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Physico-thermal properties of spinifex resin bio-polymer

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ABSTRACT

The traditional preparation of spinifex resin for use as an adhesive by Indigenous Australians involves the application of limited heat as a source of energy for processing though overheating may cause permanent degradation of the material. This paper investigates the physico-thermal properties of spinifex resin and its traditional manufactured composite materials to manipulate morphologies and properties during handling and performance. The pure resin was found to display a low glass transition temperature (T_g), and the T_g was found to increase when it was heat-treated due to the thermally induced reaction of resin functional groups. The glass transition temperature further increased when soil minerals were incorporated within the resin matrix according to the conventional theory of hindrance of molecular motion of the polymer chains. The pure resin (metabolic compounds) contained some inorganic elements (Al, Fe, Mg, Mn, Ca, etc.) because of the micro-nutrients taken up by spinifex plants during their life span. Thermo-gravimetric analysis (TGA) revealed that the pure resin displayed the lowest thermal stability. However, the thermal stability improved for resin samples that had been extracted by solvent and subsequently heat treated. This enhanced thermal stability was most likely due to the thermally induced reaction of resin functional groups to form a crosslinked network structure.

1. Introduction

A major problem with synthetic polymers derived from petroleum-based raw materials is their disposal. As landfill sites expand at an alarming rate, the quantity of solid plastic waste requiring disposal is becoming a serious global concern. Consequently, there has been a strong demand for renewable feedstock for polymer synthesis and for the incorporation of more recyclable and/or degradable components in polymer products, which would reduce the costs of solid waste disposal [1]. Increasing demand for environmentally friendly polymeric materials as an alternative to petroleum-based feedstock has encouraged researchers to explore new bio-based polymeric materials [2]. We are actively researching a bio-based polymeric plant resin derived from native Australian *Triodia* grasses.

'Spinifex' (also commonly known as 'porcupine grass') is the generic term used to describe approximately 69 species of grass (Family *Poaceae*) within the genus *Triodia*; it is not to be confused with members of the *Spinifex* genus which are perennial grasses restricted to coastal regions. Spinifex grasses cover more than 27% of the Australian continent, predominantly in the arid and semi-arid regions [3–5].

In this paper we are particularly concerned with *Triodia pungens*, a widespread resin producing species that played an important role in the traditional material culture of Indigenous Australians, perhaps most widely as an adhesive used for hafting stone implements to wooden handles, such as spears, knives, axes and adzes. While various plant genera produce substances with adhesive properties (e.g. *Xanthorrhoea*, *Corymbia*, *Eucalyptus*, *Grevillea*), *Triodia* usage was more widely spread and appears to have been used even in areas where alternatives were available, suggesting it had particularly desirable characteristics. In addition to its typical use as an adhesive, *Triodia* resin was also used for mending cracks and holes in wooden carrying dishes, as a waterproofing agent, for decorative and ornamental purposes, for the manufacture of objects used in ceremonial contexts, and additionally for medicinal applications. Prior to European colonization, *Triodia* resin was widely treated across the continent, in return for other artifacts or resources. The longevity of such *Triodia* resin use in Australia is not known definitively, however it can confidently be assumed to be at least thousands of years old, since in the mid-Holocene (ca 5000 years ago) a suite of small stone artifact types which required hafting for their effective use, proliferate in the archaeological record [6,7].

The resin is secreted from internal or external specialized cell structures of the *T. pungens* plant, and generally appears to

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play no role in the primary physiology of the plant, though may afford some secondary functional benefits. The resin extracted is primarily a mixture of volatile and nonvolatile terpenoid and/or secondary compounds [8]. Spinifex resins are considered to be bio-organic polymers which belong to the thermoplastic class of bio-polymer. Therefore, below its glass transition temperature (T_g), the resin is hard and brittle, and when the temperature reaches T_g, it becomes soft and malleable [5].

It is clear from the available ethnographic sources that some resins required the addition of other substances to improve their effectiveness as adhesives. For instance, in Western Australia, possum fur was added to *Xanthorrhoea* resin [9] and in Central Australia, kangaroo dung was added to *Leschenaultia* ("mindrie") resin [10–11] for the purpose of improving its quality and strength. With respect to traditional spinifex resin manufacturing techniques, most accounts make no explicit mention of the deliberate inclusion or exclusion of other additives; indeed, in northwest Queensland, Roth (1897:101) was adamant that no such materials were added, stating "No water, wax, or other ingredients are used in its manufacture". A recent display in the South Australian Museum suggests that in Central Australia, kangaroo dung would be added to spinifex resin to increase its strength; however, the source of this information is not attributed and it seems likely (given the weight of evidence) they have erroneously attributed this practice to spinifex resin when in fact it referred to mindrie manufacture from the same region as reported by researchers [10,11]. Nevertheless, while additives may not necessarily have been deliberately added to traditionally manufactured spinifex resin, such samples always contain a component of sediment particles as well as plant fibers, in addition to the resin itself. The quantity of such components is variable, and appears dependent to some degree on the skill with which the sample was winnowed to remove such impurities, and for how long such winnowing occurred. The presence of such materials (not technically additives since they are already present in the sample by virtue of the processing techniques, rather than being deliberately added during the process) must have been recognized by Indigenous peoples as serving a functional purpose, since the sample was not purified further so as to remove them. Our research has shown that these sediment and/or fiber inclusions serve as conventional fillers in the resin matrix, and therefore, increase the glass transition temperature as a result of a reduction of polymer chain mobility. Sand fillers also alter resin surface hardness and change the handling characteristics of resin materials to impart desired flow or thixotropic behavior to the materials [12] for easy processing during hafting.

