J.Natn.Sci.Foundation Sri Lanka 2017 45 (3): 219 - 227
DOI: http://dx.doi.org/10.4038/jnsfsr.v45i3.8186

RESEARCH ARTICLE

Synthesis of novel porous tannin-phenol-formaldehyde cation exchange resin from *Terminalia arjuna* (Kumbuk)

L.D. Sumathirathne[1] and L. Karunanayake[1,2*]
[1] *Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda.*
[2] *Center for Advanced Material Research, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda.*

Revised: 25 November 2016; Accepted: 19 January 2017

Abstract: Natural tannins have a high affinity to absorb metal ions, proteins and some other biomolecules. In this study, tannins extracted from *Terminalia arjuna* (Kumbuk) were used to synthesise renewable tannin-phenol-formaldehyde resin systems and a porous modified resin system. A series of resin systems was synthesised by varying the incorporated phenol content. The ion exchange capacities of the resins produced were studied and the resin with the highest ion exchange capacity was selected. It was sulfonated to increase the properties further. A monovalent cation, Na^+ was used to estimate the adsorption properties of both sulfonated and unsulfonated resin systems. Solubility and swelling properties of the resins were measured to check their applicability as an ion exchanger in aqueous media at different pH values. Fourier transform infrared spectroscopy (FTIR) analysis was carried out to characterise the synthesised resins. Scanning electronic microscopic (SEM) images were obtained to study the morphology of the resins produced. Sulfonated tannin-phenol-formaldehyde resin with the tannin/phenol ratio of 1:1 showed the highest adsorption capacity for the metal ion used (Na^+), which was 1.552 meq/g.

To increase the surface area and to gain an efficient flow rate, a porous tannin-phenol-formaldehyde resin system was prepared. Synthesis was carried out using hexamethylenetetramine as both the cross linker and the catalyst. Coconut oil was used as the porogenic agent to create the porous structure through emulsion templating process. Synthesised porous resin contains μm and nm scale porous structures.

Keywords: Cation exchange resin, FTIR, porous resin, SEM, sulfonation, tannin of *Terminalia arjuna*.

INTRODUCTION

Common metal removal methods are technically complicated, inefficient or costly in meeting the discharge standards for industrial effluent (Yu *et al*., 2008). Although ion exchange is more effective, a high capital expenditure is usually required for such systems. Hence, producing a resin based on natural materials is more economically viable (Yu *et al*., 2008).

The use of tannin based compounds as ion adsorbents have been reported due to the affinity of tannin towards various cations (Mitra *et al*., 1991). Randall (1977) examined the suitability of various barks as ion exchange substrates. Although tannin can adsorb ions, its high solubility in water was found to be a constraint to use tannin as an adsorbent in applications such as ion exchange resins. This problem can be overcome by polymerising it with formaldehyde to form polymers or copolymers (Arasaretnam & Karunanayake, 2010). Garro Galvez *et al*. (1997) have studied the possibility of utilising *Caesalpinia spinosa* (Tara) tannin in the manufacture of wood adhesives. Thermosetting wood adhesive resins from valonia and mimosa were developed and characterised to remove various heavy metals by Ozacar *et al*. (2006).

Simple tannin formaldehyde resins (TFRs) possess a lower ion exchange capacity (IEC), and in order to produce a resin with better IEC, introduction of functional groups to the resin is needed (Mitra *et al*., 1991). Mitra *et al*. (1991) have extracted condensed tannins from spruce, mimosa, and radiata pine bark and reacted these with formaldehyde to have tannin formaldehyde resins with a lower cation exchange capacity. They have also modified tannin resins with different functional groups, and sulfonation of the resultant resin matrix was found to be very effective. Mitra *et al*. (1991) have developed

* Corresponding author (laleenk@gmail.com)

sulfonated crosslinked tannin formaldehyde resins and tannin-phenol-formaldehyde ter-polymer resins as stable and reusable cation exchangers. They have found that the introduction of phenol units into the tannin formaldehyde matrix increased the available sites for sulfonation. Tannins extracted from *Terminalia chebula* (Aralu) were used by Arasaretnam and Karunanayake (2010) to synthesise tannin-phenol-formaldehyde resins (TPFR). They (Arasaretnam & Karunanayake, 2010) produced ion exchange resins with different tannin to phenol ratios and sulfonated these to improve the properties further. The resin with 1 : 0.5 tannin to phenol ratio showed the highest IEC for all metal ions.

Porous resins were invented as a solution for slow kinetic and low IEC in typical ion exchangers. Kunin *et al*. (1962) developed a macroreticuler ion exchanger, Amberlyst 15, which is entirely different from conventional homogeneous gels. Ortiz-Palacios *et al*. (2008) synthesised macroporous resins with specific surface areas produced by suspension polymerisation with 4-vinylpyridine (4VP) and divinylbenzene (DVB) and various proportions of porogens. When used to remove Cr^{+6} in water samples they have shown high selectivity, fast adsorption kinetics and high removal capability at pH 6.5. Zhang and Sun (2001) developed a biporous anion exchange resin for protein chromatography incorporating solid granules and solvents as the porogenic medium.

