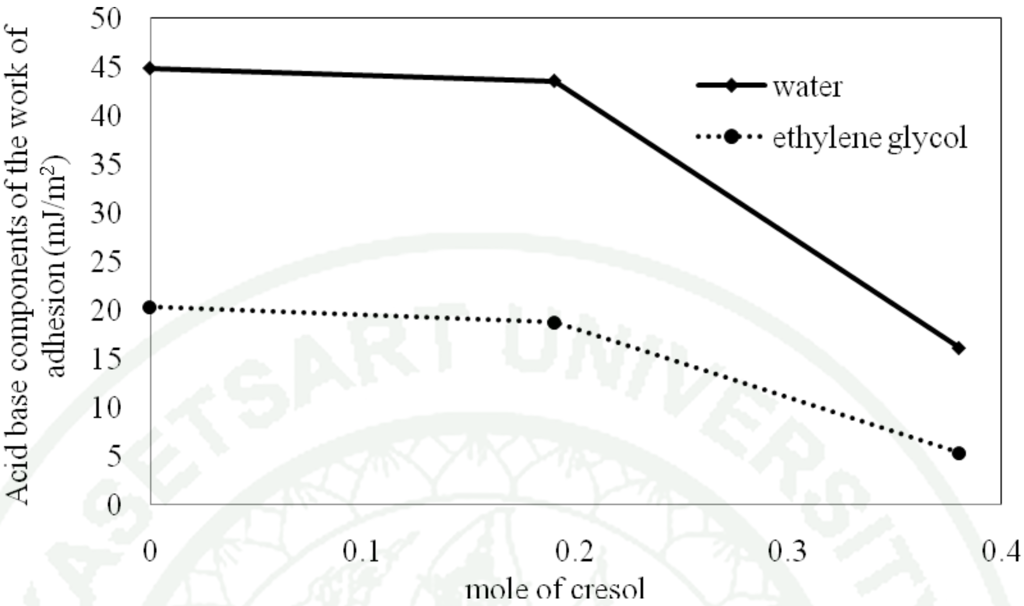


Figure 19 Effect of the cresol content on the acid-base components of the work of adhesion of water and ethylene glycol of the phenolic coatings

2.4 The effect of anacardic acid content

The following set of experiments was carried out to study the effect of AnAc content of the AnAc based-rosole type resin on the surface properties (for the fixed amounts of 3.5 moles formaldehyde and 0.38 moles cresol). Figure 20 shows the effect of AnAc content on the surface hydrophobicity via contact angle measurement. It can be seen that the addition of AnAc can suppress the hydrophobic behaviours of the coatings. The contact angle increases while γ_S^{LW} and γ_S^- decrease with increasing AnAc content (less than 1.55 moles). On the other hand, the substitution of AnAc in excess of 1.55 moles causes the contact angle to decrease while γ_S^{LW} and γ_S^- increase. These results show the reverse effect of formaldehyde content on the hydrophobic behaviours of the coatings. The optimum content of AnAc (the strongest hydrophobicity) was found at 1.55 mol, 3.5 mol formaldehyde and 0.38 mol cresol. Further increasing AnAc content leads to suppression of hydrophobic properties. The effect of AnAc content on the work of adhesion of water and ethylene glycol are shown in Figure 21. $W_{a,H_2O-re\sin}^{AB}$ rapidly decreases with the substitution of AnAc to the minimum of 16.13 mJ/m^2 at 1.55 moles AnAc. When the AnAc content is low, the surface can interact with water via hydrogen bonding with hydroxymethyl groups on the phenolic ring. High AnAc content leads to the water interaction via active *ortho* or *para* sites of each benzene ring in the polymeric film. For the acid-base property of the prepared surfaces, for AnAc content less than 1.55 moles, $W_{a,EG-resin}^{AB}$ revealed an increase in the acidic character of the resin surface due to carboxylic groups on the benzene ring of the prepared coatings that act as electron-pair acceptor. This trend continues to an optimum at 1.55 moles AnAc with $W_{a,EG-resin}^{AB}$ =5.40 mJ/m^2. However, at high AnAc content, the prevalence of hydroxymethyl groups slightly suppresses the acidic character of the surface i.e. $W_{a,EG-resin}^{AB}$ =9.96 mJ/m^2 at 2 moles AnAc.