Correlation between traditional Indigenous applications, preparation, structure and properties and more controlled laboratory extraction, purification and testing is necessary in order to evaluate the potential for developing the resins, or its derivatives, as a future renewable material. Therefore, the objective of this study was to analyze the physico-morphological aspects and thermal properties of spinifex resin and traditional composite materials. The chemical and thermal properties of various resins obtained/extracted were compared. Different chemical groups in the resin materials were identified by 'attenuated total reflection-Fourier transform infrared' (ATR-FTIR) analysis, and mineral components in the resin materials were tested by 'inductively coupled plasma mass spectroscopic' (ICP-MS) analysis. Resin molecular weight and distribution was measured by 'gel permeation chromatography' (GPC) analysis, and resin thermal properties were characterized by 'differential scanning calorimetry' (DSC) and 'thermo-gravimetric analysis' (TGA). To the best of our knowledge, this is the first published systematic study of *T. pungens* resin biopolymer morphology and its thermal behavior.

Table 1
Identification of experimental spinifex resin samples and their origins.

Sample code	Descriptions
OR	Virgin resin collected directly from spinifex plant
SR1	Acetone-extracted spinifex resin (solvent evaporated at 85 °C for 72 h)
SR2	Acetone-extracted spinifex resin (solvent evaporated at 40 °C for 72 h)
MR	Spinifex resin composite from a museum article (fresh resin)
MRT	Spinifex resin composite from a museum article (extensively heat treated)

2. Materials and methods

2.1. Materials

Three categories of samples were examined in this study (see Table 1). Pure resin droplets were collected directly from *T. pungens* plants growing around Camooweal, western Queensland, Australia using a spatula with no further treatment (sample OR). Threshed resin, in the form of a mixture of sediment, fibers and resin biopolymer prepared using the traditional Indigenous methods was obtained from the same region (sample SR1 and SR2). This involved the collection of spinifex plants, and then beating them in order to dislodge the resin particles (along with adhering sediment and plant fibers), and sieving the resultant residue (replicating the traditional winnowing).

These resins were compared with similarly traditionally prepared resin composite samples taken from objects in The University of Queensland Anthropology Museum. As Indigenous people used composite materials rather than pure resin, we have considered two spinifex resin based composite materials viz. fresh composite material (sample MR) and extensively heated composite material (sample MRT). The reason for selecting MRT was to investigate how morphological properties would change with the repeated application of heat, because a direct or indirect source of heat must be applied both for the traditional manufacture of resin and again for later hafting or alternate bonding or caulking applications, as and when required.

2.2. Resin extraction

Laboratory reagent grade acetone was used for resin extraction in all instances. Resin was extracted from the threshed sample by dissolving 1 kg of the threshed mixture in 2 L of acetone, and allowing to settle for 24 h in order to dissolve the resin completely. The resin solution was filtered (using Whatman filter paper, GF/C with particle retention of 1.2 μm) and further colloidal particles were removed by centrifugation at 3000 rpm using an Allegra® X-15R Benchtop Centrifuge (Beckman Coulter, USA) for 45 min. Solvent (acetone) was then evaporated at 40 °C and 85 °C for 72 h under flow of nitrogen in order to minimize the oxidation of resin functional groups. This extraction process is shown schematically in Fig. 1. All resin samples were kept in a vacuum oven (SalvisLab Vacucenter, Switzerland) at 35 °C for 48 h before characterization. The resin samples and associated identification codes used in this study are tabulated in Table 1.

2.3. Characterizations

Different chemical moieties in the spinifex resin samples were identified by diamond attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. All samples were scanned between 4000 cm^{-1} and 400 cm^{-1} on a diamond Nicolet 5700 ATR-FT-IR spectrometer in absorbance mode. On average 128 scans were

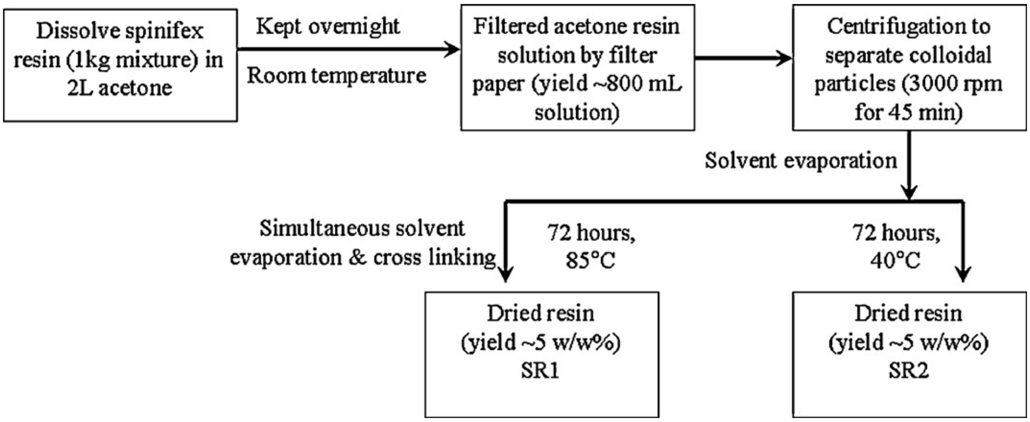

Fig. 1. Schematic of resin extraction from threshed spinifex resin mixture.

performed with a resolution of 4 cm^{-1} for each sample. OMNIC Nicolet software was used for spectral analysis. Elemental analysis of the resin and resin composite samples was carried out using inductively coupled plasma-mass spectroscopy (ICP-MS) on a Varian Vista Pro ICPOES instrument. A known amount of resin sample was digested using EPA protocol 3052.

