

Synthesis, Characterization and Membrane Properties of modified polyphenols based resin

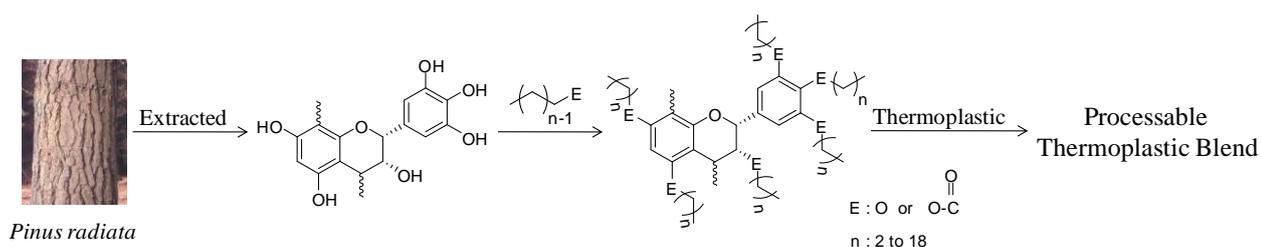
S. Arasaretnam*

*Department of Chemistry, Faculty of Science, Eastern University, Chenkalady, Sri Lanka

Abstract

Tannins are the most abundant resource of natural aromatic polyphenols and an alternative feedstock for the elaboration of chemicals and building blocks to develop value-added polymeric materials. This study is focus on extraction of tannin and modification to obtain green polymeric materials. In this challenge, the extracted tannin was modified from *Pinus radiata* bark (PBT) by coupling with different aliphatic alkyl carboxylic acid (C_2 to C_{18}). Various weight percentage of alkyl chain lengths were introduced into the tannin by esterification or etherification. The resulted modified tannins were characterized by spectroscopic techniques, namely, 1H - and ^{13}C -NMR, and thermal studies by TG analysis and DSC. Spectroscopic studies indicated that the degree of incorporation of alkyl chains depends on the feed of weight % of alkyl chains at modification process. Thermal analyses of the modified tannins reveal that thermal stability was increased for esterified and also etherified tannins compared to the neat tannins.

Keynotes: Tannins, extraction, modification, thermal stability, esterification, etherification



Schematic representation of preparation of processable thermoplastic blend

*Corresponding Author's Email: s_arasaretnam@yahoo.co.uk

<http://orcid.org/0000-0002-6656-7152>

1.0. Introduction

The term “tannin” indicates a plant material which allows the transformation of hide into leather (Ferreira *et al.*, 2000[1]). The word “tannin” is used to define three classes of phenolic compounds with different chemical natures, hydrolysable tannins, complex tannin and condensed tannins and Hydrolysable tannins are subdivided into ellagitannins and gallotannins. Hydrolysable tannins are a mixture of phenols such as gallic and ellagic acid, esters of sugars (i.e., glucose), gallic acid or digallic acid. These tannins are divided into two categories, namely, gallotannins, which produce gallic acid and its derivatives from hydrolysis and the ellagitannins, which produce ellagic acid after hydrolysis. These tannins are mainly used in the tanning industry (Ferreira *et al.*, 2000[1]).

Complex tannins are formed from an ellagitannin unit and a flavan-3-ol unit. An example of this kind of tannin is acutissimin A, which is composed of a flavagallonyl unit connected to a polyol derived from D-glucose by a glucosidic connection in C-1 and three other ester bonds. Condensed tannins represent more than 90 % of the worldwide production of commercial tannins. Having from 3 to 8 flavanoid repetition units are needed to call compound condensed tannin. These tannins are made up of associated precursors (flavan-3-ol and flavan-3, 4-diol) of carbohydrates as well as imino and amino acid traces. These tannins are generally complex with proteins. Their faculty of complexation changes according to their chemical nature. Each flavanoid is composed of two phenolic rings having different reactivity (Ferreira *et al.*, 2000[1]).

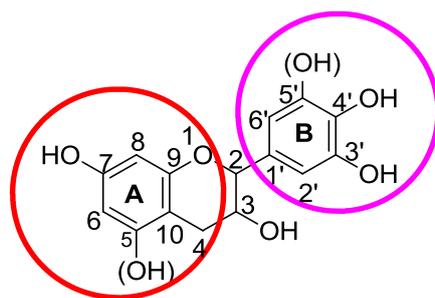


Figure 1. An example of a monoflavanoid of condensed tannin.

The structure of monoflavanoid in Figure 1 shows that it is possible to have two configurations for each ring such as with or without OH in the positions of 5 and 5'. The flavanoids from condensed tannins are mostly derived from flavan-3-ol and flavan-3, 4-diol.

Flavonoids have common features in their hydroxylation pattern and three dimensional structures. The A-ring generally has three oxygen atoms at alternate positions (5, 7, and 9). In contrast, the B-ring has variable oxygenation, though a *para*-hydroxyl, with respect to the C3 propyl chain, is often present. A second *meta*-hydroxyl is also commonly observed as is further hydroxylation (Manitto, P 1981[2]). The molecular conformation of flavonoids may adopt two forms, namely, planar or puckered. For instance, the ring systems of flavones, aurones, and chalcones are planar. On the contrary, the saturated pyran ring of anthocyanin, flavanols, flavanones, isoflavanones, and flavanonol are puckered. Polymerisation is very common among the flavonoids. Linkage occurs through atoms C-4, C-6, and C-8 *via* electrophilic substitution. The labile methylene C-4 protons give rise to a carbanion which can attack the nucleophilic centres of the A-ring. The Meta hydroxyl pattern of the A-ring encourages the electrophilic attack. Stereoisomerism of oligomers and polymers results around the inter-flavanoid bonds. These polymers can range from dimers to very large macromolecules (Cody, V 1993[3]).

A wide variety of modifications, linked with their chemical structure can be performed with tannins. Main chemical modification can be classified into three main categories (Cody, V 1993[3]).

1. The heterocycle can be opened and can lead to rearrangements of the chemical structure.
2. Reactivity of nucleophilic sites, created by OH groups present on the aromatic rings leads to electrophilic aromatic substitutions.
3. Finally, reactions can also take place directly with the OH. In each category, there are different reactions leading to new building blocks, which are of great interest for polymer synthesis.