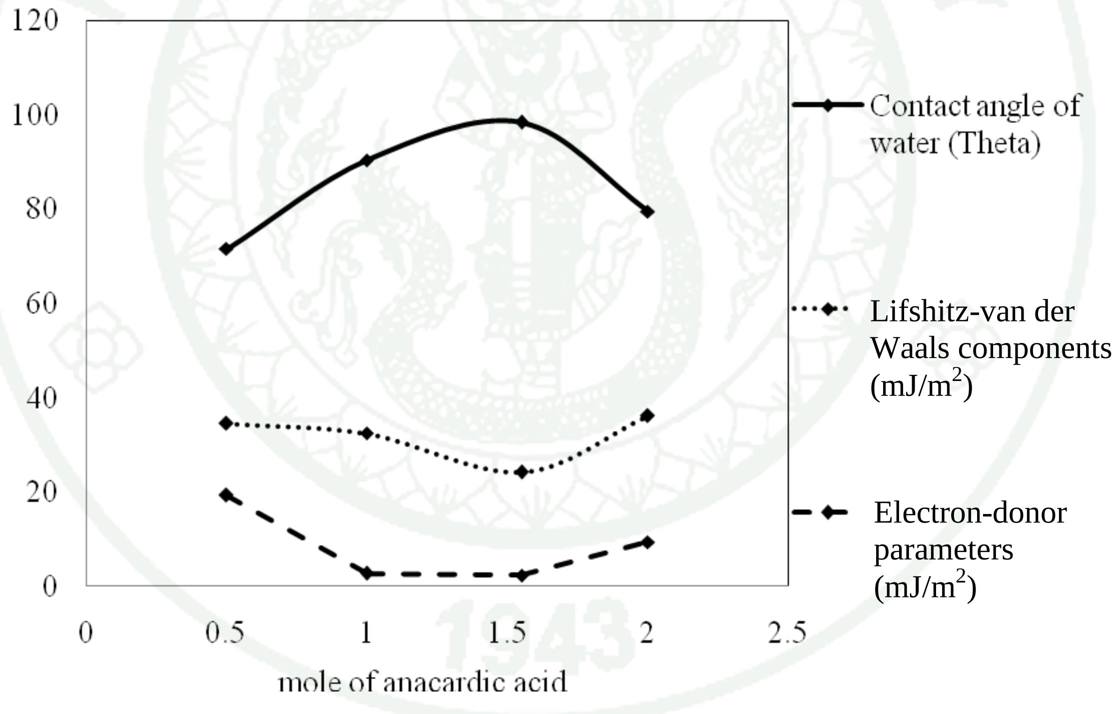


Figure 20 Effect of the anacardic acid content on the contact angle and Lifshitz-van der Waals and electron-donor components of the phenolic coatings

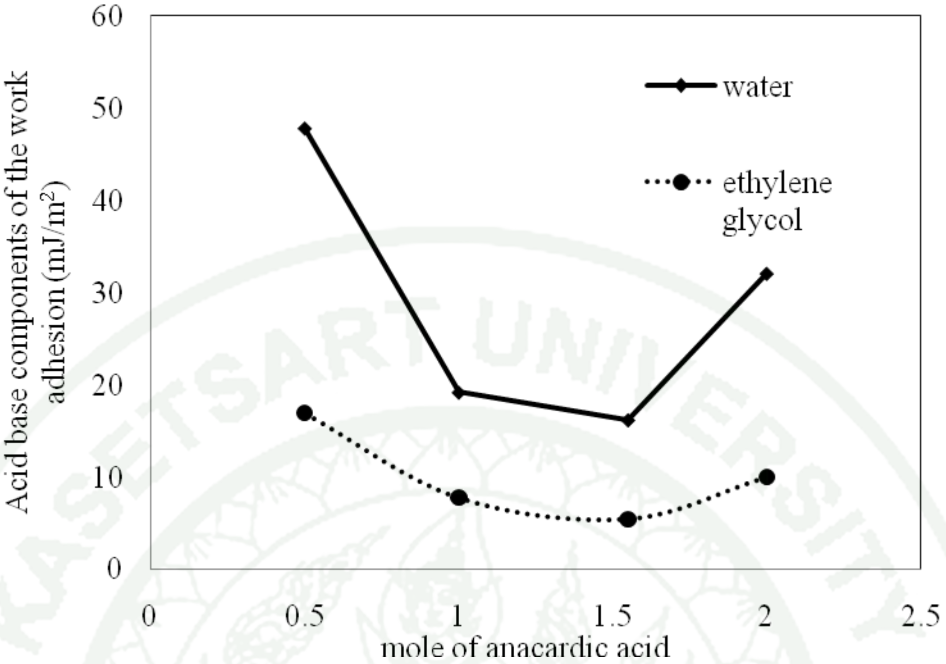


Figure 21 Effect of the anacardic acid content on the acid-base components of the work of adhesion of water and ethylene glycol of the phenolic coatings

3. Thermal and chemical properties of anacardic acid based rosole-type resin

3.1 Thermal properties of anacardic acid based resole-type resin

The maximum hydrophobic polymer was used to study thermal properties by using differential scanning calorimetry (DSC) that is a thermalanalytical technique in which the different in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The main application of DSC is for studying phase transitions, such as melting, glass transitions or exothermic decompositions. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperature (T_g). Glass transition is the transition from the liquid state to the glass or an amorphous solid. Below T_g, amorphous solids are in a glassy state and most of their joining bonds are intact. In inorganic glasses, with increased temperature more and more joining bonds are broken by thermal fluctuations so that broken bonds begin to form clusters. As the temperature increases, an amorphous solid will become less viscous. Crystallization temperature (T_c) occurs when the molecule may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. As the temperature increases the sample eventually reaches its melting temperature (T_m). When considered as this temperature of the change from solid to liquid phase.