Molecular weights (weight average, M_w and number average, M_n) and their distribution (polydispersity, PDI = M_w/M_n) were determined by gel permeation chromatography (GPC) techniques using a Waters Alliance 2690 Separations Module attached with an auto-sampler, column heater, differential refractive index detector, and a photodiode array (PDA) connected in series. HPLC grade tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1} and the total injection volume was 50 μL. The columns consisted of three 7.8 mm × 300 mm Waters Styragel GPC columns connected in series, comprising two linear UltraStyragel and one Styragel HR3 columns. Poly (styrene) standards ranging from 1000 to 2 × 10^6 g mol^{-1} were used for calibration.

Thermal properties of the resins were tested by differential scanning calorimetry (DSC) and thermo-gravimetric (TGA) analysis techniques. A Mettler Toledo DSC1 Star System calorimeter with a sub-ambient temperature attachment was used to measure the glass transition temperatures of resin materials. The heating rate was 10 °C min^{-1}, and all samples were scanned from −100 °C to 100 °C in a nitrogen atmosphere. A sample weight in the range of 5–10 mg was employed for all measurements. Glass transition temperatures (T_g) of the resin samples were identified by the baseline shift of the DSC curves. Thermal stability analyses were performed with a Mettler Toledo (TGA/DSC 1) Star^e system thermal analyzer. The thermal degradation temperatures were reported as the temperature at which 5 wt% ($T_{d5\%}$) and 10 wt% ($T_{d10\%}$) of original sample weight had been lost. Sample weight for the TGA experiments was 5–10 mg and all samples were scanned from 30–500 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The temperatures at which maximum degradation rates occurred in each sample were identified from differential thermo-gravimetric analysis (DTA) curves.

3. Results and discussion

The gel permeation chromatography (GPC) results for samples OR, SR1 and SR2 are presented in Table 2. Since the traditionally prepared museum samples MR and MRT had significant amounts of sand and other mineral fillers present, it was difficult to separate the spinifex resin bio-polymer from filler substances in THF solution, and therefore we were unable to characterize these samples using GPC. All bio-polymeric resin samples display a low molecular weight. The low polydispersity index (PDI) observed for all resin samples was most likely due to the collapsing of polymer chains in THF as samples contain a significant amount of inorganic substances. Compared to the virgin resin (OR), the molecular weights of the extracted resins evaporated at 40 °C (SR2) and 85 °C (SR1) showed slight increases accompanying the higher temperature thermal history. This is most likely due to thermally induced reactions between resin functional groups. Possible new linkages include esters (by reaction between hydroxyl and carboxylic groups) and anhydrides (as a result of the reaction between two adjacent carboxylic functionalities).

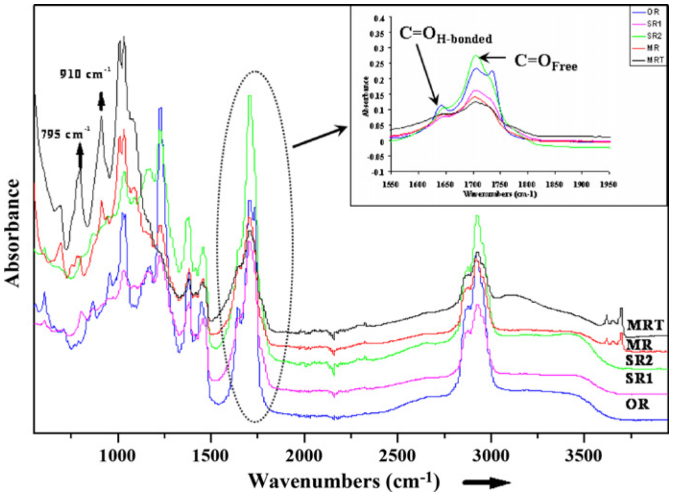

Fig. 2. ATR-FTIR spectra of spinifex resin and their composite samples.

Diamond attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) can be used to identify various chemical moieties within spinifex resin compounds [13]. Fig. 2 displays the ATR-FTIR spectra of all resin samples. All spinifex resin samples display similar spectra, however, subtle differences in peak shape are apparent due to morphological differences in the

Table 2
Gel permeation chromatography (GPC) data of selected spinifex resin samples.

Samples	^aM_n	^bM_w	^{c}PDI
OR	1131	1371	1.21
SR1	1434	1973	1.38
SR2	1231	1557	1.27

[a] Number average molecular weight.
[b] Weight average molecular weight.
[c] Polydispersity index (M_w/M_n).

resin samples. The major characteristic peaks observed are: C—H stretching of sp^2 hybridized bonding at 2870–2925 cm^{-1}, C=O stretching at 1640–1730 cm^{-1}, CH_3 bending at 1378–1380 cm^{-1}, CH_2 rocking at 1447–1456 cm^{-1}, a broad peak around 3450 cm^{-1} for OH stretching of alcohol and/or for carboxylic acid groups, a peak near 1225 and 1170 cm^{-1} for stretching of ester bonds (C—O—C), a peak at 1000–1030 cm^{-1} for bending of aromatic C—H bonds, and a peak around 865 cm^{-1} which is assigned to the unsaturated absorption of C=C groups. Two major peaks are sharpening when excessive mineral fillers are present in the resin samples. Two significant sharp peaks indicate the presence of substantive quantities of silica compounds in the resin composite samples of MR and MRT. They include the peak at around 910 cm^{-1} for —Si—OH stretching and the peak at around 795 cm^{-1} for symmetric stretching of —Si—O—Si— [14].