The preparation of resorcinol diacetate by the reaction of resorcinol with acetic anhydride in the presence of pyridine gives high purity resorcinol diacetate (Dressler, H 1994[4]). Acetylation of polyphenols offers the ability to derivatise some or all the hydroxyl groups. Patti *et al.*, 2000[5] described a method whereby the aromatic hydroxyls were protected with acetyl groups followed by the introduction of a palmitic acyl group at the 3-*O* position. The Williamson ether synthesis is a better method for preparation of more complex ethers. An alkoxide reacts with an alkyl halide *via* a SN² type reaction (Patti *et al.*, 2000)[5] .

The B-ring (pyrogallol or catechol) is less reactive compared to the A-ring. Indeed, activation due to the presence of phenol groups on the B-ring is not located on a carbon contrary to the A-ring whose activated sites are on C6 and C8. However, at high pH (approximately 10), the B-ring can be activated by anion formation. Different tannin varieties and wastewater from the tanning process have been successfully tested. Thus, it is possible to carry out this reaction regardless of the type of tannin (Patti *et al.*, 2000) [5] .

The overall aim of this study was to modify tannins into value-added products. These products may have utility in various aspects of chemistry including polymers, adhesives, and pharmaceuticals.

2.0. Materials and Methods

Materials

The *Pinus radiata* bark, mesh size: 80 and pH=3-7 was procured from Presanna enterprises, the product sourced from Indore (India). Pine bark tannin was obtained by solvent extraction of *Pinus radiata* bark followed by rotator drying of the extract liquor. Then, it was vacuum dried at 80 °C for 24 h before their use. Stearic acid and other fatty acids (acetic, propionic, hexanoic and octanoic) were purchased from Sigma-Aldrich and used as received. All fatty acids were stored in the absence of light. The 1-bromohexane (Sigma-Aldrich), sulphuric acid (H₂SO₄) and hydrochloric acid (HCl) (Rankem), acetone, ethyl acetate, methanol, ethanol, toluene, diethylether and *n*-hexane (Finar Chemicals Ltd.), sodium bicarbonate (NaHCO₃), sodium chloride (NaCl), magnesium sulphate (MgSO₄) and sodium chloride (NaOH) (SD Fine-Chem Ltd.) and molecular sieves (SD Fine-Chem Ltd.) were used as received. The dimethylformamide (DMF) (Sigma-Aldrich) was dried over molecular sieves overnight and followed by vacuum distillation. All other reagents were used without further purification.

Pre-Extraction

A pre-extraction of *Pinus radiata* bark with *n*-hexane, diethylether and toluene was performed to separate hydrocarbons, waxes, carotenoids, terpenes and lipids. This method involves soxhlet extraction for 3 hrs using *n*-hexane (500 mL) followed by toluene (500 mL), and diethylether (500 mL). The residual solvent was removed from the bark under reduced pressure and the yields were measured.

Method of Extraction of Tannin

Pine tannin was extracted from the bark of *Pinus radiata* using a standard by following procedure (Glasser *et al.*,1983)[6].

The bark grounded to pass an 80 mesh screen. The grounded bark were added in the extraction thimble and placed in the Soxhlet apparatus. A small cone of thimble was placed to prevent any loss of the specimen. It was extracted using 200 mL of ethyl acetate, acetone, methanol and methanol-water 50:50 for 6-8 h, keeping the liquid boiling briskly so that siphoning from the extractor in no less than four times per hour. After extraction with methanol-water solvents, the reaction mixture was transfers to a Buchner funnel to remove the excess solvent with suction and washes the thimble with methanol. A gummy product was obtained after separating the extract from solvent in a rotary evaporator under a reduced pressure at a temperature of 50 °C. After being removed the solvent, 100 mL of Et₂O (diethyl ether) and *n*-hexane were added respectively to the extracted product to remove any non-tannin compounds. The separated compound (condensed tannin) was analysed by the FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy, thermogravimetric analysis (TGA), differential scanning chromatography (DSC) characterisations after filtering.

Thin layer chromatography (TLC)

Silica gel 60 F254 aluminium TLC plates (Merck) were used with various solvents. Plates were visualised with ultraviolet (UV) light and/or iodine vapour staining.

Nuclear magnetic resonance (NMR) spectroscopy

All solution state NMR spectra were recorded on Avance or INOVA spectrometer in CDCl₃/DMSO-d₆ with tetramethylsilane as an internal standard and the magnetic field frequencies were 300 or 500 MHz for ¹H-NMR and 75 or 125 MHz for ¹³C-NMR measurements.

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer at a resolution of 4 cm⁻¹ using KBr optics at room temperature and a minimum of 32 scans were signal averaged. The absorbance was measured between 400-4000 cm⁻¹.

Differential scanning calorimetry (DSC)

Thermal analyses were performed by a Differential Scanning Calorimeter, DSC Q100 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Typical procedure was as follows.

The sample was, first equilibrated to $-30\text{ }^{\circ}\text{C}$ and heated (first heating) from $-30\text{ }^{\circ}\text{C}$ to maximum temperature around $200\text{ }^{\circ}\text{C}$ (chosen as per thermal stability of the sample) at $10\text{ }^{\circ}\text{C min}^{-1}$ and then it was cooled (first cooling) from maximum temperature to $-30\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ using TA, Refrigerated Cooling System 90. Then the sample was again heated (second heating) from at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and then it was cooled (second cooling) at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ between the same temperature limits of the first cycle. The second heating and cooling curves are considered for discussion.