Table 5 shows the thermal properties determined by differential scanning calorimetry (DSC) for the synthesized phenolic resin (PRS) and the AnAc based-resole type resin (PCF 3.5) at a heating rate of 20 ^oC min^{-1} (Figure 22 and 23). The effect of AnAc on T_m of PCF 3.5 has also been compared to that of non-anacardic acid resin (PRS) in Table 5. The melting temperature of PRS and PCF 3.5 was 163.52 ^oC and 184.14 ^oC, respectively. It is evident that the melting temperature markedly increased upon the substitution of AnAc for phenol possibly caused by the alkyl groups (side chain) from AnAc monomer confounded in the complex network of the polymeric film. The enthalpy of thermal decomposition of the anacardic acid base-resole type resin (ΔH) was also determined via DSC. Results show that the decomposition of PRS and PCF 3.5 are exothermic with the heat of fusion of 417.34 and 245.86 J/g, respectively. The higher heat of fusion of PRS can be related to the high crosslinking density caused by the prevalence of active sites (2 *ortho-* sites and 1 *para-* site as compared to one *ortho-* and one *para-* site for PCF 3.5) that can interact with hydroxymethyl group of formaldehyde producing ether or methylene bridges.

Table 5 Thermal properties of phenolic coatings

Sample	T_i (^OC)	T_{onset} (^OC)	T_m (^OC)	T_{stop} (^OC)	ΔH (J/g)
PRS	152.63	154.66	163.52	183.56	417.34
PCF 3.5	179.34	181.42	184.14	199.03	245.86

Where T_i is kick-off temperature, where the curing starts

T_{onset} is temperature where the first detectable heat is released

T_{stop} is temperature of end of curing

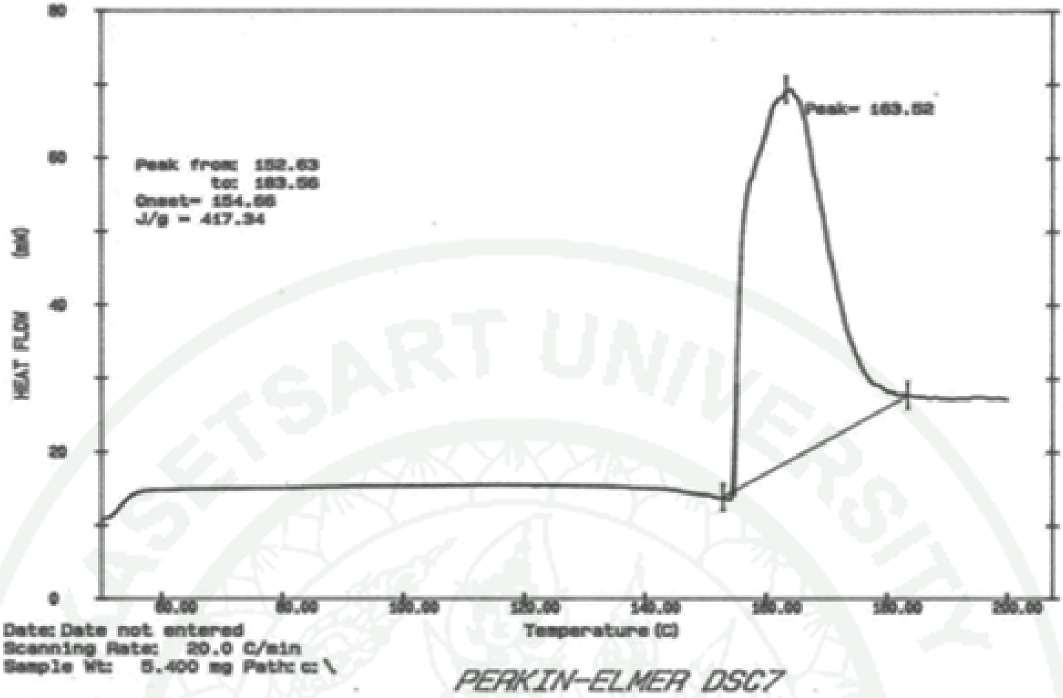


Figure 22 DSC scan of PRS (P : C : F = 1.55 : 0.38 : 3.5)