Szczurek *et al.* (2014) synthesised an environmental friendly porous monolith using natural condensed tannins. Synthesis of the new carboHIPE was carried out by using sunflower oil, tannin solution and ethoxylated castor oil as the porogenic agent, external phase and surfactant, respectively (Szczurek *et al*., 2014). The use of tannins extracted from *Terminalia arjuna* (Kumbuk) in tannin-phenol-formaldehyde synthesis has not been reported. In this study, Kumbuk tannins were used to synthesise environmental friendly sulfonated TPFR and modified porous TPFR. The emulsion templating method was followed to synthesise the modified resin and coconut oil was used as the porogenic agent.

METHODOLOGY

Extraction of tannins from dried Kumbuk bark

The bark layer of *Terminalia arjuna* (Kumbuk) (thickness about 1 cm) was collected from the Anuradhapura area of Sri Lanka. After cleaning, the dried Kumbuk bark was finely ground to reduce particle size.

Initially, the powdered sample was extracted using hexane at 68 ^{o}C for 1 h, and then extracted using petroleum ether at 45 ^{o}C for 1 h to remove nonpolar compounds. Finally, the ground bark sample was extracted using methanol at 70 ^{o}C for 2 h. The methanol extract was filtered and concentrated using a rotary evaporator under reduced pressure. The resulted dark brown coloured viscous liquid was heated to obtain tannins by evaporating the solvent in a water bath at 80 ^{o}C.

Identification of tannin types

Ferric tests, acid butanol tests and nitrous acid tests were used in order to confirm the presence of phenolic compounds, condensed tannins and ellagitannins, respectively.

Determination of total polyphenolic content

Total polyphenolic content was determined using the folin-ciocalteau method. Commercially available folin-ciocalteau reagent was diluted with an equal volume of distilled water. Then 10.00 cm^3 from that solution was pipetted out to a 100.00 cm^3 volumetric flask and made up to the mark with distilled water. A series of gallic acid solutions of 50, 55, 60, 65, 70 and 75 ppm were prepared as standards. Aliquots (1.00 cm^3) of the gallic acid standards were poured into 6 test tubes. Then 5.00 cm^3 of diluted folin-ciocalteau reagent was added to the solutions and allowed to react for 6 – 8 min. Thereafter, 4.00 cm^3 of sodium carbonate solution [7.5 % (w/w)] was added and the contents of the test tubes were mixed well. The test tubes were covered with aluminium foil and kept at room temperature for 2 h. The absorbance measurements were taken at 750 nm using a colourimeter. The absorbances of the prepared tannin samples were also measured following the same procedure. The total polyphenolic content in the extracted crude tannin sample was calculated using a calibration plot.

Preparation of TFR and TPFR

For the preparation of TFR, a 20.000 g sample of solidified tannin extract was dissolved in 50.00 cm^3 of deionised water in an Erlenmeyer flask. About 10.00 cm^3 of methanol was also added to the flask at room temperature. The pH of the reaction mixture was adjusted to 10 using a solution of NaOH [33 % (w/w)]. The required amount of formaldehyde solution [37 % (w/w)] was added dropwise at 40 ^{o}C while stirring until the gel formation occurred. The mixture was brought to 80 ^{o}C using a water bath and kept at 80 ^{o}C for 1 h.

The resultant mixture was allowed to cool and harden. It was neutralised using a dilute HCl (0.1 M) solution. The resin produced was washed with hot deionised water and filtered using vacuum filtration to remove unnecessary reagents. The resin was ground and oven-dried at 100 °C for 1 h for further crosslinking. It was sieved through a 20-mesh sieve to get uniform particle size. Finally, the resin was cooled and stored in a desiccator.

The same procedure was followed to synthesise TPFR while incorporating various amounts of phenol to the initial water tannin mixture.

Sulfonation of the resins

A sample of TFR or TPFR (10.300 g) prepared using Kumbuk tannin was refluxed with 25.00 cm^3 of H_2SO_4 [98 % (w/w)] at 105 °C for 6 h in a paraffin bath to obtain the sulfonated resin. The sulfonated resin was allowed to cool, washed with hot deionised water and vacuum filtered to remove the residual free H_2SO_4. Then the resin was neutralised and converted to its Na^+ form using 250.00 cm^3 of 1.0 M NaCl solution. The resin was washed with deionised water to remove excess NaCl, dried in an oven at 105 °C and allowed to cool in a desiccator.

