



Synthesis of micro carbonaceous material by pyrolysis of rubber wood and its effect on properties of urea-formaldehyde (UF) resin

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ABSTRACT

Micro sized carbonaceous materials were synthesized by pyrolysis of rubber wood fibers and their dispersion in urea formaldehyde (UF) was investigated. The carbonaceous material reinforced in UF has been prepared with a weight concentration up to 5%. The uniform dispersion of the carbonaceous material in the UF was achieved by mechanical stirring. All resin hybrids were characterized by solution rheology, Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffractometry (XRD) while the dispersion of carbonaceous materials was analyzed by scanning electron microscopy (SEM). FTIR spectroscopy results showed that carbonaceous materials can make hydrogen bonds with UF resins. The X-ray-based measurement of the crystallinity index (CrI) indicated that carbonaceous material increased the crystallinity of UF resin, whereas the maximum value of CrI was observed at UF-1 i.e., 85.7%. Curing reactions were examined with differential scanning calorimetry (DSC), and it was observed that the curing temperature of UF resin is affected by the addition of carbonaceous materials. Thermo-gravimetric analysis (TGA) revealed that carbonaceous materials have little effect on the thermal stability of the resin. Wood particleboards were fabricated and their performance was measured. The internal bonding strength and the modulus of rupture were measured for the particle boards, and a maximum at a 1% weight concentration was observed. The formaldehyde content of particle boards decreased with the addition of carbonaceous materials. At a 1% weight concentration, a maximum reduction of formaldehyde content was obtained using the perforator method.

1. Introduction

UF resins are, by and large, the most widely used resins because of their various positive aspects, e.g., low cost, non-combustibility, fast curing rate, and a light colour [1]. However, they also have some strong negative points, e.g., poor water-resistance and high formaldehyde discharge from the boards. However, in spite of this, UF resins are industrially vital resins, which have been used for interior grade composite wood items like particleboards, medium density fiberboards (MDF) and plywood. About 68% of the world's use of UF resin has been concerned with particle board and MDF manufacture, with about 23% employed by the plywood industry [2]. The chemistry that underlies UF

resin preparation is based on a series of multi-step reactions. The preparation of a UF resin starts with an addition reaction between formalin and urea under neutral or basic conditions [3]. A combination of mono, di, tri and tetra methylol ureas are formed in the addition reactions which then undergo condensation reactions under acidic conditions resulting in the formation of a cross-linked polymer network. UF resins are cured, ideally, under marginally acidic conditions at a temperature of around 95–130 °C.

Formaldehyde has been associated with human health problems in terms of both short and long term exposure. In 1992, the California Air Resource Board (CARB) perceived formaldehyde as a deadly air contaminant fundamentally in light of the assurance that it is a cancer-

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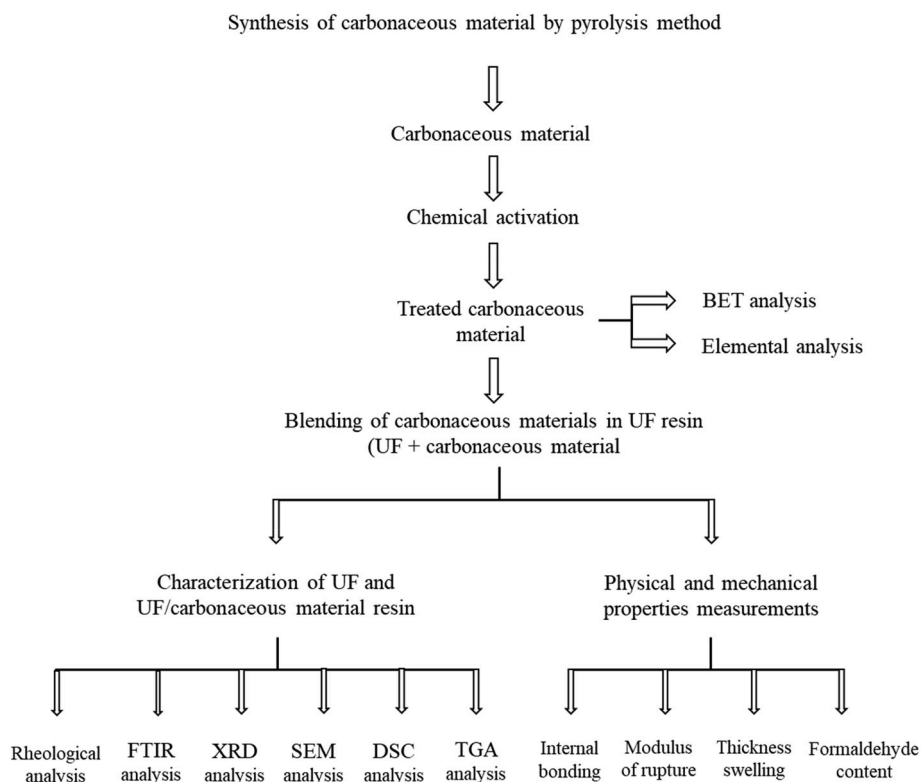


Fig. 1. Flow chart of the experimental process.

causing agent to humans with no known safe level of exposure [4]. Formaldehyde has been shown to promote non-cancerous conditions in humans, for instance, eye, nose, and throat aggravation, together with cancer health impacts. The International Agency for Research on Cancer (IARC) carried out an evaluation of formaldehyde which indicated that there was sufficient evidence that formaldehyde causes nasopharyngeal cancer in people [5].

A substantial amount of research has been done to upgrade the properties of UF resins, for example, high dimensional soundness under adversarial atmospheric situations of temperature and humidity. Nano-clay (aluminium layered silicates) incorporation in MUF resins has been utilized to enhance the properties of MUF resins thus leading to the impregnation of MUF/nano clay resins in the preparation of wood composites. The viscoelastic characteristics and storage modulus of MUF resins are likewise upgraded by the addition of nano-clay. The mechanical properties and dimensional stability of wood composites manufactured using this approach have additionally made significant strides in recent years [6–8].

Investigations into the incorporation of Na-montmorillonite (Na-MMT) in UF resins with a specific end goal of enhancing curing rate, producing a higher degree of cross-linking, in the end, resulting in enhanced the plywood properties have been conducted [9]. The impact of nano clay (Cloisite 30B) on the UF and MF (melamine formaldehyde) resin properties of storage modulus and obstruction properties upgraded by the adding of nano clays yet it defers the curing temperature of both UF and MF resins and furthermore doesn't significantly affect the properties of particleboard [10]. Investigations into the incorporation of nano crystalline cellulose in UF resins as filler have revealed that the addition of 1% of nano crystalline cellulose in a UF resin can diminish formaldehyde content by 13% and enhance bonding quality by up to 40% [11,12].