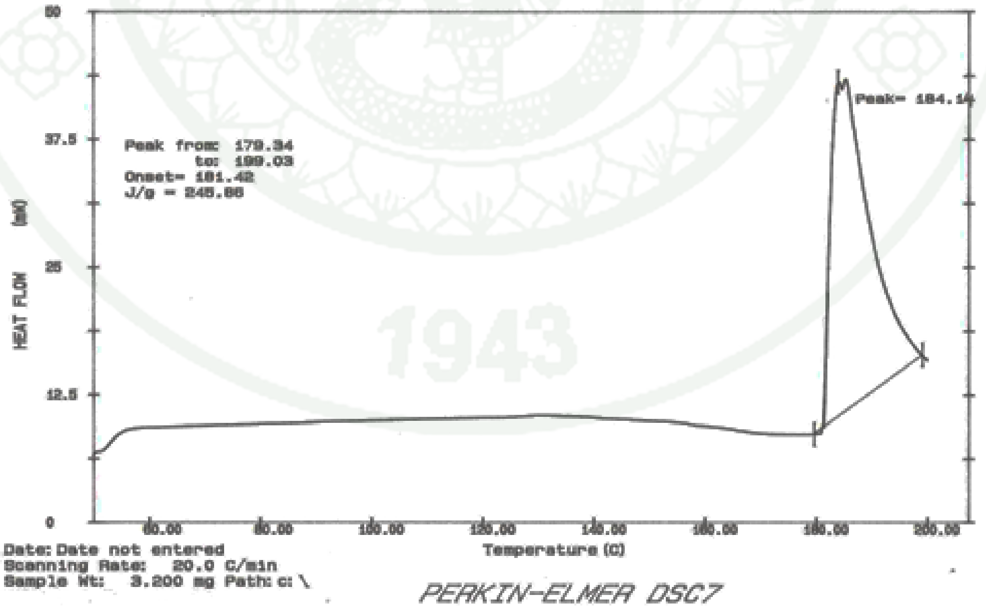


Figure 23 DSC scan of PCF 3.5 (AnAc : C : F = 1.55 : 0.38 : 3.5)

3.2 Chemical properties of anacardic acid based-resole type resin

Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. Hence, the correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample.

AnAc based-resole type resin was synthesized via two types of reaction for which the mechanism was proposed for phenolic resin (Knop and Pilato, 1985; Knof *et al.*,1988; Manfredi *et al.*, 1999). The first reaction is the addition of the formaldehyde at *ortho*- and *para*- positions of phenol (Figure 24). The other reaction is condensation with the formation of water. Two different types of condensation reactions of AnAc based-resole type resin can occur between the phenol free position and the methylolphenols producing an ether bridge, and between the methylolphenols themselves producing a methylene bridge (see Figure 25).

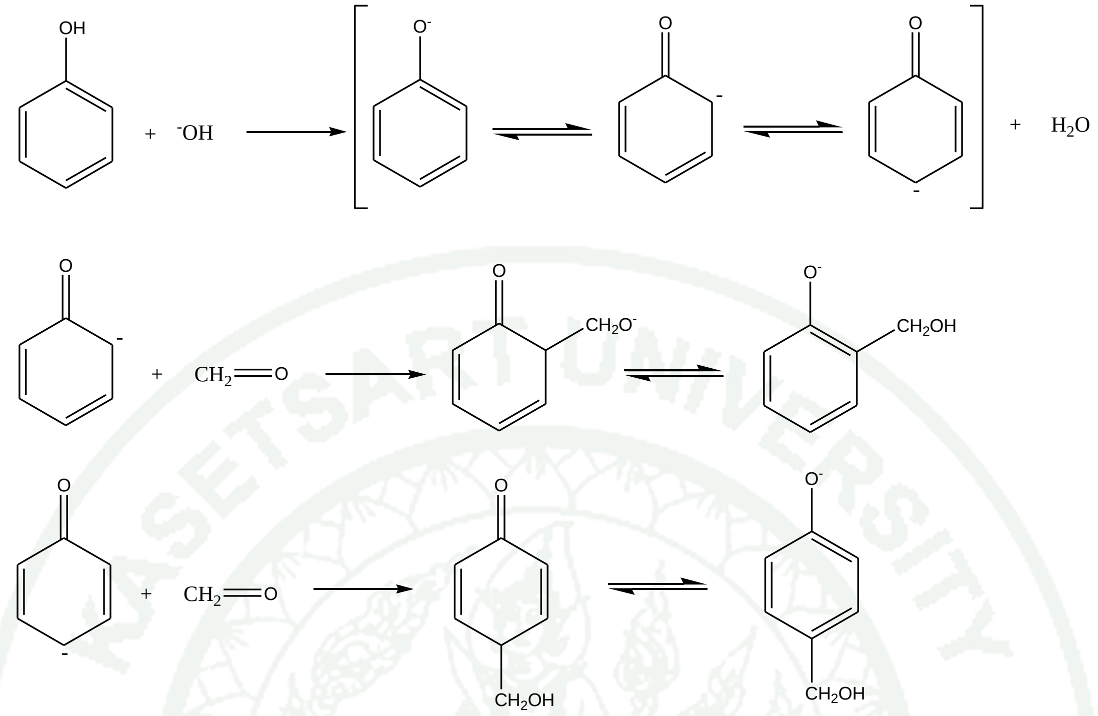


Figure 24 Reaction scheme for the prepolymer resole type resin

Source: Gibson (2001)