Preparation of modified resin

Initially, 20.000 g of tannin, 10.000 g of phenol, and 30.00 mL of distilled water were mixed in a 250.00 mL beaker and 0.700 g of pure *p*-toluene sulfonic acid (PTSA) was added to it as a catalyst. It was then mixed using a mechanical mixer at 250 rpm for 20 min. About 0.420 g [1.4 % (w/w)] of Wettam solution was added as a non-ionic emulsifier and it was mixed for further 20 min at 250 rpm to ensure homogeneity of the emulsion.

As the second part of the procedure, 50.00 mL of coconut oil was continuously added dropwise at a rate of 44 drops per min while stirring at 250 rpm. After half of the volume of coconut oil was added, 5.022 g [40 % (w/w)] of hexamethylenetetramine (hexamine) was added as a crosslinker to the emulsion. The mixing speed was increased to 900 rpm for 30 s to increase mixing of hexamine, and reduced to 250 rpm before the remaining oil was added dropwise. After adding the total volume of oil, the mixture was mixed for an additional 10 min at the same speed.

The resulting light brown coloured viscous emulsion was poured into a Petri dish and covered with an aluminium foil. It was allowed to cure in a ventilated oven at 80 °C for 20 h. A dark brown coloured tannin-phenol-formaldehyde porous resin was formed and the excess oil fraction was removed. The resin was allowed to cool at room temperature in a desiccator before being cut into small cubes and inserted to a thimble. It was refluxed in a Soxhlet extractor using acetone as the solvent for 7 ds to remove the coconut oil completely. It was allowed to cool and stored in a desiccator.

Determination of IEC for monovalent cations

About 5.000 g of the Na^+ forms of sulfonated and unsulfonated resins were allowed to hydrate in deionised water for several minutes before being packed into a burette-type column using deionised water. In this study, the IEC of the monovalent cation, Na^+ was determined. The Na^+ form of the sulfonated and unsulfonated resins were converted to H^+ form using 0.1 M HCl solution as the influent. The resin columns were then washed with deionised water until the output was free from excess H^+ ions. A 0.1 M NaCl solution was allowed to pass through the resin columns at a rate of 3 cm^3min^{-1}. The effluent was collected and H^+ ions in the effluent were estimated by titrating with a 0.1 M NaOH solution using phenolphthalein as the indicator to calculate IEC.

Scanning electron microscopic (SEM) studies

The resins were sputtered with gold and images were obtained using a scanning electron microscope (Hitachi SU6600). The images were analysed and the pore diameter was calculated using Image J software.

RESULTS AND DISCUSSION

Synthesis of tannin-phenol-formaldehyde resins (TPFR)

Although the extracted tannin was soluble in distilled water, TFR and TPFR did not dissolve. By changing the tannin/phenol ratio, different resin systems were obtained and their yields are shown in Table 1.

Synthesis of porous modified resins

Coconut oil is a commonly used vegetable oil produced in Sri Lanka. Hence, in modified resin synthesis, instead of sunflower oil, coconut oil was used. When considering the fatty acid composition, coconut oil contains a higher percentage of saturated fatty acids than sunflower oil (Table 2). As unsaturated fatty acids are more susceptible to oxidative reactions, according to fatty acid activity coconut oil is expected to be less reactive than sunflower oil. Therefore, we can assume that the use of coconut oil

as the porogenic solvent instead of sunflower oil does not lead to side reactions. As the reaction mixture is heated only up to 80 °C, the relatively low smoke point will also not affect the process.

Hexamine is considered as a hardener in industry. In this study, hexamine was used as the crosslinker in place of formaldehyde. Hexamine releases formaldehyde to the polymerisation, while releasing NH_3 as a catalyst to the reaction. Hence, we can assume that -CH_2- linkages will be formed in the polymerisation reaction as in other TPFRs discussed before. However, in the fourier transform infrared spectroscopy (FTIR) spectrum of the modified resin, there were peaks that can be assigned to C-N bonds at 1239 cm^{-1}. According to previous studies, -CH_2-NH-CH_2- linkages can occur during the tannin hexamine polymerisation (Pena *et al*., 2009; Moubarik *et al*., 2010; Zhu *et al*., 2013) (Figure 1).

Table 1: Yield of resin with different tannin: phenol weight ratios

Label of resin	Crude tannin weight (g)	Added phenol weight (g)	Required formaldehyde volume for gel formation (mL)	Yielded resin weight (g)
KRT1P0	2.500	0.000	0.65	2.295
KRT1P0.25	2.500	0.625	0.70	2.305
KRT1P0.5	2.500	1.250	0.90	2.350
KRT1P0.75	2.500	1.875	1.00	2.602
KRT1P1	2.500	2.500	0.50	2.088

Table 2: Chemical composition of coconut and sunflower oil

Type of oil		Saturated fatty acid %	Monounsaturated fatty acid %	Polyunsaturated fatty acid %	Smoke point (°C)
Coconut oil		86	6	2	177
Sunflower oil	(high oleic)	11	20	69	225
	(low oleic)	12	84	4	-