Thermo gravimetric analysis (TGA)

Thermo gravimetry curves were obtained from TGA Q-500 thermal analyser at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. Samples were heated from room temperature to $800\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Esterification of Tannin

Synthesis of Pine tannin stearate with 6 equivalents of acetylating agent

Pine bark tannin (PBT) (1.5 g, of PBT units) was dispersed in acetone (10 mL) at $70\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. The corresponding amount of stearic acid (9.1 ml) was then added aliquot into the flask with stirring of the reaction mixture with Con. H_2SO_4 (1 ml) as catalyst. Samples were taken throughout the reaction to monitor reaction progress, quenched with ethanol and analysed by TLC. After 24 h the reaction mixture was quenched with water (30 mL) and concentrated by rotary evaporation. The reaction mixture was poured into *n*-hexane (20 mL), washed with saturated NaHCO_3 solution (4 x 50 mL), HCl (0.1 mol L^{-1} , 2 x 50 mL), water (1 x 50 mL), saturated NaCl solution (2 x 50 mL), and dried with MgSO_4 . The solution was concentrated by rotary evaporation to yield a brown oily product (1.2 g). This was washed again using NaOH solution (0.5 mol L^{-1} , 4 x 50 mL) instead of saturated NaHCO_3 to yield a brown oily product (1.12 g, 75 %). The reaction was carried out using different type of fatty acids (acetic, propionic, hexanoic, octanoic,) and added at various ratios of the acids to complete esterification of all OH groups of tannin unit in the presence of Con. H_2SO_4 as a catalyst.

Etherification of Tannin

Synthesis of Pine tannin ether with 6 equivalent of 1-bromohexane (Williamson ether synthesis)

Pine tannin (10.00 g) was dissolved in DMF (100 mL) and powdered anhydrous potassium carbonate (1.38 g) was added. The solution was heated to reflux for 10 min, allowed to cool, and 1-bromohexane (0.24 mL) was added. The reaction mixture was refluxed at 110 °C for 24 h, cooled, filtered, and concentrated by rotary evaporation to yield a red liquid (7.4 g).

On work up, the reaction mixture was cooled to room temperature and neutralised with 1 M HCl, subsequently, the mixture was poured into distilled water. The resulting precipitate was recovered by filtration to yield an orange-brown solid. The product was further purified twice by extraction and precipitation with ethyl acetate-water before vacuum drying at 45 °C for 24 h. (3.7 g, 37 %). TLC and ¹H NMR spectroscopy was allowed to assessment of the reaction products.

The above reaction was repeated by using different ratios of 1-bromohexane and pine tannin in the alkaline medium to design various uploads of etherification of the tannin unit.

Preparation of blend membranes

The polysulfone (PSF) blend membranes with different compositions of PSF/PBT blends with weight ratios of 95/5, 90/10 and 85/15 were prepared according to phase inversion process in the following manner.

At first, required amount of PSF was fully dissolved in DMF under constant stirring for 4 h at about 90 °C. Then, required amount of PBT was added to PSF solution and allowed the stirring for 2 h at 70 °C to obtain a homogeneous solution. The solution was allowed to stand at room temperature for 12 h for cooling and remove the air bubbles by applying vacuum. Then, this homogenous solution was used for membrane casting on glass plate using a casting glass rod. The gelation bath for phase inversion consists of 1.0 % DMF in distilled water at 25 °C. The fabricated membrane was kept in gelation bath for 1 h, washed with excess water and followed by stored in double distilled water. The similar procedure was used to prepare blend membranes by using PSF and tannin stearate (PBTS).

3.0. Results and Discussion

Extraction of Tannin

The soxhlet technique is an important study to demonstrate the poor tannin extraction with non-polar solvents. The complexity of natural tannins molecules demands experiment test to choose the solvent. Therefore, solvents with different polarity were tried for optimal extraction in the extraction process. The results showed that a mixture of water-methanol (1:1 v/v) as the best extracting solvent. The yields of extraction was in the range of 18-20 % depends of solvent system. Highest yield (20 %) of extraction was obtained from methanol-water (50:50) extraction method. Ethyl acetate and acetone had lower extraction yields this may be due to the sugars and hemicelluloses are hydrolysed during extraction in organic solvent.

FT-IR spectrum of extract of pine bark in range of 400-4,000 cm^{-1} is shown in Figure 2. The strong band centered at 3,400 cm^{-1} is due to -OH group and aromatic C-H bands at 3,000 cm^{-1} which is overlapped with wide band of hydroxyl group. Tensile vibration of aromatic ring (C-C) is located in area of 1,610 cm^{-1} . The bending vibration of methyl group is observed at 1,325-1,450 cm^{-1} and (C-O) appears in the area of 1,033-1,203 cm^{-1} . Resulted spectrum is similar as reported by Lee *et al.*, 2006)[8] .

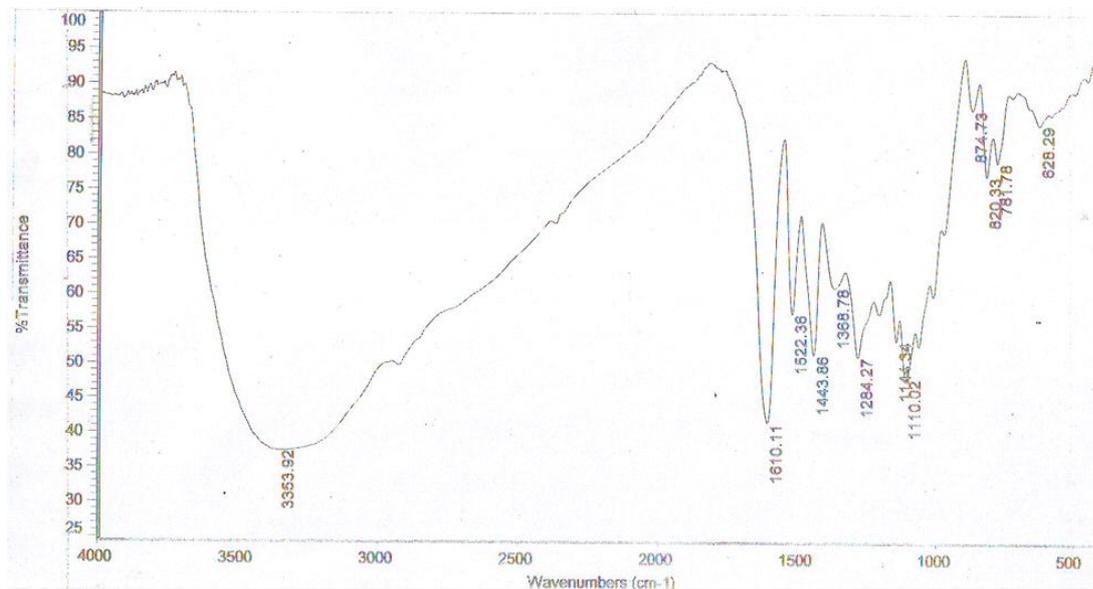


Figure 2. FT-IR spectrum of condensed tannin

$^1\text{H-NMR}$ spectroscopy was performed on all extractions to identify the composition of each sample. NMR studies have shown that the majority of the condensed tannin signal lies

between 5.82 and 7.56 ppm, due to the aromatic moiety in condensed tannins. Signals between 5.82 and 6.36 ppm correspond to the aromatic A ring and signals between 6.36 and 7.56 correspond to the aromatic B ring. The C ring proton signals lie between 3.8 and 4.6 ppm as reported by De Bruyne *et al.*, 1996[9].

