Abstract: Simple bio-based abrasive grinding wheel based on thermosetting resin matrix was developed starting with condensed tannin and furfuryl alcohol, which are mainly derived from forest and agricultural products like tree barks, wheat and crops. Fourier transform infrared spectra (FTIR) signified the acidic conditions are quiet efficient for the reaction of furfuryl alcohol, urea and glyoxal all together and the -CH2-NH- and -CH2-O-CH(OH)- groups are predominating in cross-linking of the tannin-furfuryl alcohol-urea-glyoxal (TFUG) resin. The strengthening contribution of the tannin was also confirmed by the preservation of its distinct crystallinity using X-ray diffraction (XRD). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) ensured that TFUG resin can be cured at low temperature and offer higher heat resistance compared with phenol-formaldehyde (PF) resin. The high hardness and excellent compressive strength revealed by the corresponding investigations such as Brinell hardness, compression resistance, and grinding tests suggested a strong abrasive ability using the new grinding wheel compared with lab-made grinding wheel based on PF resin. This could be ascribed to the absence of cracks and low content of formed holes as confirmed using scanning electron microscopy (SEM) and balanced reaction conditions that leads to network structure with regular local reinforcements and homogeneous crosslink density.

Keywords: Tannin; furfuryl alcohol; bio-based resin; grinding wheel

1 Introduction

Grinding wheels have widely been used in building construction, interior decoration, mechanical manufacturing and other fields [1]. It is one of the most commonly used processing materials. Phenol-formaldehyde resin (PF) as a petrochemical product is the main resin binder for preparation of grinding wheels [2,3] and other materials [4,5]. However, the toxic formaldehyde of PF based grinding wheels limited its development. Nowadays, some raw materials coming from forests are widely used to replace oil-derived resin because of the low toxicity and renewability, such as tannin [6] and lignocellulosics [7]. Tannin, which was extracted from wood bark and grape pip is the most abundant natural aromatic
bio-sources after lignin. This is the motivation for its continuous development for the replacement of PF resins [8,9]. Over the past three decades, in order to improve the mechanical strength and thermal properties of tannin resin, formaldehyde was used to crosslink it [10]. However, the toxicity of free formaldehyde associated with disposal and health hazard problems limited the further development. Furfuryl alcohol originated from agriculture with excellent thermal resistance [11] has been broadly used to react with tannin for the preparation of tannin-furanic (TF) resin based materials, such as rigid plastic [12], foams [13–16], grinding wheels [17,18] and wood adhesives [19,20]. Compared with PF based materials, these materials show excellent mechanical properties and good heat resistance. Nevertheless, the self-condensation reaction of furfuryl alcohol has been easily established under acidic conditions, which predominates to such an extent that lead to little or no co-reaction with tannin [19,20]. Thus, the cross-linking between furfuryl alcohol and tannin for preparation of TF resin was carried out under alkaline condition, which resulted in poor heat resistance due to the low reactivity of tannin under these conditions. For abrasive grinding wheel, heat resistance plays a significant role during the grinding process. Our previous work showed that for substitution of formaldehyde, glyoxal can be alternatively used as a cross-linker to react with furfuryl alcohol for the reduction of self-condensation of furfuryl alcohol under acidic conditions [21,22]. As the proportion of furfuryl alcohol in TF resin is very high [23,24], as well as its price, which imposed restriction on its industrialized development. On the other hand, urea has a low price and a good reactivity, thus can act as a substitution for parts of furfuryl alcohol and react easily with furfuryl alcohol and tannin [25,26]. Consequently, research on tannin, furfuryl alcohol, urea and glyoxal has been conducted to ascertain the feasibility of tannin-furfuryl alcohol-urea-glyoxal (TFUG) resin based abrasive grinding wheel considering presenting good mechanical properties and better heat resistance. This report deals firstly with the possibility that furfuryl alcohol, urea and glyoxal can be used to cross-link FUG resin under acidic conditions. Secondly, the tannin addition into this resin system to form the formulation of a resin matrix for abrasive grinding wheel after mixing with abrasive silicon dioxide particles. The curing process of abrasive grinding wheel was employed in oven for 4 days referring to literature reports [18,27]. In order to make the grinding wheel process more efficient, the curing process of the resin matrix incorporating abrasive particles will be done in a press machine. This study is important for the development of an environment-friendly abrasive grinding wheel, which is a step for potential replacement of the industrially-applicable PF based grinding wheels.