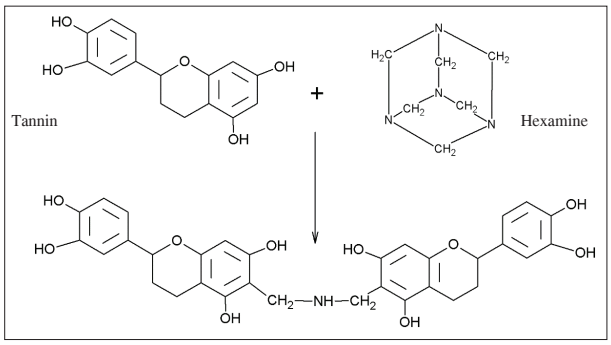


Figure 1: Possible reaction between tannin and hexamine (Moubarik *et al*., 2010)

According to literature, the new modified resin could be treated as an organic polyHIPE. As the modified resin started to float in the water filled burette, it was difficult to prepare a column to use in ion exchange studies. However, the low density of the resin indicates that it has a porous structure. In addition, when trying to pass a solvent through the modified resin system, it did not flow through, indicating that the porous structure is a closed-cell type.

Determination of IEC of resin systems

The IECs obtained for unsulfonated resin systems with different tannin to phenol ratios and the IECs of sulfonated resin systems are shown in Table 3. The highest IEC was obtained for the resin labelled KRT1P1SO_3Na, which had a tannin/phenol ratio of 1:1.

The simple tannin formaldehyde resin that does not contain phenol (KRT1P0) showed the lowest IEC. It is due to the weak acidic character of the phenolic hydroxyl groups present in the resin (Arasaretnam & Karunanayake, 2010). With increasing incorporation of phenol into the reaction mixture, the IEC increased as shown in Figure 2.

Table 3: IEC values for different polyphenolic contents of sulfonated and unsulfonated resin systems

Label of resins	Tannin: phenol (weight ratio)	Total polyphenolic content in the extract (%)	IEC Na^+ / H^+ (meq/g)	
			Cycle 1	Cycle 2
KRT1P0	1 : 0	49.12	0.0500	0.0480
$KRT1P0SO_3Na$			0.0470	0.0430
KRT1P0.25	1 : 0.25	61.40	0.5446	0.5086
KRT1P0.5	1 : 0.5	73.68	0.5221	0.5182
$KRT1P0.5SO_3Na$			0.6940	0.6040
KRT1P0.75	1 : 0.75	85.96	0.5638	0.4938
KRT1P1	1 : 1	98.24	0.7993	0.7414
$KRT1P1SO_3Na$			1.5520	1.4000

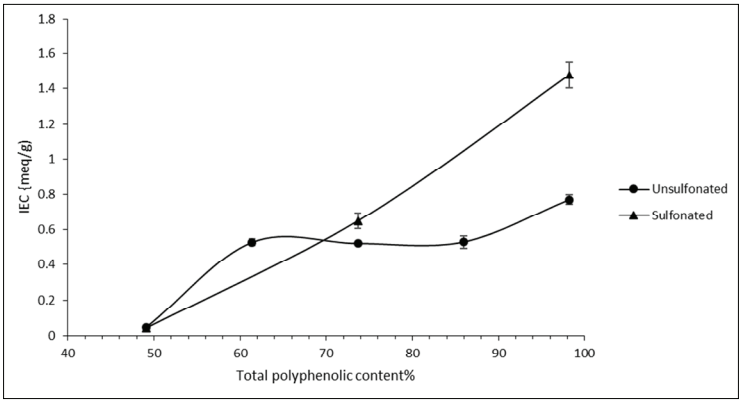


Figure 2: IEC of different resin systems with their total polyphenolic content

According to the studies of Arasaretnam and Karunanayake (2010), the highest IEC was measured in the resin with a 1 : 0.5 tannin to phenol ratio. However in this study, the highest value was shown for the resin with 1:1 tannin to phenol ratio (KRT1P1). It seems that an increase of phenol units in the TPFR system increases available ion exchange sites.

The introduction of strong acidic groups (SO_3^-) to the TFR and TPFR systems using sulfonation has increased the IEC values significantly (Table 3 and Figure 2). However, according to Figure 2, the effect of sulfonation is much higher when the phenol content is high in the resin. Tannin formaldehyde resins without pure phenol groups restrict the sites for sulfonation because of the complex branched structure of the tannin molecules. Resins formed with pure phenolic bodies reduce the steric hindrance by separating the tannin molecules, providing more sites for sulfonation in both phenol and tannin molecules.

According to previous studies sulfonated resin system with 1 : 0.5 tannin to phenol ratio showed the highest IEC for monovalent cations (H^+/Na^+) (i.e. 0.6450 meq/g) (Arasaretnam & Karunanayake, 2010). In this study, the $KRT1P0.5SO_3Na$ resin system had a similar IEC of 0.6940 meq/g. However, the highest IEC value of 1.5520 meq/g was shown for the sulfonated resin with 1:1 tannin:phenol ratio.