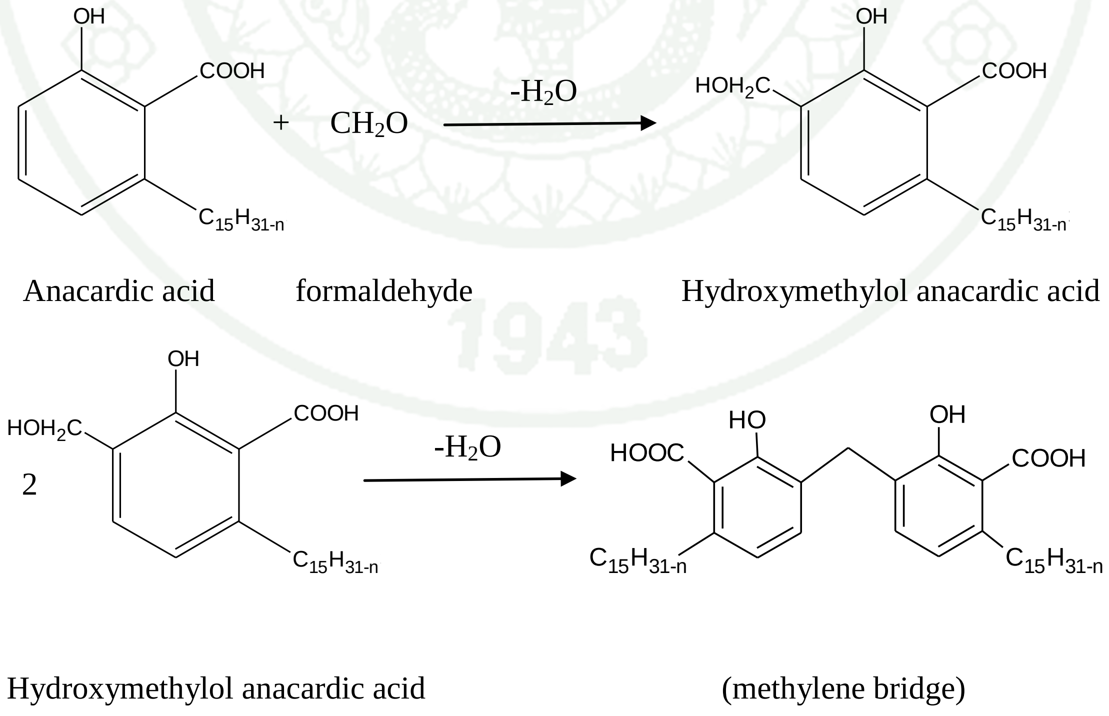
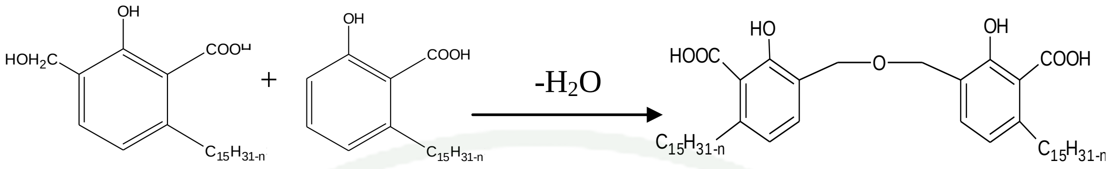


Figure 25 Reaction scheme for the methylene and ether bridge

Or



Hydroxymethylol anacardic acid (ether bridge)

Figure 25 (Continued)

Source: Gibson (2001)

FTIR spectrum (Figure 26) of AnAc based-resole type resin shows the condensation of methylolated AnAc and the degree of *ortho*- and *para*- substitution. This result revealed, in the first emission, a methylolated AnAc due to the C=O stretching from CH_2OH (1075 cm^{-1}-1117 cm^{-1}) and an intense band near 1637 cm^{-1}. The latter bands at 780 cm^{-1} and 872 cm^{-1}suggest the *ortho*- and *para*- substitution in benzene nuclei. The characteristic band at 993 cm^{-1} indicates the substitution in benzene nuclei and the band near 911 cm^{-1} and 696 cm^{-1} are attributed to three adjacent hydrogen atoms in the benzene nuclei. The intensity of peaks at 1588 cm^{-1} (C=C, stretch), 3010 cm^{-1} (C-H stretch of alkene) and 780 cm^{-1} (C-H out-of-plane deformation) imply that the polymerization progressed through the substitution of CH_2OH and not through the double bonds in the side chain. The appearance of the peaks at 2800-3000 cm^{-1} indicates the carboxylic acid group of AnAc based resole-type resin. The single band at 3376 cm^{-1} was also observed and could be relate to the presence of hydroxyl groups in the methylolated AnAc.