The IR spectra of spinifex samples show quite similar signatures, however, a closer inspection of the spectra reveals significant differences in the carbonyl group stretching region. The expanded carbonyl group stretching (υ C=O) peaks are due to the presence of carboxylic (—COOH) and/or ester (—COOR) groups, are shown in the inset of Fig. 2. The shape of peaks at 1710 cm^{-1} could be affected by the degree of hydrogen bonding of carbonyl groups present in the spinifex resins as a function of resin composition and/or processing history. The virgin resin shows a small peak around 1640 cm^{-1} due to the hydrogen bonding of carbonyl groups. The existence of both hydrogen bonded and non-hydrogen bonded carbonyl groups in the virgin resin (OR) suggests some secondary interactions between resin functional groups in its backbone structure. When the resin was extracted from the resin mixture with acetone, the weak hydrogen bonded carbonyl signature was removed due to subtle morphological changes. SR2 (40 °C evaporation) shows a single peak for non-hydrogen bonded carbonyl functional groups. A lack of hydrogen bonding could be due to the effects of acetone solvation resulting in a less dense structure (DSC thermogram supports this), but could also be due to the stronger interaction (metal complex bond formation) of resin functional groups with mineral components (ICP result). The intensity of the $C=O_{Free}$ peak for SR1 (85 °C evaporation) decreased as a result of the higher temperature processing. Thermally induced reaction between the functional groups is likely, and this formed toward more of a 3-D network morphology as opposed to a thermoplastic morphology. The museum resin sample with limited heat treatment history (MR) displayed a weak, broad peak for $C=O_{Free}$ which was due to the crosslinking and reaction of resin functional groups with other constituents. This peak further weakens and broadens when the resin composite (MRT) has been extensively heat treated due to further cross-linking and perhaps degradation.

Table 3
Inductively coupled plasma analysis of resin samples.

Elements	Unit (mg kg^{-1})					
	OR	SR1	SR2	MR	MRT	Soil[a]
Ca	175	1072	3250	8961	5397	10,890
Al	828	2140	1438	77,941	65,589	37,148
Cr	3	14	7	49	123	46
Cu	4	4	2	32	23	18
Fe	279	288	347	43,471	141,359	24,122
K	1146	276	268	9747	3868	6036
Mg	199	100	221	1542	646	1177
Mn	23	17	15	90	91	193
Na	324	389	580	2161	1433	1736
P	59	15	46	309	506	228
S	591	361	885	505	298	439
Si	1143	1274	1350	154,598	129,808	199,041
Zn	2	17	3	33	34	37

[a] ICP of soil and leaves mixture has been carried out after resin extraction.

Inductively coupled plasma (ICP) analysis results demonstrated that the virgin spinifex resin (OR) contained high concentration of Al, Ca, Na, K, Fe, S, Si, Mn and Zn etc. along with bio-organic molecules as evident in the ATR-FTIR results. In addition to these major inorganic elements, resin samples and soil also contained low concentrations of Cd, As, Co, Ni, Pb, Se, Cr and Cu etc. These elements in resins are the metabolite compounds of the micronutrients taken up by the spinifex plant, as well as some of the soil dust deposited on the resin where the plant was grown. We have analyzed the soil inorganic composition taken from where the plant was grown, as reported in Table 3. Results show that a high concentration of these mineral elements are present in the soil composition. Plant roots uptake a majority of nutrients and micronutrients [15]. Mobile mineral elements are dispersed in ground water and taken up by the plant roots for photosynthesis. Plants first solubilize these elements, and then transport them to the surface tissues of leaves. In this process, plant root tips which are slightly acidic in nature, can readily exchange H^+ ions for metal cations viz. Ca, Al, Fe, Na, Zn etc. [15–17]. The acetone-extracted threshed resin samples (SR1 and SR2) show higher concentrations of these mineral elements due to the greater access given to resin functional groups to interact, possibly by primary or secondary bonds during the extraction process. Possibilities for primary and secondary resin functional group interactions with metallic elements are illustrated schematically in Fig. 3, taking magnesium (Mg) and carbonyl groups (C=O) as particular examples. The resin composites from museum objects (MR and MRT) incorporate high concentrations of silica and other mineral components that are attributed to Indigenous methods of collecting and processing the resin which readily include mineral matter. The favorable property improvements this engenders are discussed in more detail below.