FTIR analysis

Figure 3 shows the FTIR spectra of dried Kumbuk bark and its tannin extract in the range of 640 to 3990 cm^{-1}. The

3550 to 3100 cm^{-1} broad absorption band corresponds to –OH bridging groups (Özacar *et al*., 2006) and the corresponding peak in the crude tannin sample is high in intensity compared to that of the dried bark sample. The 1600 – 1585 cm^{-1} and 1500 – 1400 cm^{-1} absorption bands can be attributed to aromatic skeletal vibrations, representing C = C stretching (Steyermark, 1976). The tannin extract from the bark has a much stronger peak compared to that of the bark sample, showing that the tannin extract from the bark has a much higher concentration of aromatic compounds (Arasaretnam & Karunanayake, 2010). The 1420 to 1330 cm^{-1} absorption band belongs to the O-H in plane deformation (Steyermark, 1976). The peaks at 1340 cm^{-1} in the crude tannin extract and 1367 cm^{-1} in the dried bark sample can be assigned to O-H in plane deformation. Again, the intensity of the band of crude tannin extract is stronger than the dried bark sample. The 1260 to 1000 cm^{-1} strong absorption band indicates C-O stretching vibrations in alcohol and phenol (Steyermark, 1976). The absorption band at 1199 cm^{-1} can be assigned to C-O stretching vibration and it has a much higher intensity in the extracted crude tannin (Steyermark, 1976; Stuart, 2005; Arasaretnam & Karunanayake, 2010).

Figure 4 shows a comparison of FTIR spectra of $KRT1P1SO_3Na$, $KRT1P0.5SO_3Na$ and the corresponding tannin extract in the range of 660 to 3990 cm^{-1}. The strong broad peaks at 1157 and 1143 cm^{-1} in $KRT1P0.5SO_3Na$ and $KRT1P1SO_3Na$ can be attributed to dimethylene ether linkages. The 840 to 730 cm^{-1} absorption bands can be assigned to the deformation vibration of C-H

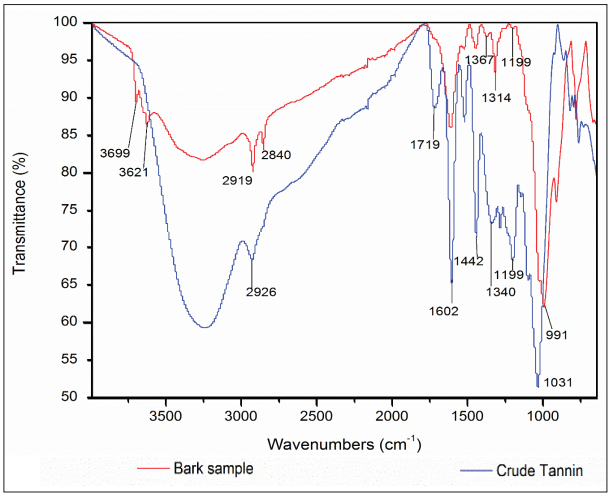


Figure 3: FTIR spectra of Kumbuk bark sample and its extracted tannin

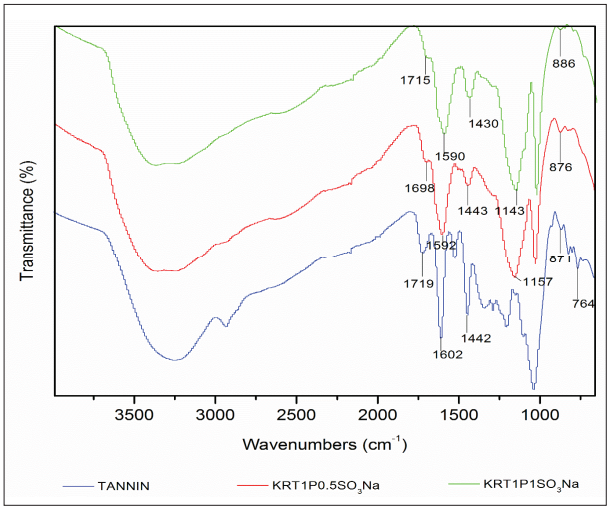


Figure 4: FTIR spectra of $KRT1P1SO_3Na$, $KRT1P0.5SO_3Na$ and tannin sample

bonds in benzene ring (Özacar *et al*., 2006). Although this bond does not participate in any chemical reaction during polymerisation, a decreased peak intensity can be observed in polymerised resin systems ($KRT1P0.5SO_3Na$, $KRT1P1SO_3Na$) compared to that of the tannin sample. This may be due to volume contraction occurring during resin polymerisation. The 1500 to 1400 cm^{-1} C = C stretching band intensity clearly decreases in the resin spectra compared to that of the tannin sample. This reduction of the band implies that crosslinking reactions have occurred with the aromatic ring.