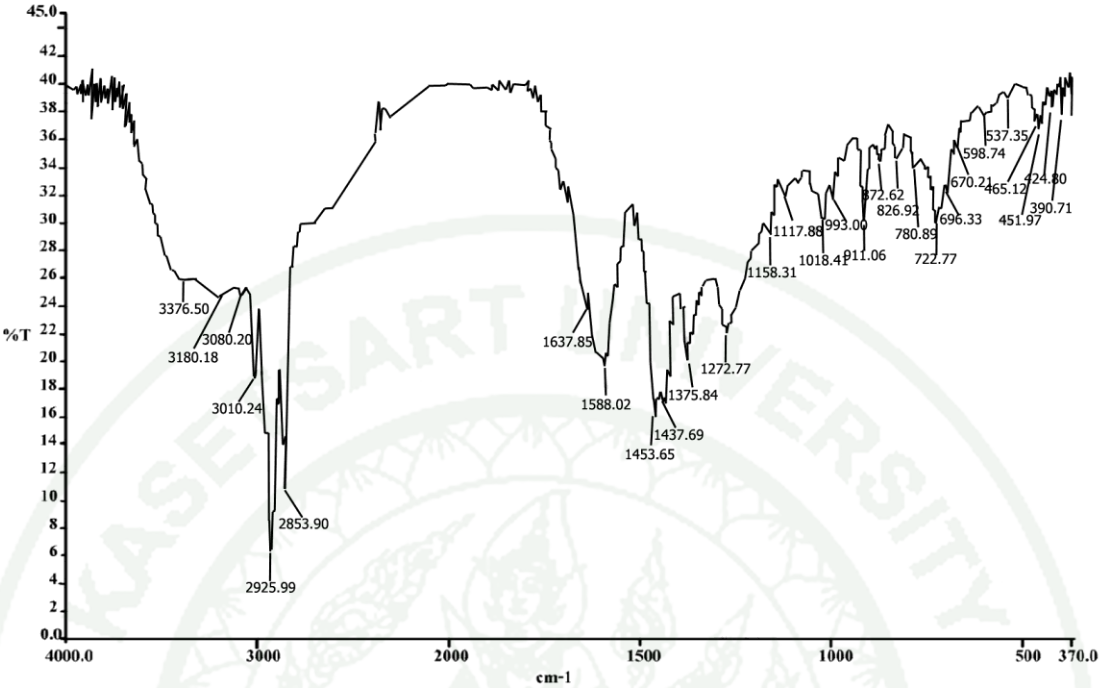


Figure 26 IR spectrum of anacardic acid based-resole type resin

4. Pressure drop and Fanning friction factor for the smooth pipe and the coated pipe

The coating (the maximum contact angle) was coated on the inner surface of 1-inch pipe. Then the pipe was rotated around the longitudinal center axis with motor 5 minutes at 80°C and cured in three steps; 2 hours at 60°C / 2 hours at 120°C / 2 hours at 180°C. The flow rate of water was controlled by adjusting the valve position, while collecting the inlet and outlet pressures.

The strongest hydrophobic surface (the molar ratio of anacardic acid : cresol : formaldehyde = 1.55:0.38:3.5) was selected for studying the pressure drop of water flow in a straight pipe. The pressure drop for both stainless steel coated with this polymer and non-coated pipe increases with increasing of volumetric flow rate. Results (Figure 27) of the pressure drop measurement for stainless steel coated with this polymer shows a significant reduction in pressure drop as much as 14.29% compared to the non-coated pipe for the water volumetric flow rate of 2.36 m^3/h.

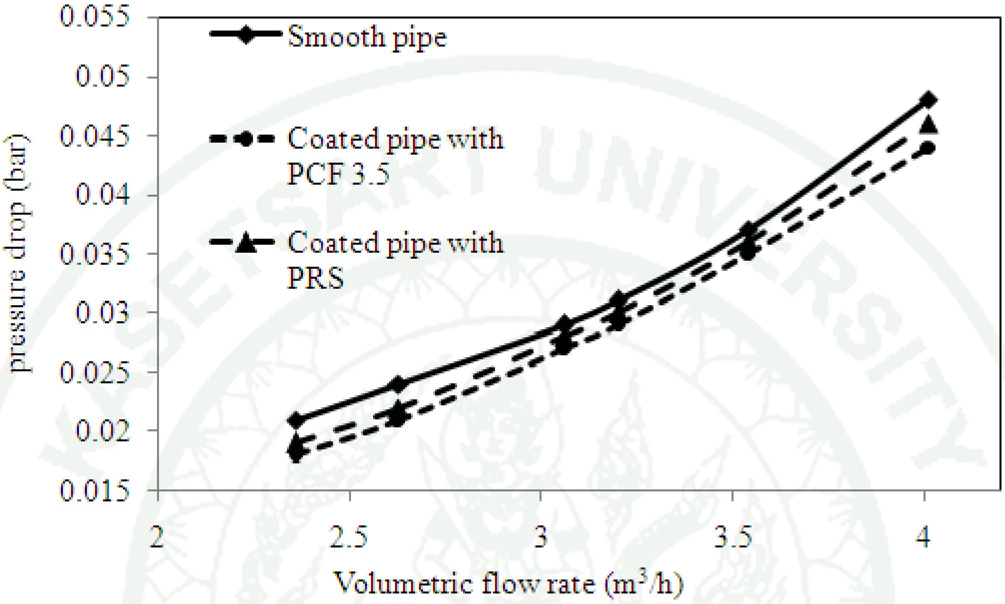


Figure 27 Pressure drop for the smooth pipe and the coated pipe

Fanning friction factor was calculated according to the measured pressure drop. Fanning friction factor versus Reynolds number of filled coatings and non-coated pipe are shown in Figure 28. These results of the Fanning friction factor decrease with increasing of Reynolds number but the non-coated pipe data have higher position. Moreover, the results of the Fanning friction factor for stainless steel coated with this polymer provide a significant reduction in pressure drop as much as 14.38% compared to the non-coated pipe for Reynolds number of 4.38E+04.