Yu et al. [13] considered the influence of nano calcium carbonate incorporation on the curing and bonding properties of a UF resin. The utilization of nano-SiO₂ as a filler in a UF resin reveals that formaldehyde content is diminished and the bonding strength of UF resin is increased

by the addition of nano-SiO₂ stacking in the UF resin. However, nano-SiO₂ addition was shown not to have any impact on the curing characteristics of the resin [14]. Zao studied the influence of low F/U molar ratios of a UF resin whilst including a nano-SiO₂ filler and observed that expansion of the nano-SiO₂ improves the formaldehyde content, curing behaviour and bonding strength [15]. The impact of aluminium oxide filler into a UF resin has further revealed decreases in formaldehyde content [16]. Carbon fibers were used as filler in medium density fiber (MDF) boards and the results obtained showed that the thermal stability of the composites based on carbon fibers were higher than the composites based on pure UF resin [17]. Multi-walled carbon nano-tubes (MWCNT) were utilized as nano-fillers in UF resins and it was observed that the curing kinetics and activation energy of UF resins were enhanced and the resin was capable of being cured at a lower temperature. In addition the formaldehyde content of fibreboard was reduced on account of the MWCNT-UF resins [18].

The properties of UF resins have been enhanced by the utilization of nano/micro scale organized fillers, for example, nano-clay, nano SiO₂, Na-MMT, MWCNT's and Al₂O₃. On the other hand, the addition of NaMMT, MWCNT, and nano-clay has have been shown to decrease the curing time of UF resins. But the industrial feasibility of these is somewhat poor and there is a critical requirement for an industrially feasible filler material.

Amongst the high cost materials like nano clay, nano SiO₂, Na-MMT, MWCNT's and Al₂O₃ which have been used as filler to improve UF resin properties, the carbonaceous material from rubber wood fibre is the most promising material as it is by far the most abundant and inexpensive woody biomass available. Carbon has been a raw material for several thousands of industrial products and their production from various bioresources is an active area of research [19,20]. In the present work we synthesized micro sized carbonaceous material from rubber wood fibres which are highly conducting and economically viable as a reinforcing agent and assessed its effect on a UF resin. The structural, morphological and thermal properties of a UF resin with carbonaceous materials were studied using FTIR, XRD, SEM, TGA and DSC. These

carbonaceous materials have been used as fillers in order to improve the properties of UF resins such as curing time, cross-link density and can improve the mechanical strength of particle boards and also reduce formaldehyde emission from the panels. The formaldehyde content from the boards was investigated by the perforator method.

2. Materials and methods

2.1. Materials

The urea-formaldehyde (UF) resin used was obtained from Dynea Malaysia Sdn. Bhd. The viscosity of the resin at 30 °C was 170 cP, pH 8.27, density 1.286 kg/m³ and gel time at 100 °C was 36 s. The fresh rubber wood fibres used for the experiments was acquired from Robin Resources Malaysia Sdn. Bhd. The mixed tropical wood fine and coarse particles were acquired from Mieco Chipboard Berhad, Malaysia.

2.2. Process of preparation of carbonaceous materials

2.2.1. Physical activation

The pyrolysis of rubber wood fibre was done in a glass furnace in an inert condition at 350–500 °C for 4 h under a constant flow rate of N₂ (250 ml/min). The carbonized wood fibres were cooled to room temperature in the same inert environment.

2.2.2. Chemical activation

The chemical activation of carbonized fibres was done with phosphoric acid (H₃PO₄) and the solution of H₃PO₄/carbonized fibres was heated at 500 °C for 3 h in a furnace with a constant flow rate of N₂ (250 ml/min) followed by to room temperature. Next, the dry mixture of activated carbon was washed with distilled water until a neutral pH was obtained. At that point, the solid particles were sifted and dried for 24 h at 105 °C, and activated carbon was acquired.

The carbonized fibres were then grinded in a Retsch Chemical Grinder ZM 200 at 18000 rpm and afterwards sieved out utilizing U.S. standard no. 80.

2.3. Experimental set-up

Fig. 1 shows the flow diagram for the experimental setup which consists of the synthesis of carbonaceous material by pyrolysis of wood fibers. The analysis of carbonaceous materials was carried out by elemental and BET analysis. Afterwards, the carbonaceous material was mixed with the UF resin and then investigated for viscoelastic properties and curing behavior by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis, while the thermal stability of the cured resin was investigated by thermogravimetric analysis (TGA). The chemical interaction/bonding between carbonaceous material and UF matrix resin was studied by Fourier transform infrared spectroscopy (FTIR), and finally, the morphology and the bonding between the UF and carbonaceous material resins were studied by scanning electron microscope (SEM) analysis. In addition, the measurement of physical and mechanical properties such as modulus of rupture (MOR) and internal bond (IB) strength, formaldehyde content and thickness swelling were also carried out and analyzed.

2.4. Elemental analysis system (CHNOS analyser)

The total carbon, hydrogen, nitrogen, oxygen and sulphur contents were determined using an elemental analyzer (Varo Macro Cube, S/N-2012/1005 made in Germany), by simple combustion process CHNOS analysis.

2.5. Brunauer-Emmett-Teller (BET) measurement

In this study, the BET measurements on carbonaceous material

samples were conducted using a Quanta chrome Nova 1200 with N₂ as the adsorbent at liquid nitrogen temperature. Before carrying out the measurement of the specific surface area of the sample, it was necessary to remove any gases and vapors that may have become physically adsorbed onto the surface. If the out-gassing is not achieved, the specific surface area may be reduced. The out-gassing conditions are critical for obtaining the required precision and accuracy.

2.6. Preparation of UF/carbonaceous material resins

Carbonaceous materials were mixed with UF resin at levels of 1, 2.5, 3.5 and 5% (w/w) and are, here-in-after, indicated with pure UF resin as UF-0, UF resin with 1 wt% carbonaceous material as UF-1, UF resin with 2.5 wt% carbonaceous material as UF-2.5, UF resin with 3.5 wt% carbonaceous material as UF-3.5 and UF resin with 5 wt% carbonaceous materials as UF-5. To obtain uniform dispersion, mechanical stirring with a Heidolph model RZR 2041 was performed for 30 min at 2000 rpm combined with ultrasonic treatment. The reason for mixing the carbonaceous material in UF resin is to improve the properties of the UF resin and to uniformly distribute the carbon particles on the board. Carbonaceous materials will decrease the curing temperature of the UF resin and will also enhance impregnation of the UF/carbonaceous material resin on the particle board. Earlier researchers have studied the use of nano clay (aluminium layered silicates) in MUF resins to improve the properties of MUF resin and in turn impregnate the MUF/nano clay resin in wood composite [6,7,21]. Nano clay decreases the curing temperature of MUF resins. For this reason, a method was developed to mix carbonaceous materials directly with resin. It was easy to mix with the resin and particles were distributed much more uniformly. The pure UF resin sample was given the name UF-0, while the mixtures were named UF-1, UF-2.5, UF-3.5 and UF-5, respectively.

2.7. Characterization methods

2.7.1. Rheological measurement

The viscosity of the UF resin and the UF/carbonaceous materials were estimated using a Brookfield digital DV-III ULTRA rheometer (Brookfield Engineering Laboratories, USA) at 50 rpm and 25 °C with spindle number 31.

2.7.2. FTIR spectroscopy

FTIR spectroscopy in transmittance mode was utilized to describe the functional groups of the resin. The pre-cured resin and samples were mixed with KBr and made into pellets to determine the bond formation. The FTIR transmittance spectra were obtained with a Spectrum 1000 PerkinElmer spectrometer in the spectral area of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹ and 50 scans.