2 Materials and Methods

2.1 Materials

Mimosa tannin, sourced by extraction from the bark of Mimosa (Acacia mearnsii, formerly mollissima, De Wildt), was obtained from the Hong Bang Biological Technology Co. (Chuxiong, China). The tannin was exposed to ethanol extraction to eliminate the majority of carbohydrates present. Furfuryl alcohol (with 98% purity), glyoxal (with a purity of 40%), para-toluene-4-sulphonic acid (p-TSA, with 97.5% purity) and formaldehyde (37% aqueous solution) were purchased from Acros Organics (Geel, Belgium). Tung oil, and silicon dioxide (SiO2) particles with a size of 0.4 mm (mess number of 40 and type of 14808-60-7) were purchased from Run Xin Materials Co. (Kunming, China). Commercial urea was obtained from Huai Ren Zhong chemical plant (Jiangxi, China). Liquefied phenol (with 80% purity) and sodium hydroxide were provided from Fisher Scientific (Loughborough, UK).

2.2 Preparation of Different Resins Matrixes

The TFUG resin matrix was synthesized by the following process: furfuryl alcohol and glyoxal with F/G molar ratio of 2 were mixed in a flat-bottomed flask fitted with a thermometer and magnetic stirrer bar at 60°C for 30 min. During this process, p-TSA (30% aqueous solution) was used to adjust the pH to 3. Then, the pH value was adjusted to 5 using 40% NaOH aqueous solution. After that, urea in powder form was added into
this system by means of mass ratio and left to react for 30 min to obtain the furfuryl alcohol-urea-glyoxal (FUG) resin. Then, tannin in powder form was mixed with the FUG resin, and the mixture was left at 60°C undergoing rotary evaporation under vacuum for 30 min (pre-polymerization) to obtain the TFUG resin. The tannin-furfuryl alcohol-urea (TFU) resin was prepared in the same way as for TFUG resin. The TF resin matrix was synthesized according to the method of Li et al. [12,18]. In brief, tannin in powder form and furfuryl alcohol by means of mass ratio were mixed in a beaker and stirred together for 5 min. Afterward, the mixture was left to react in a rotary evaporator under vacuum conditions for 1.5 h at 60°C under acidic conditions to form the TF resin. During the process, the pH was maintained at 3 using 30% aqueous solution of p-TSA. The formulations employed for the preparation of TFUG resins matrixes are shown in Table 1.

Table 1: Composition of different resins matrixes used in this study

| Sample | Tannin/g | Furfuryl alcohol/mL | Glyoxal/mL | Urea/g |
|--------|---------|---------------------|------------|--------|
| TFUG   | 20      | 40                  | 12         | 20     |
| TFU    | 20      | 40                  | 0          | 20     |
| TF     | 20      | 60                  | 0          | 0      |

The PF resin matrix was prepared according to the literature [1] at 94°C using 1 mol of phenol (80% purity) and 2 moles of formaldehyde (37% aqueous solution). During this process, formaldehyde was divided into four equal parts and each part was added at 15 min interval. The first portion of formaldehyde was mixed with phenol at 94°C; and the mixture was continuously stirred. Later, the second, third, and fourth parts of formaldehyde were added, during which the mixture was refluxed under continuous stirring. During the process, the pH of the mixture was adjusted to 10 using 40% aqueous solution of NaOH.

The solid content levels of the different resins were determined by recording the resins weights before and after drying at 120 ± 1°C for 2 h in an oven. The tu-4 viscosity cup was used to measure the viscosity of the different resins at 27°C whereas the curing times of different resins were determined in accordance to Chinese National Standard GB/T14074 (2006).