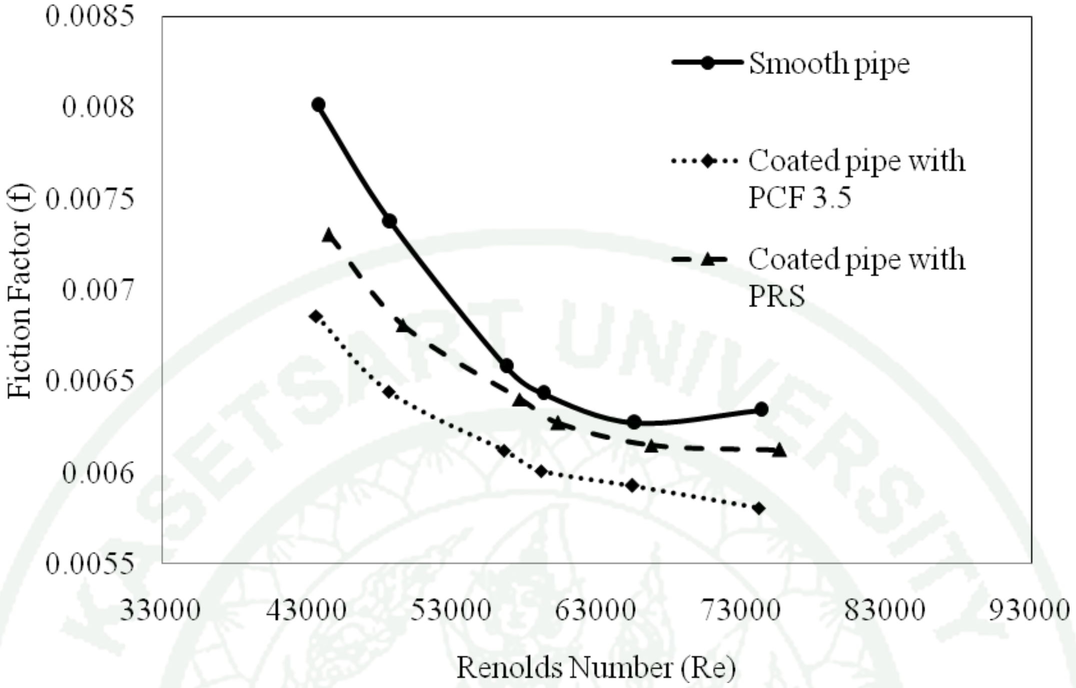


Figure 28 Fanning friction factor for the smooth pipe and the coated pipe

CONCLUSION

The maximum contact angle of anacardic acid based-resole type phenolic resin (molar ratio of anacardic acid : cresol : formaldehyde is 1.55 : 0.38 : 3.5) was 98.46^{O} suggesting highly hydrophobic properties. The results of the Lifshitz-van der Waals components, γ_S^{LW} , were the lowest value with the optimum substitution of anacardic acid, formaldehyde and cresol. The acid-base component of the work of adhesion, W_a^{AB}, between water and phenolic coatings decreased with the optimum condition of phenolic coatings. This indicated that optimum anacardic acid-cresol-formaldehyde resin has the highest resistance to water. DSC studies of phenolic coatings showed the highest melting temperature. FTIR spectrum of AnAc based-resole type resin revealed the *ortho*- and *para*- substitution and the condensation of methylolated AnAc. Stainless steel coated with this polymer provided a significant reduction in pressure drop and Fanning friction factor around 14% (compared to the non-coated pipe) for the water flow in pipe (Reynolds number = 4.38E+04).

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APPENDIX

Appendix Table 1 Surface characteristics of the effect of formaldehyde content of phenolic coatings obtained by contact angle measurement

Sample	Contact angle (theta)			Surface free energy (mJ/m^2)			
	Water	Diiodo-methane	Ethylene glycol	γ_S	γ_S^{LW}	γ_S^+	γ_S^-
1. PCF 1.5	67.7(0.58)	49.3(0.44)	67.88(0.62)	44.35	34.66	0.8	29.25
2. PCF 2.0	69.24(0.4)	51.22(0.51)	65(0.31)	39.37	33.59	0.34	24.84
3. PCF 2.5	85.16(0.61)	55.4(0.12)	69.94(0.6)	32.86	31.22	0.08	8.58
4. PCF 3.0	88.74(0.55)	65(0.51)	71(2.71)	26.44	25.07	0.02	6.41
5. PCF 3.5	98.46(0.34)	61.6(1.19)	72.08(1.53)	24.49	24.22	0.01	2.27
6. PCF 4.0	92.68(0.4)	61.6(1.19)	72.08(1.53)	27.86	27.65	0.01	3.83
7. PCF 4.5 or PC	92(0.6)	59.72(0.26)	76.5(0.84)	28.87	28.74	0	4.13
8. PCF 5.0	91.18(0.35)	47.02(0.19)	68.5(1.5)	36.96	35.92	0.08	3.27
9. PCF 5.5	89.62(0.41)	39.68(0.43)	65.12(0.95)	40.95	39.77	0.11	3.1

Where PCF is molar ratio of anacardic acid: cresol: formaldehyde = 1.55: 0.38 and number after PCF is mole of formaldehyde.