2.7.3. Scanning electron microscopy (SEM)

SEM analysis was carried out on an EVO 50 (ZEISS, USA) instrument to examine the surface morphology of the UF/carbonaceous material resins with samples mounted on an aluminium stub utilizing carbon tape. Specimens were coated with silver paint to minimise charging effects. The samples were covered with Pt-Pd by a sputter coater.

2.7.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was conducted on both UF resins comprising carbonaceous materials and on the neat resin. X-ray diffraction (XRD) was done in a XRD analyzer and the samples were examined at 2θ ranges of 3–80° at a rate of 1 deg/min. The generator was operated at Cu/30 kV/15 mA. The inter layer spacing (d002) of the carbonaceous materials was ascertained as per the Bragg equation: $2d \sin\theta = \lambda$.

The crystallinity index (CrI) was computed from Equation (1) according to the technique recommended [22].

$$\text{Crystallinity Index (Crl)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

Where Crl is the crystallinity index, I_{002} is the intensity of the diffraction from the 002 plane at $2\theta = 22.60^\circ$ and I_{am} is the intensity of the background scatter estimated at $2\theta = 18.70^\circ$

2.7.5. Differential scanning calorimetry (DSC)

DSC analysis was conducted to assess the nature of the hardening rate of UF resins comprising carbonaceous materials and their correlation with UF resin. This was carried out in a Q 1000–0567 DSC calorimeter and a TA Universal Analysis 2000 programme were utilized to analyze the data. Samples of 6 mg were placed on high-pressure aluminium crucibles. The samples were heated from 30 to 250 °C in an inert atmosphere of nitrogen maintained at a flow rate of 50 ml/min, with an identical empty crucible utilized as a source of perspective in the measurement process. The heating rates utilized were 10 °C/min to acquire the exothermic curing reaction curves.

2.7.6. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) of the UF resin and UF resins comprising different weight percentages of carbonaceous material was carried out by non-isothermal thermo-gravimetric analysis (TG, DTA) using a TA Instruments equipment. Tests (6 ± 0.2 mg) were placed in alumina crucibles. A blank alumina crucible was utilized as a reference. The samples were heated from 30 to 600 °C at a heating rate of 10 °C/min with a constant flow of N_2 of 50 ml/min.

2.8. Preparation of wood particleboard panels

The standard methodology of ASTM D1037 was followed to fabricate 250 mm x 250 mm x 9 mm wood particleboards with a target density of 800 kg/m³. A sum of 450 g of wood particles containing both coarse and fine particles with 60:40 ratios respectively at 12% moisture content were utilized to make particleboards. A rotating drum blender was utilized to consistently mix the wood particles alongside UF/carbonaceous material resin. The drum comprised of steel dowels organized in a crisscross pattern, which was expected to encourage tumbling and blending with a rotation speed of 18 rpm. The carbonaceous materials with different weight concentrations (1%, 2.5%, 3.5%, and 5%) mixed with 10% UF resin (all concentrations were calculated by weight of wood particles) were sprayed with a spray gun on the wood particles. A loose mat of 250 x 250 mm was prepared with resin sprayed wood particles, which were then pre-squeezed at 5 MPa pressure. Finally, the pre-pressed panels were hot-pressed at 180 °C for 270 s with an objective thickness of 9 mm. Except for the carbonaceous material concentration, all other parameters, for example, UF resin loading, particle moisture, pressing time and platen temperature, were kept the same in all experiments.

The boards were conditioned at a relative humidity of $65 \pm 5\%$ and a temperature of 25 °C to accomplish a uniform moisture content in the boards. The boards were then trimmed from each of the four sides, and standard samples of $250 \times 50 \times 9$ mm³ for modulus of rupture (MOR), $50 \times 50 \times 9$ mm³ for internal bonding strength (IB), and $50 \times 50 \times 9$ mm³ for thickness swelling (TS) were prepared. Ten samples were prepared from each treatment to analyze MOR, IB, and TS.

2.9. Mechanical properties measurements

The boards were tested according to ASTM standards. The mechanical properties i.e., modulus of rupture (MOR) and internal bonding (IB) were measured according to ASTM D 1037. The mechanical properties of the samples were performed on a Shimadzu UTM AG-X plug series machine, and the results were analyzed by Trapezium X-software. A total of 10 samples for MOR and 10 samples for IB were tested for the final result analysis. Equations [2,3] were used to calculate the MOR and

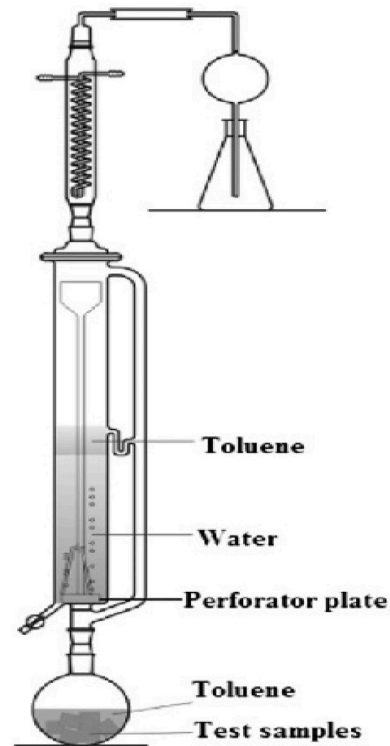


Fig. 2. The perforator apparatus.

IB, respectively.

$$\text{MOR (N/mm}^2\text{)} = 3 \times P \times L / 2 \times b \times d^2 \quad (2)$$

where P is the breaking load, L is the distance between knife edges on which the sample was supported, b is the average specimen breadth, and d is the average specimen depth.

$$\text{IB (N/mm}^2\text{)} = F/A \quad (3)$$

where F is the maximum force calculated over the entire area and A is the surface area of the specimen.

2.10. Dimensional stability tests

The thickness swelling (TS) tests were conducted in accordance with ASTM D 1037. Before testing, the weights and dimensions of the specimens, i.e., length, width, and thickness, were estimated. The samples of each kind were soaked in water at room temperature for 24 h and the samples were removed from the water, patted dry with tissue paper and measured again. Each assessment obtained represents an average from several samples.

Estimates of thickness swelling (TS) in percentages were computed utilizing equation (4):

$$\text{TS (\%)} = (T_2 - T_1) \times 100 / T_1 \quad (4)$$

where T_1 is the initial thickness of the sample and T_2 is the thickness of the wetted sample.

2.11. Formaldehyde content testing

The formaldehyde content of the particle board panels was estimated using the EN-120 (1992) standard, also called the perforator method as shown in Fig. 2.

The main principle behind this approach is to extract the formaldehyde from test pieces by boiling toluene and then transferring it into distilled water. Formaldehyde trapped by water was then quantitatively

Table 1

Synthesis parameters, chemical elemental analysis and product yields for chemically treated carbonaceous materials synthesized by pyrolysis method. In general, pyrolysis decomposed the raw materials and produced purer carbon products.