Differential scanning calorimetry (DSC), a thermal analysis technique, was performed to provide insights into the morphological structure of the various spinifex samples. The glass transition temperatures (T_g) of the spinifex resins and resin composites are compared by looking at a single heating cycle thermogram for each sample. In DSC, resins are heated at a fixed heating rate and the amount of energy required to maintain a fixed rate of temperature increase is measured. Because changes in the mobility of polymer chains in an amorphous polymer sample affect its specific heat, DSC can indirectly inform about the effects of thermal history (crosslinking) and minerals (fillers) on polymer mobility at different temperatures. The T_g of the resins is indicated by a change in heat capacity, which presents as a baseline shift in the DSC trace

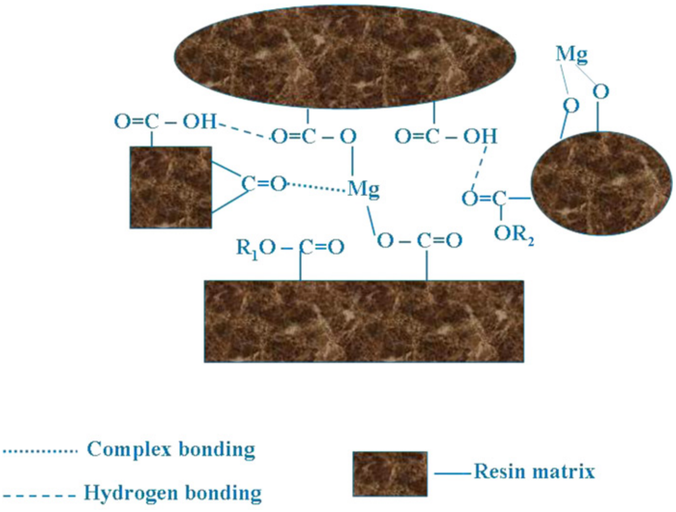

Fig. 3. Schematic of mineral elements compounded with resin functional groups taking carbonyl group and magnesium as examples.

Table 4
Glass transition (T_g) behavior of spinifex resin and their composite samples.

Samples	Onset (°C)	Midpoint (T_g) (°C)	End set (°C)	Glass transition temperature range (°C)
OR	−15.11	−12.60	−7.10	8.01
SR1	28.71	36.73	47.35	18.64
SR2	−1.40	8.64	17.43	18.83
MR	40.56	43.44	51.80	11.24
MRT	50.24	52.12	57.20	6.96

[13]. Below the glass transition temperature (T_g), polymeric materials display glass-like behavior (brittle), but above T_g, the polymers become rubber-like. Fig. 4 shows the heating cycle thermograms for spinifex resin samples, and the corresponding thermal transition data are summarized in Table 4. Analysis of this data revealed a low glass transition temperature with a midpoint of approximately (−10 °C) for virgin resin (OR). An additional small thermal transition (T_{g2}) occurs at around 26 °C. The more prominent, suppressed T_{g1} is most likely due to the fact that this virgin resin still contains many volatile components which would serve to strongly plasticize the resin and increase polymer chain mobility. The glass transition temperature of threshed resin (SR2) increases to 25 °C after extraction by acetone and the solvent evaporated at 40 °C. A combination of the loss of low molecular weight volatiles and the interaction of pure resin functional groups with mineral elements seems to be the reason for this increase. When the solvent was evaporated at higher temperature (85 °C), the glass transition temperature of threshed resin (SR1) increased further due to the formation of 3-D network as a result of reaction between resin functional groups. Indigenous people often purposefully left sand or other mineral fillers in the resin matrices in order to easily increase the volume of a batch, to alter surface hardness, improve adhesive properties, and to change the handling and performance characteristics of resin materials to impart desired flow or thixotropic behavior of the materials for easy of processing during hafting [12]. One could imagine the need to increase the softening temperature of the material so that, on an extremely hot day in the Australian desert (∼45 °C in the shade), the finished article (e.g. hafted spearhead) would still be robustly held in place by the resin “composite”. With this in mind, we observe that both the thermally induced network and the addition of mineral fillers impart molecular hindrance to the polymer chain mobility (Fig. 5), thereby increasing the glass transition temperature.

The approximate values of $T_{d5\%}$ and $T_{d10\%}$ (the temperature of degradation at which the weight losses are 5% and 10% respectively), and T_{DTA} (T_{Max1} and T_{Max2}, corresponding to temperatures at which the maximum degradation would occurred) for resin