In the spectrum of sulfonated phenol-modified resin ($KRT1P0.5SO_3Na$), there is a new peak that appears at 1157 cm^{-1} and this broad, intense peak can be attributed to S=O groups. The peak appearing in the 3550 – 3500 cm^{-1} range, that can be assigned to phenolic –OH has been shifted from lower wave numbers (3200 cm^{-1}) to higher wave numbers (3350 cm^{-1}). Further, the appearance of a shoulder (3200 cm^{-1}) can be seen in the sulfonated resin spectrum. The shoulder has close wave numbers to the –OH peak of tannins and unsulfonated resins, and indicates the presence of two different types of –OH groups. The peak around 3500 cm^{-1} can be assigned to free –OH groups. Hence, it can be concluded that sulfonation has liberated some of the hydrogen bonded –OH groups. It also shows that sulfonation has left some unaffected –OH groups represented by the shoulder around 3200 cm^{-1}. This results show that the phenolated resin has been successfully sulfonated (Steyermark, 1976; Stuart, 2005; Pena *et al*., 2009; Arasaretnam & Karunanayake, 2010).

When comparing the spectrum of the modified resin with KRT1P1SO$_3$Na, similar basic features and a few different peaks are observed (Figure 5). The spectrum of the modified resin also shows the –OH strong broad peak with a small shoulder in 3500 – 3200 cm^{-1}. The 2922 cm^{-1} absorption band can be attributed to C-H and -CH$_2$ vibrations of aliphatic hydrocarbon in the modified resin and it is weak in the other spectrum. The peak assigned to C-O-C aliphatic ether bonds of the KRT1P1SO$_3$Na resin was at 1143 cm^{-1}. However, the corresponding peak in the modified resin was shifted to 1105 cm^{-1}, with decreased peak intensity. Instead of the above peak, there was a new peak that arose at 1239 cm^{-1}, that can be due to the presence of C-N stretching coupled with the stretching of adjacent bonds in molecules (Steyermark, 1976; Pena *et al*., 2009). According to above comparison of FTIR spectrum, it can be assumed that the modified resin system contains –CH$_2$ linkages formed by C-O-C bonds and also considerable amounts of CH$_2$-NH-CH$_2$ linkages (Pena *et al*., 2009; Moubarik *et al*., 2010; Zhu *et al*., 2013)

Scanning electron microscopic (SEM) image analysis

According to SEM images of the original resin system in both µm and nm scale, it is difficult to observe a clear porous structure (Figure 6). However, it shows some heterogeneities and those can be due to high condensed and low condensed areas of the polymerised resin matrix.

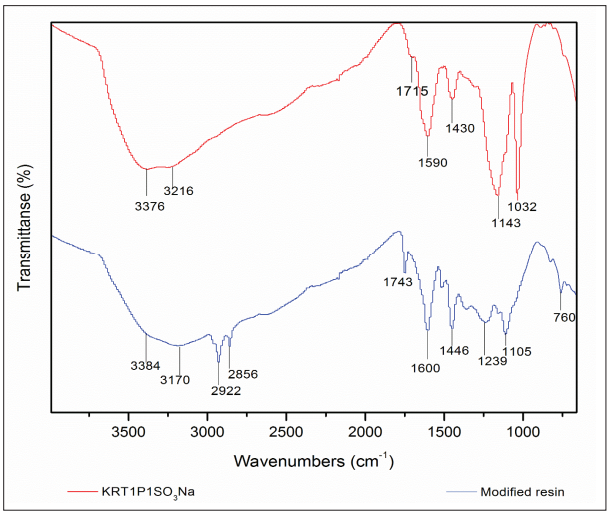


Figure 5: FTIR spectra of KRT1P1SO$_3$Na and modified resin systems

In SEM images of the modified resin system [Figure 7 (a) to (f)], it can be clearly observed that the resin system contains µm and nm scale pores and also some heterogeneities. Figure 7 (a) provides evidence that the prepared porous resin system is composed of both closed cell and open cell structures. Figure 7 (b) is a closed cell structure while Figure 7(c) and (d) are open cell structures in both µm and nm scale.