Synthesis Conditions			Chemical Composition					
Sample	Temperature (°C)	Time (Hours)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	*O (wt%)	Yield (%)
Rubber Wood Fiber	Raw (0)	0	45.28	6.75	0.56	0.017	47.39	100
	350	1	65.58	4.67	0.61	0.178	28.96	44.34
	350	2	68.32	4.54	0.62	0.182	26.34	41.28
	350	3	71.42	3.88	0.63	0.190	23.88	36.78
	350	4	73.56	3.61	0.64	0.195	21.99	33.23
	400	1	69.4	4.22	0.628	0.186	25.56	40.20
	400	2	72.3	3.73	0.63	0.189	23.15	34.98
	400	3	74.01	3.62	0.65	0.197	21.52	31.16
	400	4	74.8	3.56	0.66	0.201	20.78	29.86
	450	1	72	3.74	0.64	0.188	23.43	35.3
	450	2	74.09	3.63	0.65	0.198	21.43	30.56
	450	3	74.9	3.46	0.66	0.206	20.77	29.20
	450	4	75.4	3.32	0.68	0.216	20.38	27.80
	500	1	74.68	3.53	0.66	0.199	20.92	30.72
	500	2	75.3	3.34	0.67	0.212	20.48	27.90
	500	3	75.9	3.30	0.69	0.218	19.89	26.20
	500	4	76.22	3.122	0.71	0.222	19.726	22

determined using a UV spectrophotometer after treatment with acetyl acetone and ammonium acetyl methods.

Extraction of formaldehyde was performed using the perforator set-up, and the samples were cut from the centre of the panel. Square samples (25 mm by 25 mm) were used for production purposes. The samples were weighed to an accuracy of 0.1% on a watch glass and dried in an oven at a temperature of 103 ± 2 °C until a constant mass was achieved (approximately 12 h). The test was conducted in the R & D laboratory of Robin Resources (Malaysia) Sdn Bhd.

3. Results and discussion

3.1. Elemental composition of carbon materials

The carbon materials were determined from their elemental analysis, such as carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulphur (S). These elements are found in ligno-cellulosic materials; therefore, measurement of these elements is able to show the effect of pyrolysis on the sample. This method has been applied widely in the carbon material characterization procedure where an elemental analyzer is used [23].

The percentage of the elements of the bio carbons processed at different operating temperatures (350–500 °C), over times of 1–4 h were analyzed and the results are as listed in Table 1.

The values of CHNOS are shown in Table 1 after being operated at temperatures of 350–500 °C for 1–4 h, which gives a clear view of the transformation trends. The carbon content increases with an increase of temperature. The value of oxygen decreased when the temperature was raised from 350–500 °C. In addition, the value of hydrogen shows a slightly decreasing trend, while nitrogen and sulphur display an increasing trend. Carbonization of this complex mixture is accompanied by an experimental mass loss as seen in Table 1. With a change in reaction temperature, the effect on mass yield is significant. The theoretical carbonization mass loss for the pure rubber wood fiber (100%) at 500 °C for 4 h was 22%. The maximum value of carbon, i.e., 76.22% is obtained at 500 °C after 4 h. Therefore; this carbonaceous material was used for further study as filler in the UF resin and also for the preparation of particle boards.

3.2. Brunauer-Emmett-Teller (BET) measurement

The surface properties of the carbonaceous material used in this work were studied by a gas adsorption technique. Fine details of the porous texture can be deduced from the shape of the N₂ adsorption-desorption isotherms. The surface properties of the carbonaceous

Table 2

Surface properties of carbonaceous materials synthesized by the pyrolysis method.

Material	Temperature (°C)	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
Carbonaceous Material	350	9.6262	0.0243
	400	10.014	0.0238
	450	10.612	0.0233
	500	10.632	0.0231

Table 3

Rheological properties of the UF and UF/carbonaceous materials resin.

Adhesive	Solid Content %	Viscosity (cP)	pH
UF-0	65.0%	178	8.7
UF-1	66%	196.5	8.28
UF-2.5	67.5%	252.5	8.1
UF-3.5	68.5%	339.6	7.9
UF-5	70%	404	7.5

materials as synthesized are shown in Table 2. The surface area values and pore volumes of the carbonaceous materials at 350, 400, 450 and 500 °C are nearly the same for all samples because of the similarity of the synthetic procedures and materials. The measured BET surface area of the carbonaceous material was ~ 10 m² g⁻¹ with a pore volume of ~ 0.0238 cm³ g⁻¹. The observed relatively lower surface area is partly due to the dense nature of the particles and their packing, which results in a reduced porosity.

3.3. Characterization of resin interactions with carbonaceous materials

3.3.1. Rheological properties

The rheological properties of UF and UF/carbonaceous material resins are summarized in Table 3. The solid content of the solution was calculated using the oven dry method.

The pure UF resin (UF-0) exhibits a low viscosity because of the low solid content. When the carbonaceous material is increased to 5 wt%, the solid content of resins and their viscosities are also increased from 178 cP (UF-0 resin) to 404 Cp (UF-5), however, the pH decreases with the addition of carbonaceous material. The pH of the resin influences the wood adhesion and the variations in the pH of the resin and its components affects activity and properties of the resin. Too high a pH causes the resin to cure slowly and too low a pH causes it to cure too fast.

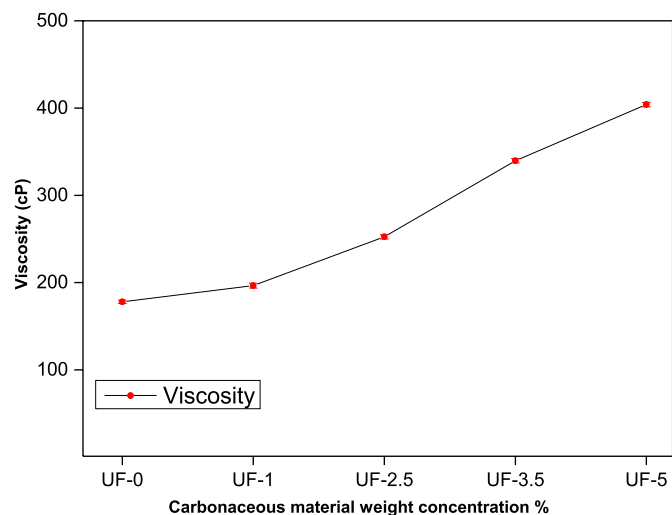


Fig. 3. Viscosity of UF resin as a function of different weight percentage of carbonaceous material in UF resin.

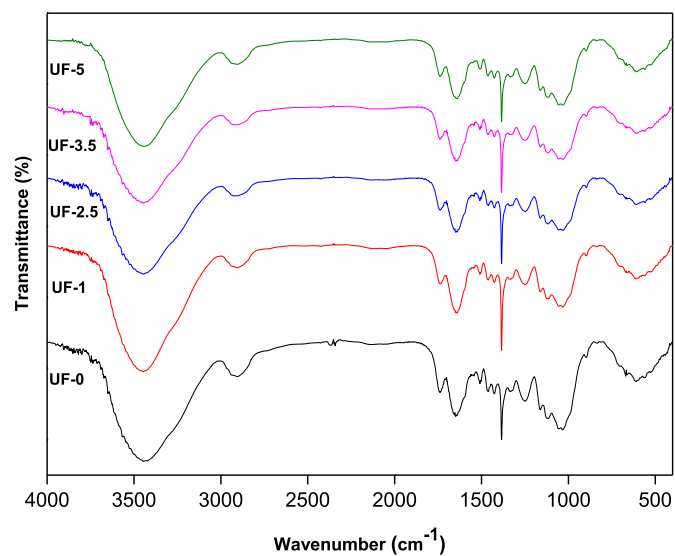


Fig. 4. FTIR spectra of pure UF resin and UF carbonaceous material resins.