2.3 Preparation of Different Grinding Wheels

First, 50 g of each of the different resins listed in Table 1 was agitated mechanically in a beaker for 1 min. Next, 5 g of tung oil and SiO2 particles were added and mixed well with these resins. Tung oil was used to improve the tenacity of these samples and SiO2 particles were used as abrasive particles. The mass ratio of SiO2-to-resin used was 1.5:1 based on the previous work by Lagel [18]. Then the mixture was poured into a mould of 50 mm diameter and 15 mm thickness. The mould was placed under a press, model Instron 4467, for 1.5 h at 150°C under a pressure of 7.8 MPa to achieve the curing process. After that, cooling was provided on the grinding wheel and a 16 mm diameter hole was then drilled at the centers to produce the corresponding TFUG, TFU, TF and PF resins-based grinding wheels, respectively, which will be denoted TFUG-G, TFU-G, TF-G and PF-G through this study. A schematic illustration for the preparation of the TFUG-G is shown in Fig. 1.

2.4 Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Diffraction (XRD)

Avarian1000 Infrared spectrometer (Varian, Palo Alto, CA, USA) was used to record the infrared spectra of the different type of resins. One g of KBr and 0.01 g of cured resins powder were mixed to prepare the sample for testing. The scan range of wavenumbers was 500 cm⁻¹ to 4000 cm⁻¹.
The crystalline characteristics of different resins were studied using an X-ray diffractometer (D/max-RB, Rigaku, Japan) with CuKα target operating at 40 kV and 50 mA. A diffraction angle range of 40–5° was used during the analysis. The resins were freeze-dried for 48 h before they were crushed into powder for testing. A software (Jade 5.0, Livermore, CA, USA) was used to analyze the diffractograms and the relative crystallinity was calculated by estimating the area under the curve using a software (SeaSolve Software Peak Fit v4.12, Framingham, USA).

Figure 1: Schematic illustration of the preparation of a grinding wheel based on TFUG resin incorporating silicon dioxide particles
2.5 Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA)

A DSC analyser (DSC 204 F1, Netzsch, Germany) operated under nitrogen atmosphere was used to investigate the curing behavior of different resins with a heating rate of 15°C/min over the temperature range from 30°C to 250°C.

A thermogravimetric analyzer (TGA) (TG 209 F3, Netzsch, Germany) operated also under nitrogen atmosphere was used for testing the thermal resistance of the resins under a heating rate of 20 °C/min over the temperatures range from 30°C to 900°C.

2.6 Scanning Electron Microscopy (SEM)

Microscopic observation was carried out on the surfaces on grinding wheels with dimensions of 5 mm × 5 mm × 4 mm using scanning electron microscope (Model S 4800, Hitachi, Tokyo, Japan) at 50× magnification.

2.7 Brinell Hardness, Compression and Abrasiveness Measurements

The Brinell hardness (HB, daN·mm$^{-2}$) measurements were accomplished according to the Chinese testing norm of GB/T 231.1-2009 using strength testing instrument (Instron model 1193, Boston, USA) working with a 10 mm steel ball diameter under 2452 N loading and 2 mm/min loading rate. The Brinell hardness was given by Eq. (1):

$$
HB = \frac{3.18F}{1000P}
$$

where F is the force determined for the retained depression (N); and P is the depth of depression of the ball (mm).

The compression test was implemented following the ASTM D695-10 using the strength analysis instrument (Instron model 1193, Boston, USA) operated at a loading rate of 2 mm/min.

The wear index (I, %) was measured on the surface of a commercial particleboard (100 × 100 × 19 mm$^3$) after 500 cycles were elapsed using the abrasion meter of Taber Abraser machine (Tape 5130, Taber Industries, USA) installed with the prepared grinding wheel in this study, following the ASTM_D4060-01 standard. Meanwhile, a calibrated grinding wheel H-18 (North Tonawanda, USA) was used for comparison and the mass ratio of glass particles (40 mesh number)-to-PF resin used was 1.5:1 with butadiene styrene rubber as a tenancity agent. For the different properties, each result was the average reading of six replicates. The wear index was given by Eq. (2):

$$
I = \frac{(A - B)1000}{C}
$$

where A is the weight of particleboard before abrasion (mg); B is the weight of particleboard after abrasion (mg); and C is the number of abrasion cycles record.