The majority of the carbohydrate signals were between 3.10 and 4.26 ppm as shown in Figure 3. Signals between 5 and 5.5 ppm correspond to the anomeric protons.

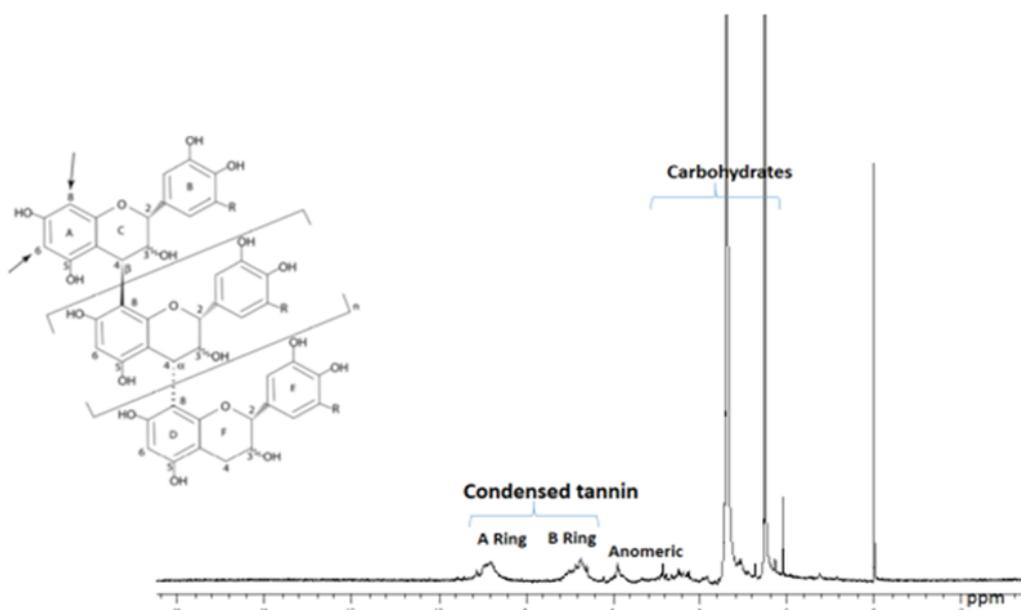
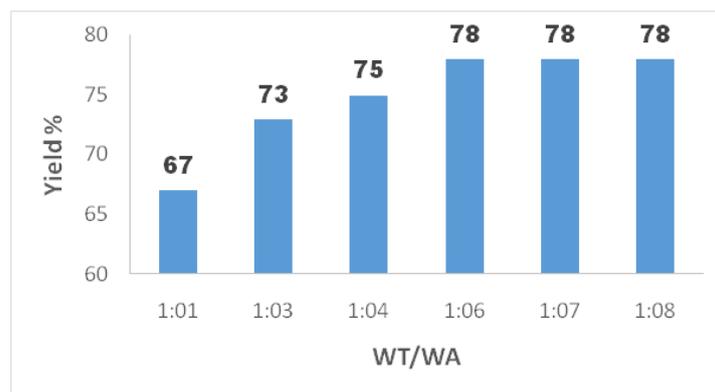


Figure 3. $^1\text{H-NMR}$ spectrum of condensed tannins with peak assignment.

Esterification of Tannin

Pine bark tannin stearates having various degrees of esterification were produced by the coupling of the respective tannin extract with different fatty acids. Tannins extracted from *Pine radiata* bark were having inherently differing flavonoid units due to their respective hydroxylation patterns and interflavan linkages.



WT/WA- weight ratio of pine tannin (WT) to stearic acid (WA)

Figure 4. Esterification ratio and isolated yield of pine bark Tannin stearates

Table 1.0. Esterification ratio and isolated yield of Pine bark Tannin ester using different alkyl fatty acids

S. No.	Reagents ratio (w/w)		Yield of esterified tannin (%)
	Tannin	Acid	
CH₃COOH			
1.	1	1	28
2.	1	3	33
3.	1	6	61
CH₃(CH₂)₁₆COOH			
4.	1	1	67
5.	1	3	73
6.	1	4	75
7.	1	6	78
8.	1	8	78
CH₃(CH₂)₈COOH			
9.	1	3	57
10.	1	6	52
CH₃(CH₂)₄COOH			
11.	1	6	42
12.	1	6	45
CH₃(CH₂)₆COOH			
13.	1	6	41

Yields percentages of esterification of pine tannin with different fatty acids are shown in Table 1. The results indicated that the tannin stearate showed greater yield percentage compared to the other used fatty acids. The equivalent ratio of tannin (based on flavonoid

unit) to stearic acid was varied from 1 : 1 to 1 : 8 with the latter ratio designed to promote full esterification of the tannin unit (Table 1). Acetone was selected as solvent and the reactions were carried out at reflux temperatures for at least 24 hrs to promote complete reaction. In attempting to move toward more benign chemistry approaches, acetone solvent was used as reaction media and ethanol in work up, where product isolation was simplified by its precipitation into ethanol. This procedure ensured removal of stearic acid and unwanted by products, which were increasingly present at higher stearic acid ratios. Figure 4 shows the isolated yields of the various tannin stearates from the series of esterification. These yields ranged from 67 to 78 % for the various tannin stearate products.