Table 4

FTIR peaks observed for UF resin and UF carbonaceous material resins samples.

Wavenumbers/cm ⁻¹					Functional group	Explanation
UF-0	UF-1	UF-2.5	UF-3.5	UF-5		
3429	3452	3458	3460	3461	(NH) 2° amine & OH	The spectrum of UF/carbonaceous material resins shows strong absorption band between 3452–3461 cm ⁻¹ region and 3429 cm ⁻¹ for pure sample. The methylenization reaction happen during cross-linking.
1642.0	1649.1	1640.0	1640.0	1642.8	(C=O) in -CONH ₂ (amide I)	These peaks are assigned to the stretching C=O of amide-I in CONH ₂
1508.6	1509.0	1509.7	1509.18	1509.1	(NH) in NH-CO in 2° amine (amide II)	The strong absorption bands to the -NH (amide-II)
1459.3	1459.1	1459.1	1462.9	1462.9	CH- deformation; Asymmetric in -CH ₃ -and -CH ₂ -	The multiple peaks at 1450–1470 cm ⁻¹ might be attributed to C-H bending vibrations of the CH ₂ -N group.
1385.5	1380.0	1384.5	1383.4	1384.3	(CH) in CH ₂ /CH ₂ OH/ N-CH ₂ -N	The smaller peaks in the region of 1350–1450 cm ⁻¹ represent by the C-H bending mode in CH ₂ /CH ₂ OH/N-CH ₂ -N.
1247.9	1249.1	1248.1	1249.1	1250.9	(C-C-O)	The strong and broad peak at 1247 cm ⁻¹ is assigned to C-N extending vibrations of amide II
1115.7	1161.9	1161.1	1162.7	1162.7	(N-CH ₂ -N), ν(C-O-C) of ether linkage	The 1115 cm ⁻¹ top is ascribed to both the asymmetric stretch of N-CHO-N and the asymmetric stretch of -C-O-C- of ether linkages
1032.2	1031.7	1032.7	1033.7	1034.2	(H-N-H-CH ₂ -CH ₃) 1° amine	The strong 1032 cm ⁻¹ peak is due to the C-O stretching mode of the CH-OH
609.8	608.4	608.23	608.6	608.6	(-CH)	The weak small peak at 600–650 cm ⁻¹ ascribed the -CH bending mode

The viscosity of the resin is an important parameter in the manufacturing of composite wood products. The resin should possess free spray-ability over wood particles. The viscosity of the modified resin shows an increasing trend with an increasing weight percentage of carbon. The internal friction of a moving fluid resists motion because of its molecular makeup, which increases internal friction as shown in Fig. 3. A fluid having a low viscosity flows easily because its molecular makeup results in much less friction when it is in motion.

3.3.2. FTIR analysis

UF resins are poly (methylene ether hydroxymethylureas) formed by the condensation reaction of urea with a liquid form of formaldehyde. Carbonaceous materials have free surface carbon, hydrogen and nitrogen, which react with macromolecular end groups and mostly with hydroxyl groups by means of condensation reactions [24]. 1,3-bis-hydroxymethyl urea (dimethylolurea) is formed amid the initial step of an addition reaction amongst urea and formaldehyde, which has 2 hydroxyl groups and could interact with carbon and frame a C-OH extending mode. To check this amid the development of UF/carbonaceous materials resins, all samples were examined with FTIR spectroscopy, and the recorded spectra are displayed in Fig. 4.

Amid the curing procedure, a three-dimensional system is formed and this procedure is irreversible and brings about an insoluble resin. Owing to the intricacy of the polymer structure, numerous and broad peaks in the pure UF resin (UF-0) spectra are shaped. The FTIR peaks observed for the UF resin and UF resin with carbonaceous materials are listed in Table 4.

The broad peak at 3429–3461 cm⁻¹ can be accredited to the hydrogen bonded O-H and N-H in the spectrum of the UF resin. The broad nature of this band might be assigned to monomers, for example, water and formaldehyde, whose O-H groups may form hydrogen bonds with reactive functional groups, for example, CH₂OH, NH₂, and NH [25]. It is vital to mention that the free -NH₂ group has a typical peak at 3452 cm⁻¹. The strong absorption band is observed in the spectra between 1600–1650 cm⁻¹ are assigned to stretching C=O (amide-I) in -CONH₂ group. These peaks are assigned to CO extension of amide I and II, and the -N-H scissors of amide I. The overlapped peaks in the zone 1500–1650 cm⁻¹ are attributed to the -N-H bending vibrations of amide II. The multiple peaks at 1450–1470 cm⁻¹ might be attributed to C-H bending vibrations of the CH₂-N group, while smaller peaks in the region of 1320–1450 cm⁻¹ can be assigned to extending C-N vibrations of amide I and II, while it has additionally been assigned to C-H extending and -O-H bending vibrations of alcohol [26]. The strong and broad peak at 1247 cm⁻¹ is assigned to C-N extending vibrations of amide II [27].

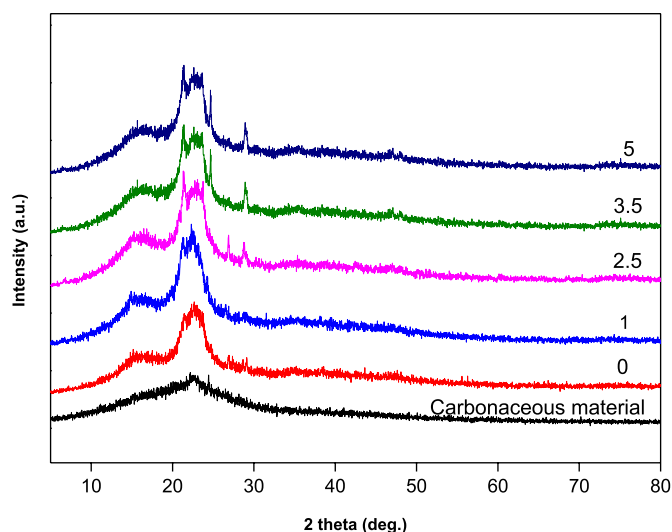


Fig. 5. XRD patterns of carbonaceous material, pure UF resin and UF resin with different carbonaceous materials.

Table 5

XRD data results of UF and UF/carbonaceous material resins.

Samples	2-theta (deg)	Crystallinity Index (CrI) %
UF-0	22.57	74.9
UF-1	22.37	85.7
UF-2.5	21.43	77.0
UF-3.5	21.50	76.4
UF-5	21.51	72.5

The 1115 cm^{-1} top is ascribed to both the asymmetric stretch of N-CHO-N and the asymmetric stretch of -C-O-C- of ether linkages [28]. The strong 1032 cm^{-1} peak is due to the C-O stretching mode of the CH-OH, lastly, the weak small peak at $600\text{--}650\text{ cm}^{-1}$ can be ascribed to the -CH bending mode.

3.3.3. XRD analysis

The X-ray diffraction profiles of the carbonaceous material, pure UF resin (UF-0) and UF/carbonaceous material resin compositions are presented in Fig. 5.