3 Results and Discussions

3.1 FTIR and XRD Analyses

Fig. 2 shows the infrared spectra of mimosa tannin aqueous solution (T) and TFUG resin. The spectrum of T reveals absorption peak at 1286 cm$^{-1}$, resulting from C-OH stretching vibration of the phenolic hydroxyl groups [28,29]. On the other hand, the spectrum of TFUG presents absorption peak, corresponding to C-OH stretching vibration of the benzene ring, shifted to 1289 cm$^{-1}$, which confirms that urea or glyoxal interfered with the chemical environment of mimosa tannin. Meanwhile, the single peak observed at 1630 cm$^{-1}$ in the spectrum of TFUG resin can be attributed to carbonyl groups of urea, implying that the structure is not symmetric. Namely, the electrophilic reaction between urea and aromatic ring under acidic conditions easily produces C-N single bond and p-π conjugation [29]. These results indicate that one end of the
carbonyl group of urea was linked to tannin and the other end was linked to furfuryl alcohol or to glyoxal. The absorption peak observed at 1451 cm$^{-1}$ in the spectrum of T is ascribed to O-H bending vibration of phenolic hydroxyl groups. However, it was perturbed to 1438 cm$^{-1}$ in the spectrum of TFUG, which was most likely attributed to the electrophilic substitution reaction of phenolic hydroxyls at the ortho positions, which caused altering of the chemical environment of the phenolic hydroxyls. Further, there was a strong absorption peak at 1500 to 1530 cm$^{-1}$, revealing C=C stretching vibration of the aromatic rings. On the contrary, these peaks almost disappeared in the spectrum of TFUG, which signifies that the symmetrical electrophilic reaction on ortho positions of phenolic hydroxyl group weakens the absorption. The peak of 1072 cm$^{-1}$ was attributed to the ether bond (C-O-C) symmetric and anti-symmetric stretching vibration between glyoxal and furfuryl alcohol. These results indicate that cross-linking between tannin, urea, furfuryl alcohol and glyoxal had been accomplished.

The X-ray diffractograms of T, TF and TFUG are displayed in Fig. 3. The patterns of TF and TFUG are very parallel with that of T, which translates into the addition of furfuryl alcohol, urea and glyoxal did not change the aggregation state of tannin.

Figure 2: FTIR spectra of mimosa tannin and TFUG resin

Figure 3: XRD patterns of mimosa tannin, TF and TFUG resins
3.2 Characteristics of Laboratory-Made Resin Matrixes

The different prepared resins in laboratory were characterized and the results are shown in Fig. 4. It can be seen that the gel time of TFU was longer than that of TF and TFUG. Moreover, the solid content and viscosity of TFUG resin are higher than that of TF resin. Compared with the TF resin, the TFUG resin has a shorter gel time, which could be caused by some reasons. For the TF resin, the cross-linking between tannin and furfuryl alcohol under acidic conditions below 100°C is difficult to form the -CH₂-bridge because of the self-condensation of furfuryl alcohol, which was proven in some previous studies [30–32], and is presented in Scheme 1a for demonstration. However, our previous work showed that the glyoxal is easily converted into the tetrahydroxy ethane after hydration reversible reaction in water under the acidic conditions and then its reaction with furfuryl alcohol reduces the self-condensation of furfuryl alcohol [20,22] (Scheme 1b). Based on this, the reaction among tannin, furfuryl alcohol, urea and glyoxal is easily established below 100°C, which has been proven also via FTIR as shown in Fig. 2 and clarified in Scheme 1c.

Fig. 5 reveals the relevant DSC thermograms of T, TF, TFU, TFUG and PF resins. All of them showed one exothermic peak after freeze drying. Namely, the peak of T appeared between 63°C–82°C whereas that of TF appeared between 120°C–160°C. This indicates that the curing temperature of tannin increased due to the linear self-polymerization of furfuryl alcohol which requires a higher temperature [28]. For TFUG resins, the peak assigned in the range 62°C–72°C was lower than that of TFU resin, which showed a peak at the range of 70°C–85°C. Compared with TFU and PF resin, the curing temperature of TFUG decreased significantly, which can be correlated with the gel time to recognize that the glyoxal made the reaction between tannin, furfuryl alcohol and urea easier.