In the case of the pine bark tannin stearates, the yields were relatively similar with products obtained in the range of 70-80 % isolated yield. These products were qualitatively assessed by FTIR and NMR spectroscopic techniques and used to confirm the degree of esterification in each product (Figure 5). FTIR initially provided evidence of successful ester formation and an indication of the extent of product esterification (Figure 6).

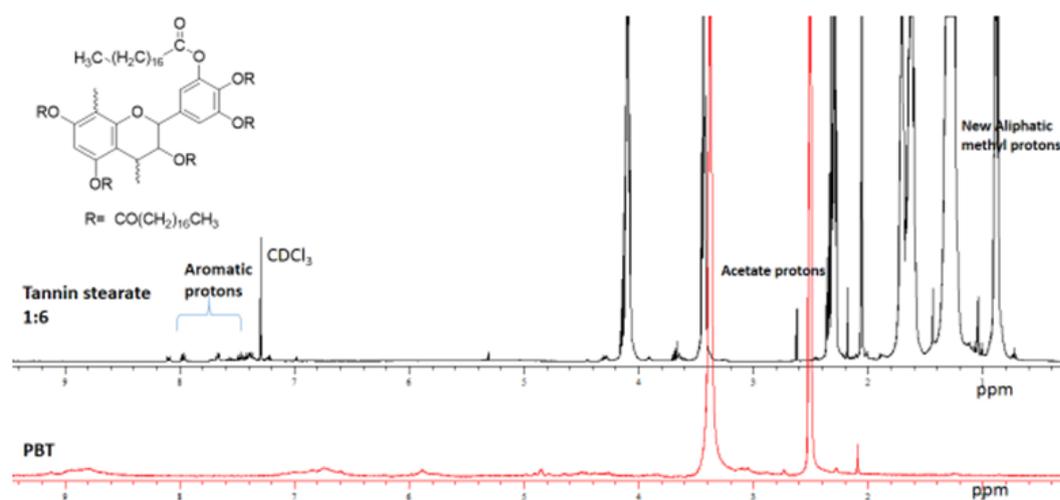


Figure 5. ¹H-NMR spectra of condensed tannin (PBT) and esterified tannin with peak assignment.

Figure 5 shows the NMR spectra of pine bark tannin (PBT) and tannin stearate. The distinct regions were respectively attributed to the aromatic protons (8.0-6.0 ppm), methine protons (5.5-5.8 ppm) and acetate protons (O=C-CH₃; 2.28-2.30 ppm). ¹H-NMR allowed a good evidence of the insertion of the acetate groups onto the tannins. In the ¹H-NMR of PBT showed the presence of Gallotannin (pentagalloyl glucose) in the region of 2.5-3.5 ppm. During the esterification of tannin glucose moiety may be possible to remove from the

condensed tannin which could be confirmed by disappearance of some peaks in region of 2.5-3.5 ppm.

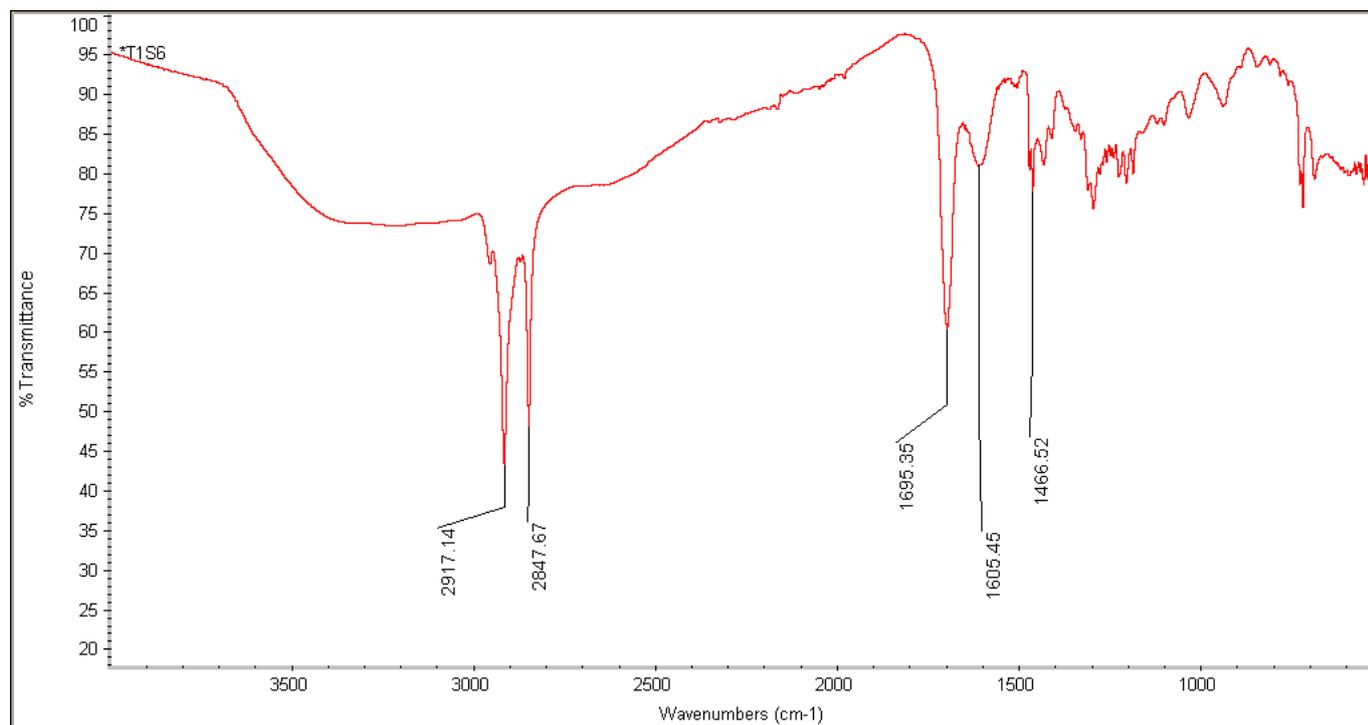


Figure 6. FT-IR spectrum of esterified tannin with assignment

FTIR spectra of pine tannin stearates have strong absorptions at 2925-2840 (ν CH₂) and 1695 (ν C=O) cm⁻¹ attributable to the stearate ester carbonyl (Figure 6). The broad absorption between 3000 and 3700 cm⁻¹ attributable to hydroxyl stretching vibrations was also observed to decrease. The relative substitution of pine tannin stearate products could be compared by FTIR spectra normalized with the tannin aromatic ring stretching vibration (1612 cm⁻¹). Evident as the ratio of tannin to stearic acid increased from 1:1 to 1:8 was a greater relative intensity of the key stearate peaks 2925, 2850, and 1770 cm⁻¹. This indicated that a trend for greater esterification with higher reaction ratio across pine tannin products. However, the degree of esterification appears to be maximized at the higher reaction ratios of 1:6 and 1:8 as similar ester carbonyl intensities were observed for these reactions with the condensed tannin type.