The carbon treated with phosphoric acid had a sharp peak at 2θ values of 22.7° from the 120 plane. The peak at a 2θ value of 22.7° , typical of carbon materials, is observed in the XRD pattern. Interestingly, only the diffraction peaks typical of carbon were seen in the XRD pattern and no indication of impurities were observed. This indicates the effectiveness and also the significance of the phosphoric acid (H_3PO_4) treatment. The UF resin with 1 wt% carbonaceous material (UF-1) exhibits a sharp peak of 22.57° compared with the pure UF resin which demonstrates a broader and weaker peak at 22.37° as shown in Fig. 5. The crystallinity index (CrI) of the cured UF resin is lower compared with that of the UF resin with 1 wt% carbonaceous material. The stronger peak of the cured UF resin with 1 wt% carbonaceous material resin compared to pure UF resin can be in all probability attributed to the higher degree of order of the as-developed micro- carbonaceous material in the UF resin than in the pure UF resin. The crystalline regions of the cured UF resin are fundamentally impacted by the presence of micro/nano materials as reported in previous research [22].

It can be seen from Table 5 that unlike UF-1, the CrI reduced with the addition of carbonaceous materials, as can be seen in UF-2.5, UF-3.5 and UF-5. This can be attributed to the existence of a cross-linked structure in the UF/carbonaceous material resins, which promotes agglomeration in these resin compositions. The reduction in the CrI implies that the percentage of the amorphous regions in the UF/carbonaceous material resins increased. A higher CrI of the UF resin can be accomplished by the addition of a small amount of carbonaceous material in light of the fact that as the carbonaceous material is increased the CrI is decreasing. The lowest CrI is found in UF-5 as listed in Table 5.

3.3.4. Scanning electron microscopy (SEM) analysis

SEM is an efficient medium for the morphological analysis of a polymer matrix.

Fig. 6(a) relates to the UF resin with 1 wt% carbonaceous material (UF-1), which demonstrates good interaction and the dispersion between the UF resin and the carbonaceous material. Fig. 6(b) illustrates the UF resin with 5 wt% of carbonaceous material (UF-5), where it is clearly seen that agglomeration of the carbonaceous material has occurred. In other words, at the higher loadings of carbonaceous material, enhanced tendencies towards agglomeration occurs.

3.3.5. Effect of carbonaceous materials on resin cure behavior

DSC examination was utilized to assess the cure characteristics of the unmodified UF resin (UF-0) and the UF/carbonaceous materials. In Fig. 7, the DSC curves of all samples for a heating rate of $10^\circ\text{C}/\text{min}$ are

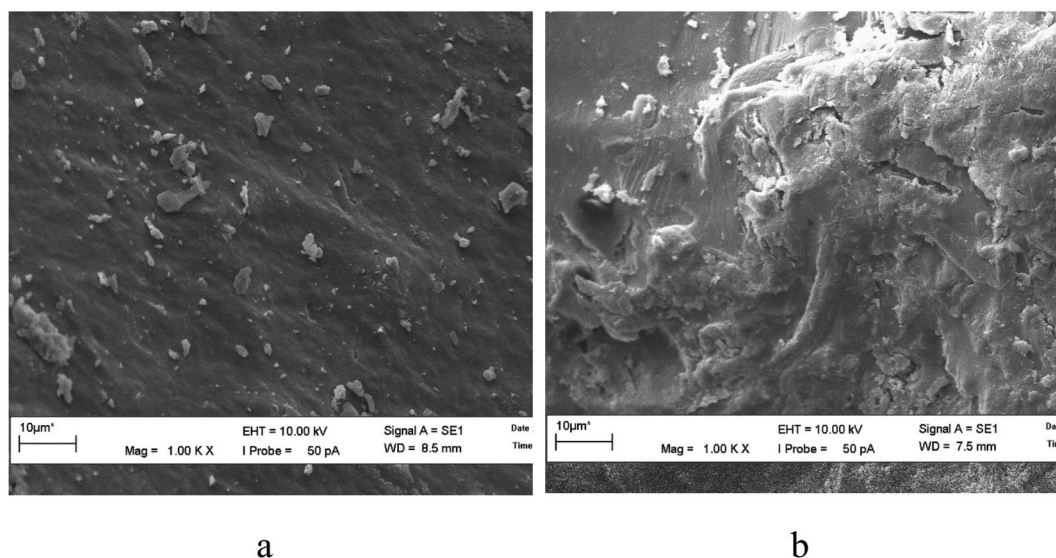


Fig. 6. SEM micrographs of the surfaces of the UF resin (a) with 1 wt% carbonaceous material (b) with 5 wt% carbonaceous material.

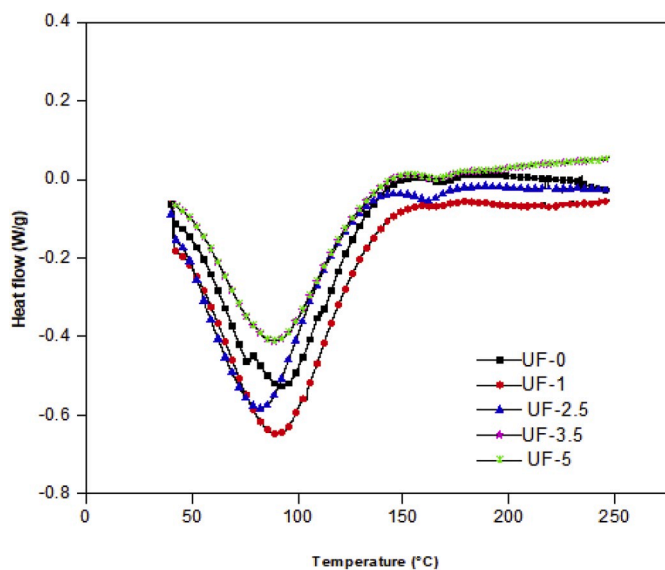


Fig. 7. DSC curves of UF-0, UF-1, UF-2.5, UF-3.5 and UF-5 for a heating rate of 10 °C/min.

Table 6
Thermal properties UF resin and UF resin containing carbonaceous materials.

Sample	Start °C	Onset (T_o) °C	Maximum (T_p) °C	ΔT (T_p-T_o) °C	Stop °C
UF-0	50.0	60.8	92.4	31.6	168.5
UF-1	50.0	69.1	99.6	30.5	165.2
UF-2.5	50.0	67.3	92.6	25.3	162.8
UF-3.5	50.0	69.5	97.8	28.3	165.3
UF-5	50.0	69.7	98.8	29.2	167.3

shown.

It is observed that all resins display a similar curing pattern. On account of pure UF resin i.e., UF-0, the maximum peak temperature is recorded at 92.39 °C, while in the samples comprising UF/carbonaceous materials, the peaks are marginally moved to higher temperatures, i.e., 99.6, 92.6, 97.8 and 98.8 for UF-1, UF-2.5, UF-3.5 and UF-5 respectively. In spite of the fact that the increases are small, this suggests that the carbonaceous materials impede the UF resin cross-linking reactions. A likely cause may be that the carbonaceous materials interact with the polymer chains, potentially by forming bonds or by taking part in the condensation reactions which occur on resin cure. Therefore, in both cases, the polymer chain needs more vitality to crosslink.