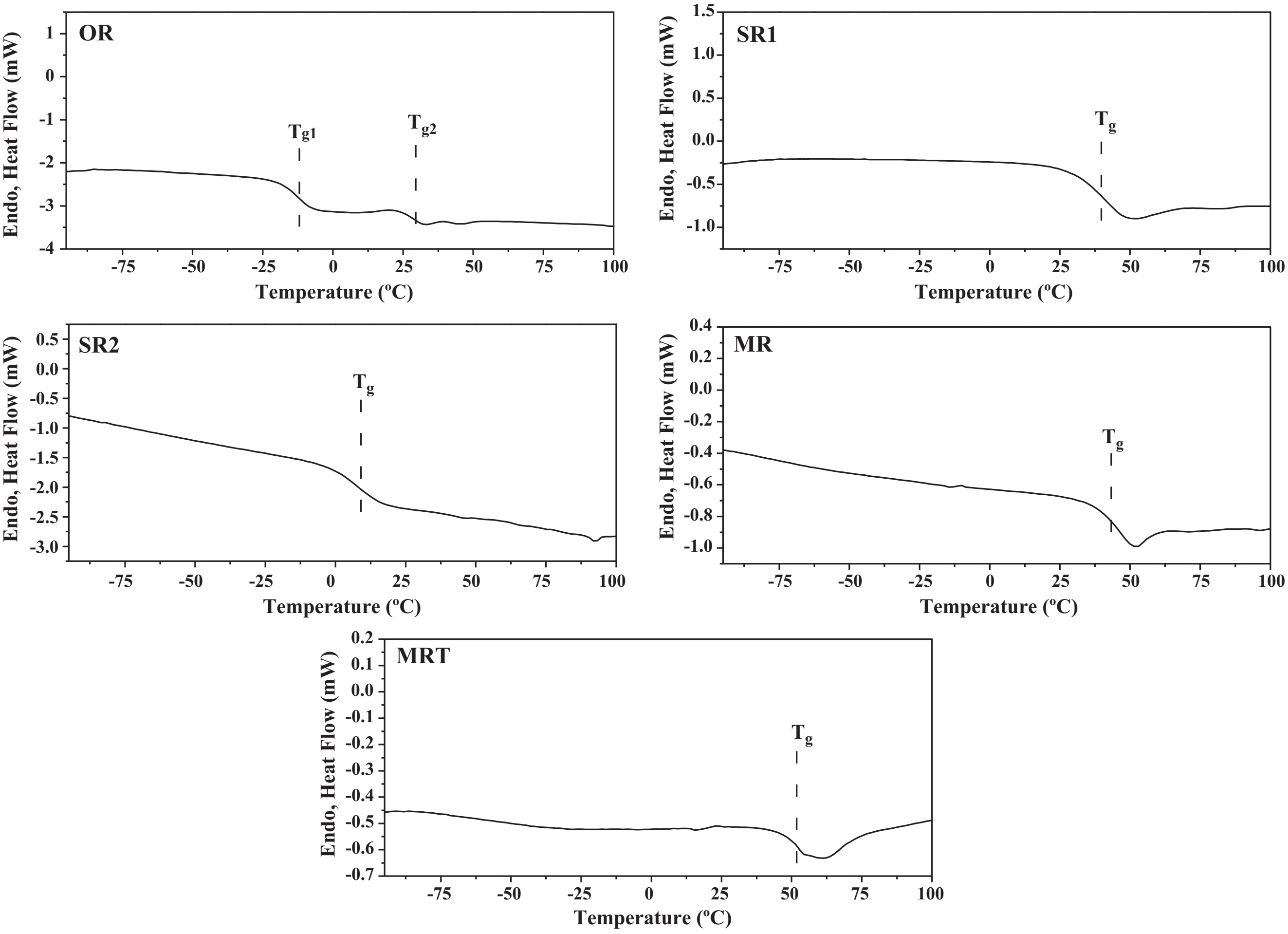

Fig. 4. Glass transition temperature of spinifex resin and their composite samples.

Table 5
Thermal degradation behavior of spinifex resin and their composite samples.

Samples	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	T_{Max1} (°C)	T_{Max2} (°C)	Char yield (%) at 500 °C
OR	190	225	285	413	6
SR1	215	239	316	415	5
SR2	200	229	315	407	5.1
MR	244	273	287	404	58.4
MRT	273	312	300	416	73.7

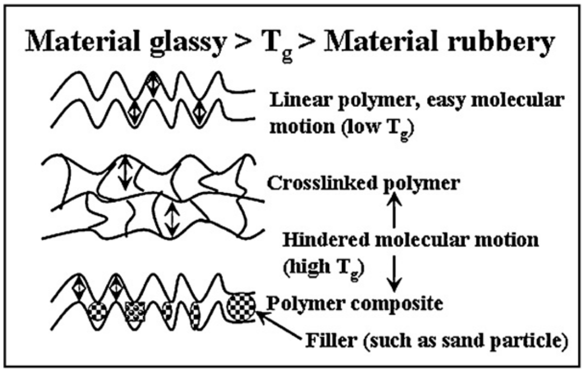

Fig. 5. Schematic of glass transition behavior of linear, cross-linked and filler filled polymer matrices.

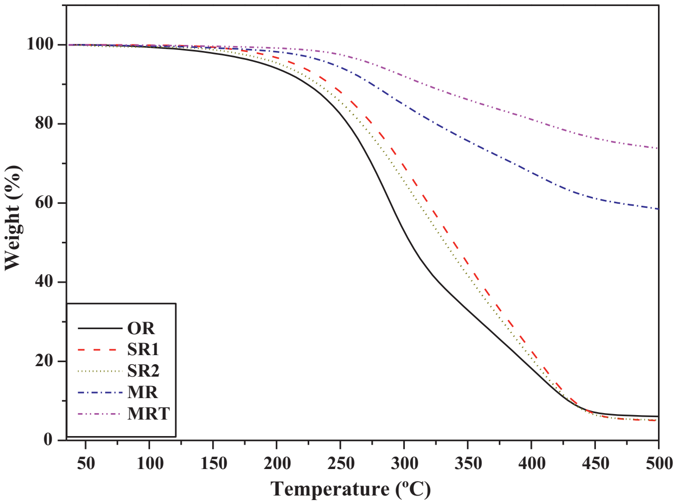

Fig. 6. Thermal degradation of resin samples with respect of temperature.