Thermal analysis of esterified tannin

The thermal degradation profiles of PBT and PBT stearate were analysed by TGA under nitrogen atmosphere. The PBT stearate showed a few differences in the thermal degradation

profile compared to the neat PBT as shown in Figure 7. The loss of mass around 100 °C for neat PBT was observed. This was due to water loss from tannin which is hydroscopic. In contrast, the PBT stearates were more hydrophobic did not show weight loss at 100 °C.

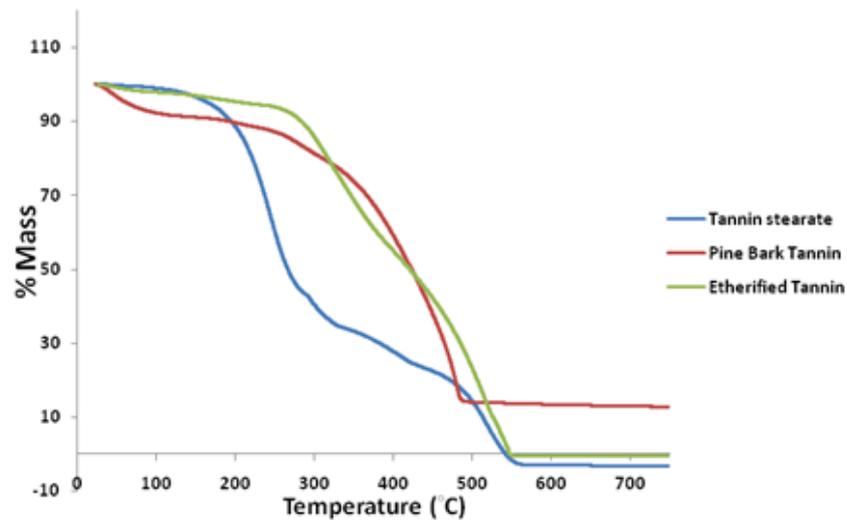


Figure 7. TGA thermograms of pine bark tannin (PBT), PBT stearate and etherified tannin. Increasing the onset temperature of degradation is beneficial for high temperature processing or applications. For instance, the incorporation of modified tannins into thermoplastics, which often requires temperatures above 180 °C to process with thermoplastics, namely, polyethylene or polypropylene.

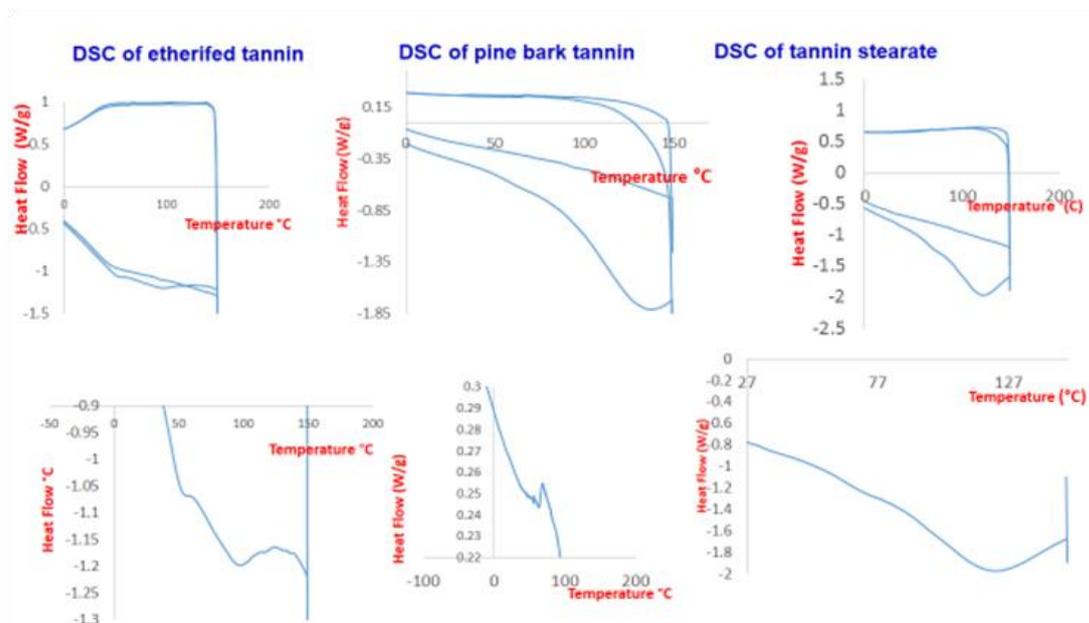


Figure 8. DSC thermograms of PBT, etherified tannin and esterified tannin (on second heating and cooling cycles).

The thermal transitions of PBT stearate were compared with neat PBT by DSC studies. However, in the first heating cycle of PBT showed a broad transition at 80 °C which was not present in the second cycle (Figure 8). This may be due to the elimination of water. The more substituted PBT showed strong thermal transitions above 77 °C, presumably melt behaviours. In contrast, PBT and esterified showed a broad transition with a maximum at about 125 °C. This suggested that a high degree of substitution is required for the material to adopt thermal characteristics similar to those of stearic acid (low melting point). The detail study is required to confirm the thermal behaviour of these materials.

Etherification of tannin

Figure 9 shows ¹H-NMR spectra of the PBT and hexylated PBT. The distinct regions were attributed to the aromatic protons (8.0-6.0 ppm), methoxy protons (O-CH₂: 4.06-4.1 ppm) and the new aliphatic methyl protons of PBT chains (1.4-0.5 ppm). ¹H-NMR allowed a good evidence of the insertion of the alkyl groups onto the tannins.