DSC was utilized to examine the changes in properties of pure UF resin (UF-0) in comparison to UF/carbonaceous material resins (UF-1, UF-2.5, UF-3.5, and UF-5). In Table 6, the onset temperature (T_o), and maximum temperature (T_p) are presented, which was spontaneously generated by the TA universal analysis software and the rate of curing (ΔT) was calculated from the maximum temperature (T_p) minus the onset temperature (T_o).

From Table 6, it can be seen that in the samples comprising the carbonaceous materials, curing started late and achieved a peak faster than for the unmodified UF resin. The ΔT value is 31.6 °C for UF-0 it declines to 30.5 °C, 25.3 °C, 28.3 °C and 29.2 °C for UF-1, UF-2.5, UF-3.5 and UF-5, respectively. The higher value of ΔT for the unmodified UF resin demonstrates a lower rate of curing, though for the samples comprising the carbonaceous materials, curing started at a higher temperature however achieved its peak faster. Therefore, it is presumed that UF containing carbonaceous materials had a higher rate of curing. The higher onset temperature of the UF/carbonaceous materials show greater activation energies for the initiation of curing, and, following

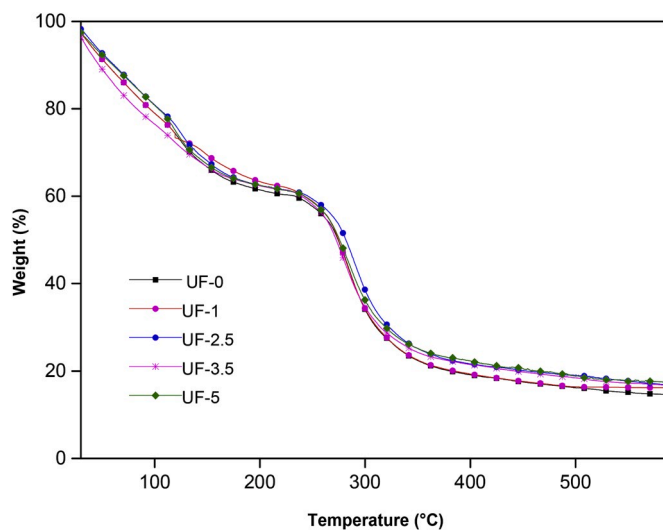


Fig. 8. TG curves of all samples: UF-0, UF-1, UF-2.5, UF-3.5, and UF-5 with a heating rate of 10 °C/min.

Table 7
TGA properties observed for UF resin and UF resin containing carbonaceous materials.

Samples	Char yield at different temperatures (%)						T_{max} (°C)
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	
UF-0	75.8	63.4	34.9	19.4	16.4	8.6	260
UF-1%	79.5	61.6	35.1	19.2	16.2	14.5	270
UF-2.5%	80.5	62.3	37.6	21.6	18.9	16.5	270
UF-3.5%	77.8	62.8	37.3	21.7	18.6	16.8	270
UF-5%	81.4	62.7	37.3	22.4	18.9	17.3	270

initiation, the curing process progressed at a very high rate.

3.3.6. Effect of carbonaceous materials on the thermal stability of the resins

In Fig. 8, the TG curves for all five samples are presented. Previous work has shown that the incorporation of carbonaceous materials into organic polymers can lead to improved levels of thermal stability [29, 30]. This was also expected in the present study, and thermogravimetric analysis was employed to evaluate this.

From Fig. 8, it is clear that the TG curves can be divided into two degradation steps [31]. The first is related to the evaporation of moisture from all the samples between 50 and 100 °C. A slow formaldehyde emission at temperatures of 100–200 °C also occurs, but it is too low to be counted as significant. Above 200 °C, the second degradation step is apparent which begins with chain scission reactions and the radicals formed actuate the development of cyclic structures in the polymer chains [32]. This process brings about substantial polymer crumbling. Degradation of cured resin starts with the release of formaldehyde from dimethylene ether groups [28]. The maximum degradation rate happens when the methylene ether linkages deconstruct [33]. Contrasting the weight loss curves of all examples over 200 °C; it can be found in Table 7 that the samples comprising carbonaceous materials have little impact on the thermal stability of the resin.

With such a small deviation in the TG curves, it is very difficult to study the effect of carbonaceous materials on the thermal stability of a UF resin. Thermal stability shows a positive correlation with carbonaceous material content, which increases when carbonaceous materials increase from UF-0 to UF-5. Carbonaceous materials have a tendency to restrict the emission of decomposition products. In any case, this can't

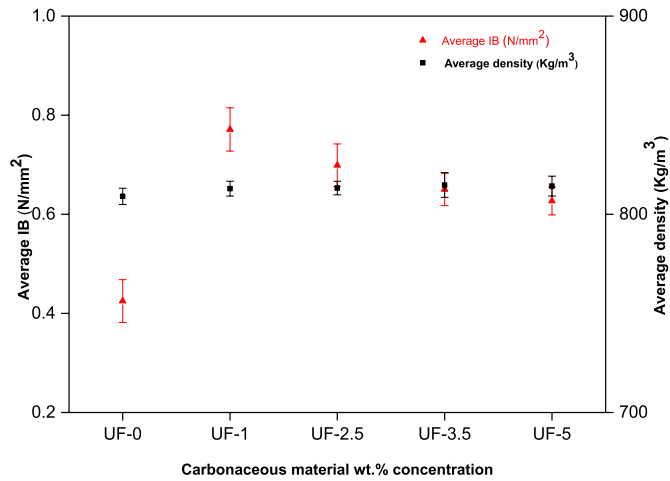


Fig. 9. A comparison of the internal bonding strength of different types of board.

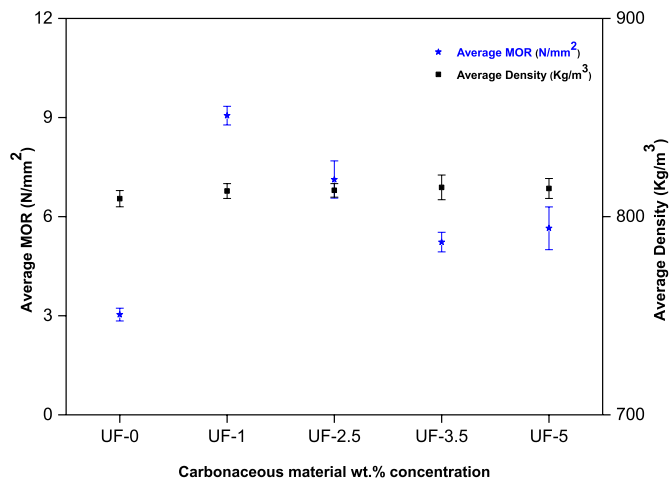


Fig. 10. Comparison of modulus of rupture (MOR) between control particle board and particle boards with different carbonaceous material loadings.

be affirmed from this investigation in light of the fact that there is no distinct thermal stabilization of the framework. This could be because of inadequate filler distribution caused by the decision to use mechanical stirring as research practice and furthermore in light of the fact that the amount of the carbonaceous materials utilized was small (maximum 5 wt%). Besides, carbonaceous materials are thermally stable at temperatures up to 600 °C [34], which results in increased levels of char yield at the higher carbonaceous material concentrations.