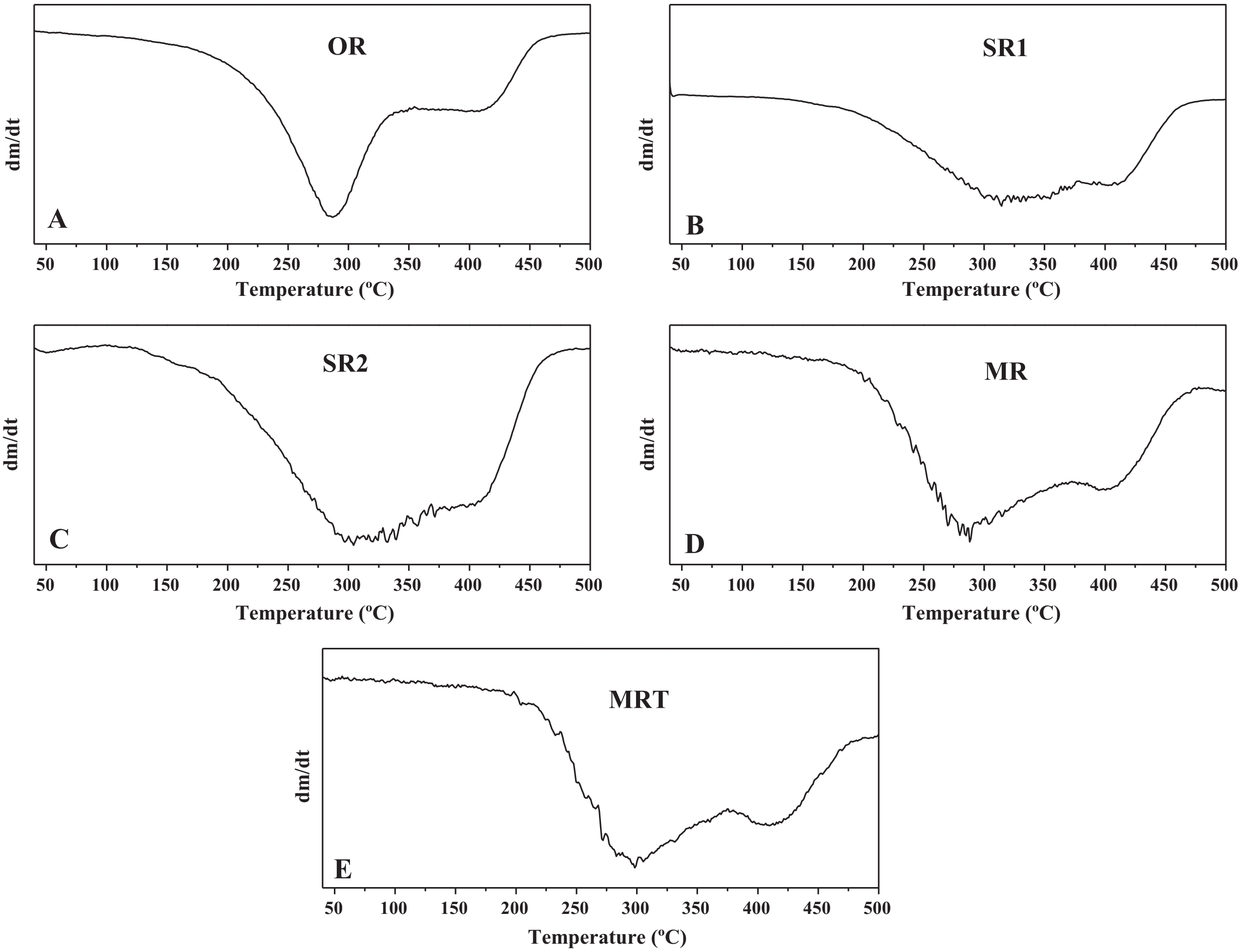

Fig. 7. Derivative of thermo-gravimetry analysis to measure maximum degradation temperature.

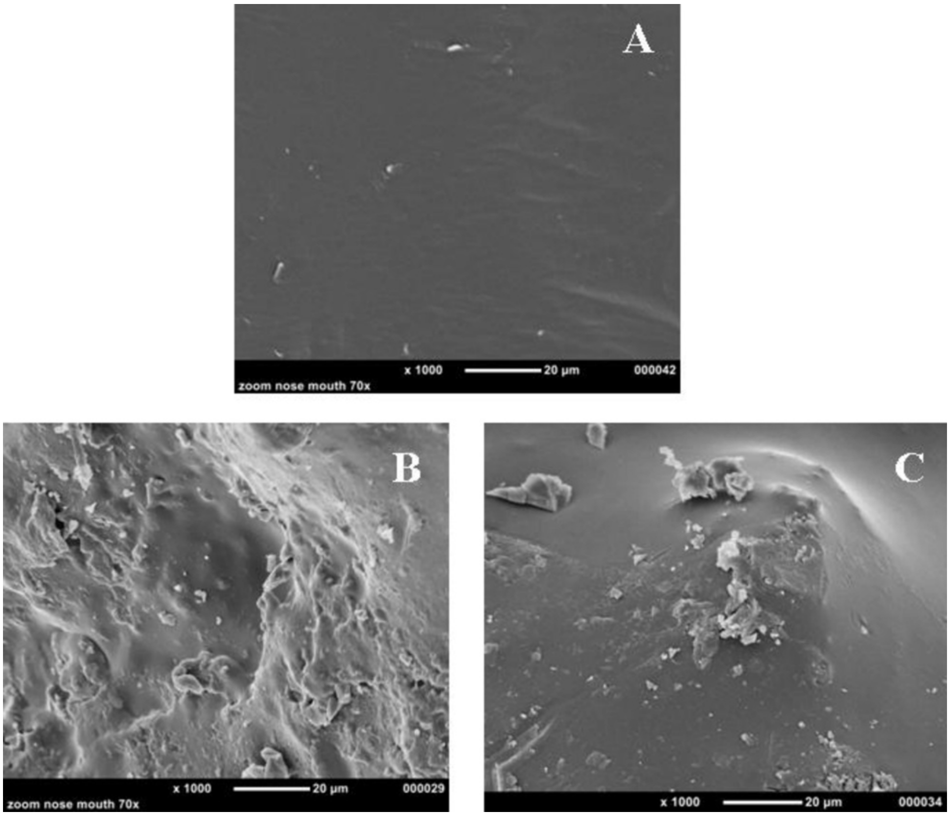

Fig. 8. (A) Surface morphology of original spinifex resin (OR); (B) surface morphology of spinifex resin composite (MR); and (C) heat treated spinifex resin composite (MRT).