In the ¹H-NMR of PBT showed the presence of Gallotannin (pentagalloyl glucose), the corresponding signal observed at 2.5-3.5 ppm. During the etherification of tannin glucose moiety may be possible to remove from the condensed tannin which could be confirmed by disappearance of some peaks in region of 2.5-3.5 ppm.

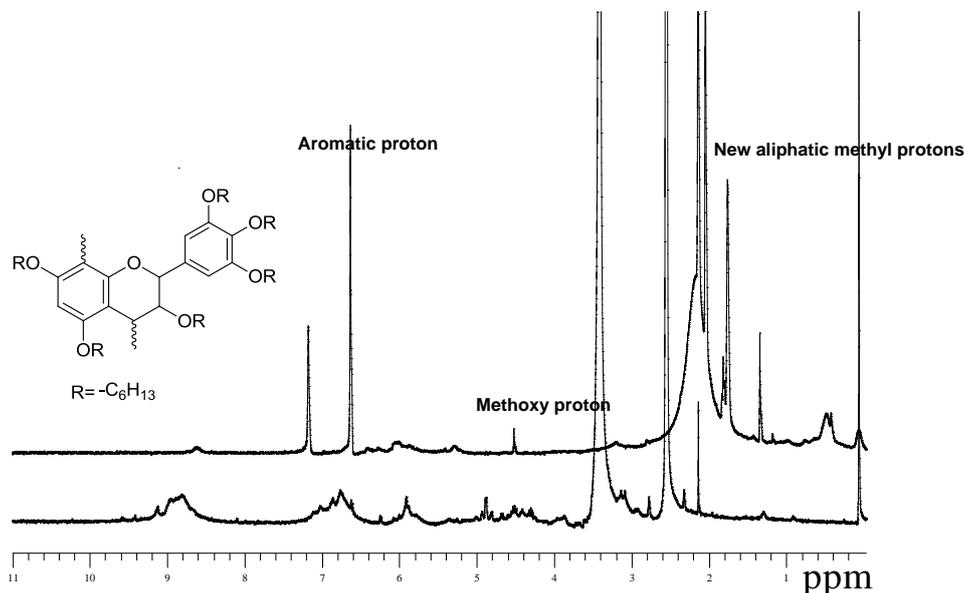


Figure 9. ¹H-NMR spectra of condensed tannin (PBT) and etherified tannin with peak assignment.

FT-IR spectrum of etherified tannin is explained that strong -CH₂ bands were observed at 2925-2855 cm⁻¹. Aromatic group C-H stretching was pointed out at 3,000 cm⁻¹ which is

located under wide band of hydroxyl group. Tensile vibration of aromatic ring (C-C) is located in area of 1610 cm^{-1} . The C-O band appeared in the area of $1033\text{-}1203\text{ cm}^{-1}$. Resulted spectrum is similar to one presented by Lee *et al.*, 2006[8] and they observed OH group in area of $1330\text{-}1420\text{ cm}^{-1}$. However, using FTIR spectroscopy, the presence of a strong peak at $1014\text{-}1114\text{ cm}^{-1}$ confirmed the presence of C-O group in methoxy linkages.

Thermal analysis of etherified Tannin

Thermal behaviours of etherified tannins were studied by using TGA and DSC. TGA curves of etherified tannin (Figure.7, 8) provided an insight to the thermal stability. It was generally observed that hexylation increased the thermal stability compared with neat PBT. A product with higher molar substitution of hexyl ethers showed a higher thermal degradation profile compared to the neat PBT. However, with higher molar substitution, the onset of degradation was increased. The PBT etherified were relatively more hydrophobic than neat PBT because of that we could not find water loss signal around $100\text{ }^{\circ}\text{C}$. Increasing the onset temperature of degradation is beneficial for high temperature processing or applications. The introduction of ether groups to flavonoids changed the thermal characteristics relative to the starting polyphenol.

DSC curves of etherified tannin showed several thermal transitions including possible glass transition behaviour (Figure 8). Most obvious was the endothermic event at $80\text{-}100\text{ }^{\circ}\text{C}$ observed on the first heating cycle of all PBT hexyl ethers. This was likely to be water loss, hence was not observed on the second heating cycle. However, the sharp nature of the transition suggested that it may be melt behaviours. On the second heating cycle, the signal became unstable at temperatures greater than $100\text{ }^{\circ}\text{C}$. As shown by TGA curve, etherified tannin has high temperature stability, with degradation starting at temperatures as low as $100\text{-}200\text{ }^{\circ}\text{C}$. Accordingly, this signal instability was attributed to degradation, possibly concurrent with melting.

The most significant observation was the glass transition (T_g) as a result of hexylation. Two trends were observed with regard to this T_g feature. First, the T_g value changed on the first and second heating cycles. This may be due to the thermal history of the product or the influence of water or trapped solvents. After the first heating cycle, all products had the same thermal history; therefore measurements of T_g were obtained from the second heating cycle.

The glass transition of etherified tannin as a result of etherification may be explained by two mechanisms, as previously described in the literature (Glasser *et al.*,1983)[6]. The conversion of phenolic hydroxyls to secondary hydroxyls disrupts the intermolecular hydrogen bonding. Thus, pseudo-cross-links were eliminated allowing increased molecular motion and as a result the T_g was lowered. However, variations of T_g in relation to the extent of substitution suggest another, potentially greater effect. This could be explained in terms of the free volume of the macromolecule. As bulky substituents were added to the macromolecule, the free volume would increase, thereby lowering the T_g . These effects have been reported on many occasions for other molecules such as lignin (Glasser *et al.*,1983)[6]. The results obtained in this study suggested similar processes were occurring for PBT hexyl ethers.

Tannin and polysulfone blends for membrane application

Blending of two or more distinct materials to create potential ultrafiltration membranes have the advantage of easy preparation by the phase inversion method for desired properties (Nunes *et al.*, 2013)[7].