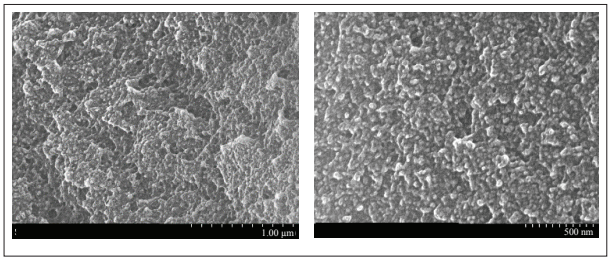


Figure 6: SEM images of KRT1P1SO$_3$Na system (original resin) in µm and nm scale

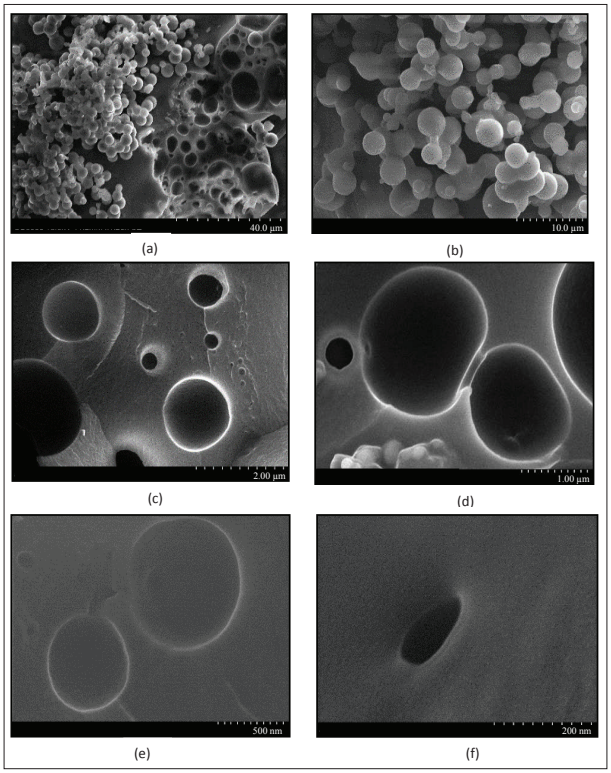
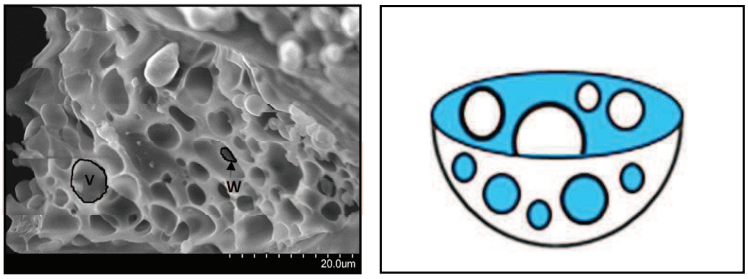


Figure 7: (a-f) SEM images of modified resin system in µm and nm scale



(a) (b)

Figure 8: (a) SEM image of modified tannin-phenol-formaldehyde resin (V - void, W - window); (b) a cross section model of an open cell structure unit in a typical polyHIPE

As in Figure 8 (a), there are some large cells with open voids and embedded windows. These structures are similar to open cell structures of a typical polyHIPE. Closed cell structures can be considered as connected hollow spheres and their voids and windows are difficult to observe [Figure 7 (b)].

Figure 9 shows pore diameter distribution of the modified TPFR system. The histogram provides evidence that the modified resin contains both µm and nm scale pores. According to the histogram, a large proportion of the pores are in µm scale. However, a considerable amount of nm scale pore structures can also be seen.

According to literature, better porous resin systems with a fewer closed cell structures can be synthesised by increasing the fraction of oil used as the porogenic solvent. There are several factors that affect pore sizes, pore structure and their distribution. Hence, by controlling those factors we can obtain a high surface area and low density porous polymeric resin system (Szczurek *et al*., 2014).

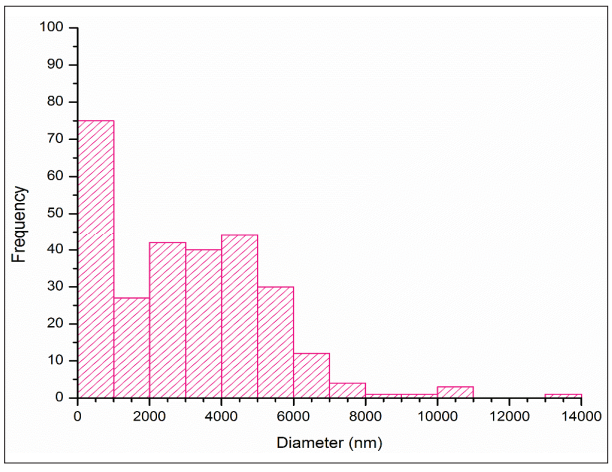


Figure 9: Pore diameter distribution of the modified TPFR system

CONCLUSION

Tannin obtained from the dried bark of *Terminalia arjuna* (Kumbuk) can be used to synthesise formaldehyde based resins with a considerable IEC. This value can be increased by the incorporation of phenol molecules that can impart extra flexibility to the polymer molecules. When changing the tannin to phenol ratio, IEC also increased with the highest value obtained in the 1:1 ratio resin system. Further, the IEC can be improved considerably by sulfonation using concentrated H_2SO_4. The highest adsorption capacity was shown by the sulfonated TPFR with tannin to phenol ratio of 1:1 for Na^+, which was 1.552 meq/g.