Values in parentheses are the standard deviation for the data set of five.

Appendix Table 2 Lewis acid-base components of work of adhesion of the effect of formaldehyde content between phenolic coatings and liquids

Sample	Lewis acid-base components of work of adhesion	
	Water	Ethylene glycol
1. PCF 1.5	63.59	27.26
2. PCF 2.0	56.19	21.76
3. PCF 2.5	32.41	11.95
4. PCF 3.0	27.06	9.02
5. PCF 3.5	16.13	5.4
6. PCF 4.0	20.29	6.13
7. PCF 4.5 or PC	20.18	6.1
8. PCF 5.0	21.18	8.98
9. PCF 5.5	21.18	9.49

The unit of Lewis acid-base components of work of adhesion is mJ/m^2

Appendix Table 3 Surface characteristics of the effect of anacardic acid content of phenolic coatings obtained by contact angle measurement

Sample	Contact angle (theta)			Surface free energy (mJ/m^2)			
	Water	Diiodo-methane	Ethylene glycol	γ_S	γ_S^{LW}	γ_S^{+}	γ_S^{-}
1. PCAnAc 0.5	71.58(0.39)	49.44(1.63)	61.64(0.38)	37.6	34.59	0.12	19.29
2. PCAnAc 1.0	90.38(1.3)	53.26(3.18)	64(0.81)	33.19	32.44	0.05	2.79
3. PCAnAc 1.55 or PC or PCF 3.5	98.46(0.34)	61.6(1.19)	72.08(1.53)	24.49	24.22	0.01	2.27
4. PCAnAc 2.0	79.54(0.37)	46.64(0.19)	60.32(2.13)	36.78	36.13	0.01	9.4

Where PCAnAc is molar ratio of formaldehyde: cresol : anacardic acid = 3.5: 0.38 and number after PCAnAc is mole of anacardic acid

Values in parentheses are the standard deviation for the data set of five.

Appendix Table 4 Lewis acid-base components of work of adhesion of the effect of anacardic acid content between phenolic coatings and liquids

Sample	PCAnAc 0.5	PCAnAc 1.0	PCAnAc 1.55	PCAnAc 2.0
Water	47.83	19.13	16.13	32.05
Ethylene glycol	16.88	7.7	5.4	9.96

The unit of Lewis acid-base components of work of adhesion is mJ/m^2

Appendix Table 5 Surface characteristics of the effect of cresol content of phenolic coatings obtained by contact angle measurement

Sample	Contact angle (theta)			Surface free energy (mJ/m^2)			
	Water	Diiodo-methane	Ethylene glycol	γ_S	γ_S^{LW}	γ_S^+	γ_S^-
1. PCC 0 (no cresol)	78.88(1.26)	45.26(0.26)	68.4(0.16)	42.3	36.87	0.53	13.8
2. PCC 0.19	83.96(1.52)	60.94(1.75)	77.1(0.66)	25.85	28.03	0.39	13.65
3. PCC 0.38 or PC or PCF 3.5	98.46(0.34)	61.6(1.19)	72.08(1.53)	24.49	24.22	0.01	2.27

Where PCC is molar ratio of anacardic acid : formaldehyde: cresol = 1.55: 3.5 and number after PCC is mole of cresol

Values in parentheses are the standard deviation for the data set of five.

Appendix Table 6 Lewis acid-base components of work of adhesion of the effect of cresol content between phenolic coatings and liquids

Sample	PCC 0	PCC 0.19	PCC 0.38
Water	44.91	43.61	16.13
Ethylene glycol	20.32	18.79	5.4

The unit of Lewis acid-base components of work of adhesion is mJ/m^2

Appendix Table 7 Fanning friction factor for the smooth pipe and the coated pipe

Volumetric flow rate (m^3/h) (Q)	Reynolds number (Re)			Pressure drop (ΔP) (bar)			Fanning friction factor (f)		
	smooth pipe	PRS	coated pipe	smooth pipe	PRS	coated pipe	smooth pipe	PRS	coated pipe
2.36	43772.64	44518.46	43647.64	0.021	0.019	0.018	0.00801	0.00730	0.00686
2.63	48780.52	49611.67	48641.22	0.024	0.022	0.021	0.00737	0.00681	0.00644
3.06	56756.05	57723.09	56593.97	0.029	0.028	0.027	0.00658	0.00640	0.00612
3.2	59352.73	60364.01	59183.24	0.031	0.03	0.029	0.00643	0.00627	0.00601
3.54	65658.95	66777.69	65471.46	0.037	0.036	0.035	0.00627	0.00615	0.00593
4.01	74376.39	75643.65	74164	0.048	0.046	0.044	0.00634	0.00612	0.00581

Where the coated pipe was coated by phenolic coatings with molar ratios of AnAc: F: C = 1.55: 3.5: 0.38

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