samples are reported in Table 5 and their thermal degradation behavior is shown in Figs. 6 and 7. Under the influence of thermal energy, in addition to the loss of low molecular weight volatiles, the resin bio-polymers and their composites are degraded due to the breakdown of bonds (C—C and C—H) in the bio-organic resin and the formation of gaseous degradation products (CO_2 and H_2O) which results in weight loss [18]. The pure resin (which we know includes more volatiles) loses mass more readily when heated in comparison to the resin samples extracted with acetone. Furthermore, thermal degradation properties were further improved when the resin was heat treated. Consistent with previous discussion, more network structure imparts large steric hindrance effects on the resin molecular chain [18].

Researchers studying resins from another Australian native plant, *Xanthorrhoea*, were able to correlate volatile loss, oxidation processes and the increased brittleness of the resultant resin when these materials were repeatedly heated [19]. For spinifex, the thermal degradation properties appear to improve significantly when the resin matrix is filled (MR and MRT) with inorganic fillers (in this case sediment particles). It is also well known that inorganic fillers in polymer matrices can induce a ‘barrier effect’ which delays the release of thermal degradation products in comparison to the virgin polymer, and subsequently decelerate the degradation of bio-polymeric materials [20–22]. Silica compounds serve as additional cross-linking sites (FTIR results) with resin functional groups, which also increases the resistance to thermal degradation. The MRT resin composite sample has even better thermal degradation properties than MR. Extensive heat treatments removed any existing volatile matter and provided additional cross-linking to the three dimensional structure. Therefore, the inorganic component and the higher crosslink density most probably account for the best thermal stability of MRT among all of the selected resin samples [23].

Fig. 6 shows that the residues left after reaching 500 °C for MRT and MR are more than 60% (MR and MRT contain at least 30% and 35% respectively of soil filler which were calculated from ICP analysis, Table 3); so it seems that in this degradation temperature range (30–500 °C), part of the spinifex polymers are degrading and the rest are remaining together with fillers as the mineral filler particles have much better thermal stability than the bio-polymer. The improvement of thermal stability of soil-particle filled spinifex resin can be ascribed to the improved overall bond strength of the bio-polymer, where Si—O bonds of the silica particles with bio-polymer positively contribute [24]. The derivative (DTA) curves (Fig. 7) revealed two-step degradations, and the majority of mass loss occurred around 300 °C in the first stage of degradation. The first step of this biopolymer decomposition is probably dominated to the chain-scission reactions, side-reactions, and cyclization reactions. The last step of degradation corresponds to the advanced fragmentation of the chains formed in the first stage of decomposition, as well as the secondary reactions of dehydrogenation and gasification, and decomposition of the char formed in the previous step [25–27]. Broadening of DTA peaks for the resin samples (SR1 and SR2) and their composites (MR and MRT) signifies that maximum degradation is occurring over a wide temperature range, possibly due to the cross-linking network structure formation, and the primary and secondary bond formation with the pure resin matrix.

Surface morphologies of original spinifex resin (OR) and their composites (MR and MRT) were examined by SEM observations (Fig. 8). SEM micrograph images revealed uniform film-like surface images of composites, and minerals are mostly entrapped by the polymer films even at higher concentration of mineral fillers. This may be attributed to the strong interfacial adhesion of hydroxyl groups of —Si—OH and —Si—O—Si— containing fillers with spinifex resin functional groups. The homogeneous matrix of these composites is a good indication of their structural integrity [28].

4. Conclusions

In this paper, we have presented results from the morphological and thermal characterization of spinifex resin and their composite samples. Experimental results revealed that pure resin contains some inorganic elements (Al, Fe, Mg, Mn, Ca, Na, K, S, P, Zn, etc.) because of micro-nutrients taken up via groundwater by spinifex plants during their life span. ATR-FTIR displayed quite similar peak positions for all resin samples, however, close inspection revealed significant difference in carbonyl group stretching and few peaks sharpening in the composite materials. Pure resin displayed a low glass transition temperature and the material was soft at room temperature. Both thermal degradation and glass transition temperature of resin samples increased when resins were heat treated owing to the thermally induced reaction between the functional groups. Reinforcements of fillers in the resin matrix further increased glass transition temperature and improved thermal degradation properties because of the network structure formation by the interaction of resin functional groups and mineral compounds in the resin matrix. Further systematic study of the morphology and thermal behavior of spinifex resin/composites, that builds upon the findings in this paper, would make a significant contribution to the effective processing of this kind of biopolymer both for the manufacture of traditional Indigenous artifacts and for developing novel advanced biopolymer-based materials. Chemical modification of this kind of interesting bio-polymeric material to improve their properties is underway in our laboratory.

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