The images of the top surfaces of the neat PSF and blend membranes are shown in Figure 10. The morphology of the top surfaces of the blend membranes showed dissimilar features compared to the neat PSF membrane. Amphiphilic copolymers that are composed of both hydrophilic and hydrophobic segments are mainly used as additives to blend with PBT and relevant host polymers.

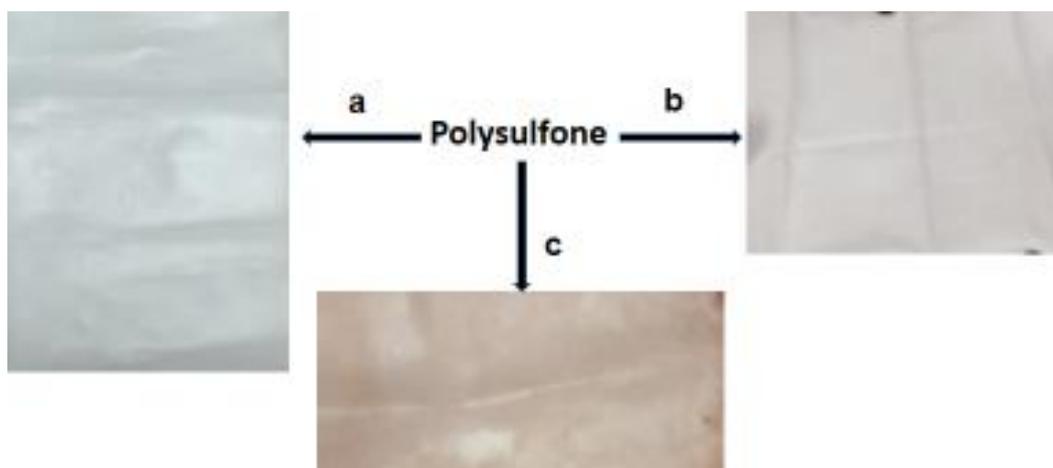


Figure 10. Images of membrane surface of (a) PSF, (b) PSF₉₀PBT₁₀ and (c) PSF₈₀PBTS₂₀.

Table 2. Compositions of polymers solutions for casting membranes.

Membrane code	PSF (wt. %)	PBT (wt. %)	DMF (wt. %)
PSF	100	0	80
PSF90PBT10	90	10	80
PSF80PBT20	80	20	80
PSF80PBTS20	70	30	80

The hydrophilic segments are useful for improving membrane hydrophilicity while the hydrophobic segments are useful for improving their compatibility with host polymers.

This study reports the preparation of a different type of blends using PBT and esterified PBT with polysulfone (Table 2). The blend membranes prepared by using similar methods which is already reported work explained that the prepared blends showed higher water flux oil rejection (Rajasekhar *et al.*, 2015)[10]. Therefore, the fabricated membranes are to be characterized by different analytical techniques and also to be investigated for the membrane antifouling properties and separation of oil-water emulsion under various conditions.

Conclusion

Chemically modify polyphenols can be potentially used to create value-added products or materials for further synthetic utility. The introduction of long-chain alkyl groups was shown to increase the hydrophobic nature of polyphenols. Tannin stearates having various degrees of esterification were prepared. The resulted compounds were characterized by spectroscopic methods and thermal behaviour by TGA and DSC and compared their characteristics with un-modified tannin. Changes in the thermal behaviour were observed upon esterification. Etherification of polyphenols provided a further method to alter the chemical and physical properties. Etherification of tannin was found to change the thermal properties, such as the glass transition temperatures and thermal degradation profiles. The modified polyphenols may find application in a range of areas, potentially adding value to increase the membrane antifouling properties, preparation of membranes for oil-water emulsion and separation of waste product of the forestry industry. Moreover, polyphenol esters may hold potential as sunscreen additives or associated cosmetics, while the tannin ethers showed potential as a thermoplastic material which could find application in a range of products.

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REFERENCES

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- [1]. Ferreira, D.; Xing-Cong, L. **2000**, Oligomeric proanthocyanidins: naturally occurring *O*-heterocycles. *Natural Product Reports*, 17:193-212.
- [2]. Manitto, P. **1981**, *Biosynthesis of Natural Products*. 1st edition, Ellis Horwood, Chichester.
- [3]. Cody, V. **1993**, Molecular conformation of flavonoids and their protein binding interactions. In *Polyphenolic Phenomena*, Scalbert, A., Ed. INRA Editions: Paris.
- [4]. Dressler, H. **1994**, *Resorcinol: Its Uses and Derivatives*. Plenum Press: New York.
- [5]. Patti, A., Mario, P., Giovanni, N. **2000**, Use of *Mucor miehei* lipase in the preparation of long chain 3-*O*-acylcatechins. *Journal of Molecular Catalysts B: Enzymatic*, 10:577-582.
- [6]. Glasser, W. G., Barnett, C., Rials, T., and Kelley, S. S., **1983**, Synthesis and characterization of several different hydroxyalkyl lignin derivatives. *International Symposium on Wood Pulping Chemistry*, TAPPI, Japan.
- [7]. Nunes, S.P., and Car, A., **2013**, From charge-mosaic to micelle self-assembly: block copolymer Membranes in the last 40 years, *Industrial & Engineering Chemistry Research*, 52:993-1003.
- [8]. Lee, W.J., and Lan, W.Ch., **2006**, Properties of resorcinol tannin-formaldehyde copolymer resins prepared from the bark extracts of Taiwan acacia and China fir, *Bio resource Technology*, 2:257-264.
- [9]. De Bruyne, T., Pieters, L.A.C., Dommisse, R.A., Kolodziej, H., Wray, V., Domke, T., and Vlietinck, A.J., **1996**, Unambiguous Assignments for Free Dimeric Proanthocyanidin Phenols from ²D NMR, *Phytochemistry*, 43:265-272.

[10]. Tota Rajasekhar., Mummuluri Trinadh., Poliseti Veera Babu., Annadanam V. Sesa Sainath., and Reddy, A.V.R., **2015**, Oil-water emulsion separation using ultrafiltration membranes based on novel blends of poly (vinylidene fluoride) and amphiphilic tri-block copolymer containing carboxylic acid functional group. *Journal of Membrane Science*, 481: 82-93.