The thermal degradation profiles of the different cured resins were collected using TGA and the results are exhibited in Fig. 6. The temperatures that correspond to weight losses of 5%, 15%, 30% and 50% are referred to as T5%, T15%, T 30% and T 50%, respectively. It is obvious that the cured TFUG resin is thermally stable up to 150°C, whereas the cured PF and T were thermally stable only up to 100°C. Even worse, the cured TFU started to be influenced by the heat at 50°C. Interestingly, T5% of TF is higher than that of TFUG while T15%, T30% and T50% of TFUG are higher than TF. This could be justified by considering the curing process is more efficient and crosslink density is higher in case of TFUG. Further, the mimosa tannin extracts, being a biological extracts, includes other substances and the
self-condensation of furfuryl alcohol leads to no or less reaction with tannin. Obviously, the addition of glyoxal and urea caused decrease of the self-condensation of furfuryl alcohol and the chemical bridging between tannin and FUG resin was proven as evidenced by FTIR technique and is thought to be responsible for the better heat resistance of TFUG compared with TF. At temperature around 800°C, the

**Scheme 1:** Proposed reaction routes of tannin-based resin system

**Figure 5:** Curing exotherms of mimosa tannin (T), TFUG, TFU, TF and PF resins
residual weight of TFUG resin was 37%. In this manner, TFUG resin is advantageous because it can be cured at a relatively low temperature and acquires high heat resistance.

3.3 Macroscopic and SEM Observation of Grinding Wheels

The various tannin-based grinding wheels were prepared in laboratory and each one acquired a smooth surface lacking of cracks, TFUG-G is an example as shown in Fig. 7. On the contrary, tannin-furanic resin based grinding wheel was reported in a previously [18] to possess some defects and cracks.

![Thermo-gravimetric traces of mimosa tannin (T), TFUG, TFU and PF cured resins](image)

**Figure 6:** Thermo-gravimetric traces of mimosa tannin (T), TFUG, TFU and PF cured resins

Additional deeper insight was accomplished by microscopic observation of the different samples using scanning electron microscopy (SEM) as illustrated in Fig. 8. From Fig. 8b, the surface of TFU-G exhibited obvious cracks in the matrix flesh. In contrast, no cracks could be detected in TFUG-G, TF-G and PF-G.

![Digital image of the grinding wheel based on TFUG resin matrix](image)

**Figure 7:** Digital image of the grinding wheel based on TFUG resin matrix
grinding wheels (Figs. 8a, 8c and 8d). It is worthy to note that the gel time of TFU resin at 100°C was longer than that of the other resins and its curing temperature was higher than that of TFUG resin. This explains the condensation reaction between urea, furfuryl alcohol and tannin as well as the self-condensation of furfuryl alcohol was difficult to be completed through a rotary evaporation process at 60°C. This means that more reactions steps had been established during press at high temperature of 150°C and accordingly the liberated water during the curing process caused formation of cracks and imperfections in the grinding wheel. Meanwhile, extensive number of holes was observed in TF-G as compared with TFUG-G. In case of TF resin, the self-condensation of furfuryl alcohol predominates to such an extent that leads to little or no co-reaction with tannin. This was proven by detecting some residual tannin in the resin matrix, causing the resin mixture to trap air. Hence, when the sample of TF-G was cured, some holes were noticed on the surface (marked with arrow in Fig. 8c). Glyoxal as a cross-linker can react with furfuryl alcohol and improve the reactivity of furfuryl alcohol and tannin resulting in no or less holes in case of TFUG-G. For the grinding wheel derived from PF-G, tiny number of holes was observed (marked by arrow as shown in Fig. 8d) as a consequence of the high viscosity of PF resin (shown in Fig. 4) causing difficulty of homogenous blending with particles.