The formation of tannin formaldehyde, tannin phenol formaldehyde and its sulfonation was confirmed using FTIR spectra. When considering the swelling property, the lowest volume change of the resin was observed in the solution at pH 7. Stability of the resin system in all pH values was confirmed by the solubility test.

Synthesis of tannin-phenol-formaldehyde porous resin was carried out using coconut oil as the porogenic agent and hexamine as the crosslinker cum-catalyst. Its porous structure was confirmed by the SEM images. According to SEM images, the modified resin contained µm and nm scale pores, while the unmodified resin did not contain a clear porous structure. There were some closed cell structures in the modified porous resin and some of the open cell structures (windows) were

embedded in large voids. According to FTIR spectra it confirms that the modified resin system is similar in the bond formation and polymerisation mechanism to the unmodified TPFR systems.

REFERENCES

1. Arasaretnam S. & Karunanayake L. (2010). Synthesis, characterization, and metal adsorption properties of tannin phenol formaldehyde resins produced using tannin from dried fruit of *Terminalia chebula* (Aralu). *Journal of Applied Polymer Science* **115**: 1081 – 1088. DOI: https://doi.org/10.1002/app.31098
2. Garro Galvez J., Riedl B. & Conner A. (1997). Analytical studies on tara tannins. *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood* **51**: 235 – 243.
3. Kunin R., Meitzner E., Oline J., Fisher S. & Frisch N. (1962). Characterization of amberlyst 15 macroreticular sulfonic acid cation exchange resin. *Industrial and Engineering Chemistry Product Research and Development* **1**: 140 – 144. DOI: https://doi.org/10.1021/i360002a016
4. Mitra N., Banerjee R. & Sarkar A. (1991). Studies on renewable polyphenol-based cation exchange resins of moderately high capacity. *Journal of Applied Polymer Science* **42**: 2499 – 2508. DOI: https://doi.org/10.1002/app.1991.070420915
5. Moubarik A., Charrier B., Allal A., Charrier F. & Pizzi A. (2010). Development and optimization of a new formaldehyde-free cornstarch and tannin wood adhesive. *European Journal of Wood and Wood Products* **68**: 167 – 177. DOI: https://doi.org/10.1007/s00107-009-0357-6
6. Ortiz Palacios J., Cardoso J. & Manero O. (2008). Production of macroporous resins for heavy-metal removal. I. Nonfunctionalized polymers. *Journal of Applied Polymer Science* **107**: 2203 – 2210. DOI: https://doi.org/10.1002/app.27243
7. Özacar M., Soykan C. & Şengïl İ.A. (2006). Studies on synthesis, characterization and metal adsorption of mimosa and valonia tannin resins. *Journal of Applied Polymer Science* **102**: 786 – 797. DOI: https://doi.org/10.1002/app.23944
8. Pena C., De La Caba K., Retegi A., Ocando C., Labidi J., Echeverria J. & Mondragon I. (2009). Mimosa and chestnut tannin extracts reacted with hexamine in solution. *Journal of Thermal Analysis and Calorimetry* **96**: 515 – 521. DOI: https://doi.org/10.1007/s10973-007-8352-9
9. Randall J. (1977). Variations in effectiveness of barks as scavengers for heavy metal ions. *Forest Products Journal* **27**(11): 51 – 56.
10. Steyermark A. (1976). *Spectrometric Identification of Organic Compounds* (eds. R.M. Silverstein, G.C. Bassler & T.C. Morrill), p. 340. Wiley, New York, USA.
11. Stuart B. (2005). Infrared spectroscopy. *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley Online Library.
12. Szczurek A., Fierro V., Pizzi A. & Celzard A. (2014). Emulsion-templated porous carbon monoliths derived from tannins. *Carbon* **74**: 352 – 362. DOI: https://doi.org/10.1016/j.carbon.2014.03.047
13. Yu H., Covey G.H. & Oconnor A.J. (2008). Innovative use of silvichemical biomass and its derivatives for heavy metal sorption from wastewater. *International Journal of Environment and Pollution* **34**: 427 – 450. DOI: https://doi.org/10.1504/IJEP.2008.020808
14. Zhang M. & Sun Y. (2001). Cooperation of solid granule and solvent as porogenic agents novel porogenic mode of biporous media for protein chromatography. *Journal of Chromatography* **922**: 77 – 86.
15. Zhu J., Njuguna J., Abhyankar H., Zhu H., Perreux D., Thiebaud F., Chapelle D., Pizzi A., Sauget A. & De Larminat A. (2013). Effect of fibre configurations on mechanical properties of flax/tannin composites. *Industrial Crops and Products* **50**: 68 – 76. DOI: https://doi.org/10.1016/j.indcrop.2013.06.033