3.4 Brinell Hardness, Compression and Abrasive Measurements

From Tab. 2, compared with the sample of TF-G prepared in laboratory and the tannin-furanic resin based grinding wheel reported by Lagel [18], the addition of urea and glyoxal in tannin-furanic resin system for the preparation of TFUG-G could reduce the amount needed of furfuryl alcohol. In addition,
TFUG-G exhibited compressive strength (229.67 MPa) and hardness (11.78 daN·mm$^{-2}$) higher than that of TF-G, 210.25 MPa, 10.67 daN·mm$^{-2}$, respectively. The FTIR techniques signified the facile reactivity of glyoxal and urea towards furfuryl alcohol under acidic conditions, which in turn leads to enhancement of the reaction of tannin and furfuryl alcohol with each other. This has been demonstrated from SEM imaging in the previous section, where holes were developed on the surface of TF-G. This defect is in charge of the low hardness and compressive strength of TF-G. However, it is difficult to elucidate whether the strength reinforcement was acquired by the urea alone or the combined action of glyoxal and urea. To distinguish whether any improvement in the hardness and compressive strength is generally related to the urea or glyoxal or their combination, TFU was prepared for comparison with TF-G and TFUG-G. It was clear that the sample of TFUG-G was harder and had a higher compressive resistance relative to that of TFU-G, which exhibited a compressive strength of 167.38 MPa and Brinell hardness of 8.35 daN·mm$^{-2}$. In addition, the compression strength and brinell hardness of TF-G are also higher than the relevant values of TFU-G, which corroborates that glyoxal reacted efficiently with furfuryl alcohol in such a way that decreased the self-condensation of furfuryl alcohol and its activity extended to condensate with tannin to form a robust network structure that afforded reinforcing of the grinding wheel. Thanks to urea that greatly hampered the reaction between tannin and furfuryl alcohol in absence of glyoxal. This has been identified for TFU-G with plenty of surface cracks as described by SEM, Fig. 8b. This explains reason beyond which the compression strength of TFU-G is lower than that of TF-G. Moreover, TFUG-G and TF-G exhibited excellent hardness and compression strength compared with the laboratory-made PF-G. The XRD study in the previous section indicates that tannin itself plays the role of a reinforcing agent because of the aggregation and aromatic nature. Thus, it is a good sign for the preparation of a high quality grinding wheel.

The abrasiveness of the different grinding wheels could be characterized by the wear-resistance and the results are given in Tab. 3. The commercial Taber Calibrade wheel H-18 was also tested for comparison with the laboratory-made grinding wheels. It was found that TFUG-G had better resistance against wear than TF-G and TFU-G with a mass loss around 0.125%, which can be attributed to an excellent blending between the resin and particles compared with the recipe in case of TF-G.

| Graveling wheel type | Cycle/r | Wear index | Mass loss of grinding wheel/% |
|----------------------|---------|------------|-----------------------------|
| TFUG-G               | 500     | 12.57 E-05 | 0.125                       |
| TFU-G                | 500     | 11.56 E-05 | 0.391                       |
| TF-G                 | 500     | 11.68 E-05 | 0.253                       |
| PF-G                 | 500     | 11.59 E-05 | 0.265                       |
| Reference: Wheel H-18| 500     | 3.92 E-05  | 0.107                       |

Furthermore, the high Brinell hardness translates into better abrasive strength in comparison to TF-G. This can be further demonstrated by TG analysis in the previous section, in which TFUG showed a
higher heat resistance than TF-G, which is conducive to mass loss as a result of the high temperature during the rotation of the grinding wheel. Furthermore, comparison of TFUG-G with oil-derived resins-based abrasive materials such as PF-G can be conducted. The corresponding wear index value (12.57 E-05) is above that of PF-G (11.59 E-05) which exhibited a mass loss up to two times higher than that of TFUG-G. Therefore, TFUG-G is candidate as a very abrasive material because of its admirable wear index, which is up to four times the related value of the commercial Taber Calibrade wheel H-18. Interestingly, compared with the grinding wheel suggested in a previous work [18], in which it was formulated with tannin-furanic resin with a wear index value of 9.79 E-05, the wear resistance of TFUG-G prepared with low amount of furfuryl alcohol was more dominate along with the more viability of its formulation for industrial production.

4 Conclusions

A new renewable environmentally friendly bio-based grinding wheel, based on mimosa tannin, can be simply fabricated at low curing temperature from a resin mixture with suitable viscosity, comprising furfuryl alcohol, urea and glyoxal, while incorporating silicon dioxide particles, which allows achieving the curing process in short time. The grinding wheel exhibited good appearance with no visual cracks and less holes, which led to interesting features such as higher hardness and stronger resistance to compression along with better abrasiveness, compared to PF grinding wheel and commercial Taber Calibrade wheel H-18. The excellent thermal resistance acquired by the grinding wheel, with about 43% residual weight at temperature as high as 800°C, can be accounted for by the distinct homogeneous crosslinking of the network structure and further reinforcing action provided by the presence of the abrasive silicone dioxide particles. Based on the low cost and green route of fabrication, it is pretty feasible to consider this material a very promising bio-based abrasive product to replace the industrially applicable grinding wheels formulated from phenolic resins.

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References

1. Anna, L. A., Dixon, K. C. (1974). Referencing styles for journals-resin bonded grinding wheel containing gas-filled thermal plastic resin beads and method of making it. Patent, 3925034, USA.
2. Robie, N. P. (1957). Referencing styles for journals-abrasive bodies. Patent, 2806772, USA.
3. Rowse, R. A., Stinchfield, C. P. (1959). Referencing styles for journals-phenolic resin boned grinding wheels. Patent, 3041156, USA.
4. Xu, F., Zhu, S. Z., Ma, Z., Liu, Y. B., Li, H. Z. et al. (2020). Improved interfacial strength and ablation resistance of carbon fabric reinforced phenolic composites modified with functionalized ZrSiO₄ sol. Materials and Design, 191, 108623. DOI 10.1016/j.matdes.2020.108623.
5. Pizzi, A., Vosloo, R., Cameron, F. A., Orovan, E. (1986). Self-neutralizing acid-set PF wood adhesives. Holz Roh-Werkst, 44, 229–234.
6. Raknes, E. (1997). Durability of structural wood adhesives after 30 years ageing. Holz als Roh- und Werkstoff, 55 (2–4), 83–90. DOI 10.1007/BF02990523.
7. Zhang, J. F., Ahmed, K. B., Xing, D., Liu, W. Y., Wang, Q. W. et al. (2020). Improving lignocellulose thermal stability by chemical modification with boric acid for incorporating into polyamide. *Materials & Design, 19*, 108589. DOI 10.1016/j.matdes.2020.108589.

8. Pasch, H., Pizzi, A., Rode, K. (2001). MALDI-TOF mass spectrometry of polyflavonoid tannins. *Polymer, 42*(18), 7531–7539. DOI 10.1016/S0032-3861(01)00216-6.

9. Sauget, A., Zhou, X., Pizzi, A. (2014). Tannin-resorcinol-formaldehyde resin and flax fiber biocomposites. *Journal of Renewable Materials, 3*(3), 173–181. DOI 10.7569/jrm.2013.634128.

10. Pizzi, A. (1994). *Advanced wood adhesives technology*. New York: Dekker.

11. Guigo, N., Mija, A., Vincent, L., Sbirrazzuoli, N. (2007). Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization. *Physical Chemistry Chemical Physics Pccp, 39*, 5359–5366. DOI 10.1039/b707950h.

12. Li, X., Nicollin, A., Pizzi, A., Zhou, X. J., Sauget, A. et al. (2013). Natural tannin-furanic thermosetting moulding plastics. *RSC Advances, 3*(39), 17732–17740. DOI 10.1039/c3ra43095b.

13. Zhou, X. J., Li, B., Xu, Y., Essawy, H., Wu, Z. G. et al. (2019). Tannin-furanic resin foam reinforced with cellulose nanofibers (CNF). *Industrial Crops and Products, 34*, 107–112. DOI 10.1016/j.indcrop.2019.03.052.

14. Celzard, A., Zhao, W., Pizzi, A., Fierro, V. (2010). Mechanical properties of tannin-based rigid foams undergoing compression. *Materials Science and Engineering: A, 527*(16–17), 4438–4446. DOI 10.1016/j.msea.2010.03.091.

15. Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Garcia, D. et al. (2013). Bioresourced pine tannin/furanic foams with glyoxal and glutaraldehyde. *Industrial Crops and Products, 45*, 401–405. DOI 10.1016/j.indcrop.2012.12.032.

16. Lacoste, C., Pizzi, A., Laborie, M. P., Celzard, A. (2014). Pinus pinaster tannin/furanic foams: part II. Physical properties. *Industrial Crops and Products, 61*, 531–536. DOI 10.1016/j.indcrop.2014.04.034.

17. Lagel, M. C., Zhang, J., Pizzi, A. (2015). Cutting and grinding wheels for angle grinders with a bioresin matrix. *Industrial Crops and Products, 67*, 264–269. DOI 10.1016/j.indcrop.2015.01.046.

18. Lagel, M. C., Pizzi, A., Basso, M. C., Abdalla, S. (2015). Development and characterization of abrasive grinding wheels with a tannin-furanic resins matrix. *Industrial Crops and Products, 65*, 343–348. DOI 10.1016/j.indcrop.2014.11.020.

19. Abdullah, U. H. B., Pizzi, A. (2013). Tannin-furfuryl alcohol wood panel adhesives without formaldehyde. *European Journal of Wood and Wood Products, 71*(1), 131–132. DOI 10.1007/s00107-012-0629-4.

20. Zhang, J., Xi, X. D., Liang, J. K., Pizzi, A., Du, G. B. et al. (2019). Tannin-based adhesive cross-linked by furfuryl alcohol-glyoxal and epoxy resins. *International Journal of Adhesion and Adhesives, 94*, 47–52. DOI 10.1016/j.ijadhad.2019.04.012.

21. Wu, Z. G., Lei, H., Cao, M., Xi, X. D., Liang, J. K. et al. (2016). Soy-based adhesive cross-linked by melamine-glyoxal and epoxy resin. *Journal of Adhesion Science and Technology, 19*, 1–10.

22. Zhang, J., Wang, W. L., Zhou, X. J., Liang, J. K., Du, G. B. et al. (2019). Lignin-based adhesive crosslinked by furfuryl alcohol–glyoxal and epoxy resins. *Nordic Pulp & Paper Research Journal, 34*(2), 228–238. DOI 10.1515/npprj-2018-0042.

23. Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Garcia, D. et al. (2013). Bioresourced pine tannin/furanic foams with glyoxal and glutaraldehyde. *Industrial Crops and Products, 45*, 401–405. DOI 10.1016/j.indcrop.2014.07.019.

24. Beckert, M., Menzel, M., Töll, F. J., Bruchmann, B., Müllhaupt, R. (2015). Nitrogenated graphene and carbon nanomaterials by carbonization of polyfurfuryl alcohol in the presence of urea and dicyandiamide. *Green Chemistry, 17*(2), 1032–1037. DOI 10.1039/C4GC01676A.
27. Zhang, J., Luo, H., Pizzi, A., Du, G. B., Deng, S. D. (2015). Preparation and characterization of grinding wheels based on a bioresin matrix and glass sand abrasives. *BioResources*, 3, 5369–5380.

28. Tondi, G., Pizzi, A., Pasch, H., Celzard, A. (2008). Structure degradation, conservation and rearrangement in the carbonisation of polyflavonoid tannin/furanic rigid foams–A MALDI-TOF investigation. *Polymer Degradation and Stability, 93*(5), 968–975. DOI 10.1016/j.polymdegradstab.2008.01.024.

29. Nasrazadani, S. (1997). The application of infrared spectroscopy to a study of phosphoric and tannic acids interactions with magnetite (Fe₃O₄), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). *Corrosion Science, 39*(10–11), 1845–1859. DOI 10.1016/S0010-938X(97)00060-7.

30. Pizzi, A., Tondi, G., Pasch, H., Celzard, A. (2008). Matrix-assisted laser desorption/ionization time-of-flight structure determination of complex thermoset networks: Polyflavonoid tannin-furanic rigid foams. *Journal of Applied Polymer Science, 110*(3), 1451–1456. DOI 10.1002/app.28545.

31. Tondi, G. (2017). Tannin-based copolymer resins: synthesis and characterization by solid state ¹³C NMR and FT-IR spectroscopy. *Polymers, 6*(1), 223–239. DOI 10.3390/polym9060223.

32. Nonaka, G. I., Nishioka, I., Nagasawa, T., Oura, H. (1981). Tannins and related compounds. I. Rhubarb (1). *Chemical & Pharmaceutical Bulletin, 29*(10), 2862–2870. DOI 10.1248/cpb.29.2862.