3.4. Mechanical testing

3.4.1. Internal bonding (IB)

The term internal bonding (IB) represents the strength of the bonding of the UF resin crosslink network with wood particles after hot pressing to form panels. Fig. 9 shows internal bonding values of particle board panel specimens manufactured using unmodified UF resin and UF/carbonaceous material combinations.

The IB of the particle boards were enhanced significantly by the carbonaceous materials. The bonding strength outcomes demonstrated that the composites containing 1 wt% showed the highest IB strength, i. e., 0.7711 in contrast with other samples. This could be because of better bonding between the matrix (urea formaldehyde and carbonaceous materials) and wood particles, which causes tension concentration in the particle boards. It is seen from Fig. 9 that unlike 1 wt% of carbonaceous

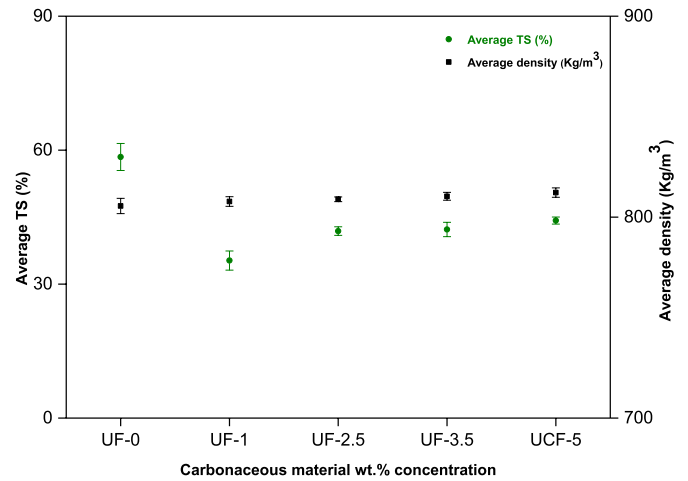


Fig. 11. The thickness swelling of particle board panels with different weight percentages of carbonaceous materials.

materials, the IB strength reduced with the increasing concentration of carbonaceous materials at 2.5 wt%, 3.5 wt% and 5 wt%. This decrease in bonding strength can be linked to an increase in the probability of agglomeration, which can result in stress concentrations that require less energy to propagate cracks. This is predictable with the outcomes reported by most researchers [35–37]. Overall, the results of the IB strength tests demonstrated that the particle board, which contains 1 wt % carbonaceous material, had the most elevated bonding strength value.

3.4.2. Modulus of rupture (MOR)

Fig. 10 shows the modulus of rupture (MOR) of particle board panels. The MOR of the panels improved significantly using carbonaceous materials. Carbonaceous materials improved the stiffness of UF resin, which is why the MOR of the particle board panels improves. In Fig. 10, the average values of MOR at different percentages of carbonaceous materials are shown.

This outcome agrees with the general perception that the addition of micro/nano-sized particles into the polymer matrix increases strength. The improvement can be effectively comprehended on the grounds that carbonaceous material conveys more stiffness to the composites [35]. The maximum value of MOR is found in particle boards with 1 wt% of carbonaceous materials, i.e., 9.058 N/mm², which may be because of the enhanced adhesion between the resin matrix and wood particles in the particle boards. The MOR of particle boards at higher carbonaceous material loadings reduces with the increment from 2.5 to 5 wt%. The depletion of MOR with increasing carbonaceous material loading can be attributed to the existence of agglomeration. It has been acknowledged that the modulus of composites at higher carbon nanotube (CNT) loadings might not due to the formation of CNT agglomerates [36].

3.5. Thickness swelling test

The thickness swelling of the particle board panels is shown in Fig. 11, which shows the percentage of water uptake for the composites after immersing in water for 24 h.

TS is decreased by adding 1% carbonaceous materials compared with the boards without including carbonaceous materials. The addition of 1% reduces TS with a slight increase occurring from 2.5% to 5% and for this situation, the TS is improved only at 1 wt% of carbonaceous materials. This might be because of better adhesion of carbonaceous materials and UF resin. The TS for UF-0 is 58.47% and it is reduced by adding 1 wt% of carbonaceous material, i.e., 35.27%. It is evident that the lower loading level of micro particles had a positive effect on TS while as, higher loading levels had an adverse effect on the thickness swelling properties.

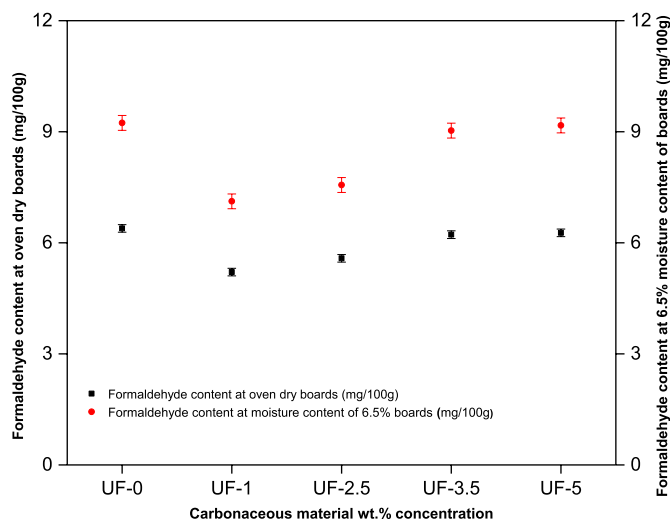


Fig. 12. Formaldehyde content of particle boards using the perforator method with different concentrations of carbonaceous materials.

Table 8

Formaldehyde contents from particle boards with different concentrations of carbonaceous materials.

Testing/Type of Boards	UF-0	UF-1	UF-2.5	UF-3.5	UF-5
Formaldehyde Content at Oven dry boards (mg/100 g)	6.39	5.21	5.58	6.22	6.27
Formaldehyde Content at moisture content of 6.5% boards (mg/100 g)	9.24	7.12	7.56	9.03	9.17

3.6. Formaldehyde emission

Fig. 12 shows formaldehyde content results as obtained by the EN-120 (1992) perforator method. The formaldehyde content was determined from oven dry samples and samples with 6.5% moisture content.

The formaldehyde content was 6.39 and 9.24 mg/100 g for the oven dry and 6.5% moisture content particle boards respectively for results based on the UF-0 resin. As indicated in Fig. 11, formaldehyde content decreased with the addition of carbonaceous material in the UF resin. The highest decrease in formaldehyde content was from the UF-1 sample, as shown in Table 8.

This decrease in the formaldehyde content for the 1% and 2.5% systems is likely caused by the capability of the microstructure of the carbonaceous materials to absorb free formaldehyde in the particle board [38,39]. Carbonaceous materials have chemical compounds that are positively charged and polar in nature, triggering the adsorption of polar formaldehyde. The presence of numerous minute pores on the surface of carbonaceous materials enables them to act as an absorbent [40]. However, UF-1 shows a greater reduction in free formaldehyde content as compared with the UF-2.5, UF-3.5 and UF-5% respectively, indicating that no higher concentration of carbonaceous materials is required.

4. Conclusions

This study explored the impact of carbonaceous materials as fillers on a UF resin. FTIR spectroscopy results have shown that carbonaceous materials can produce hydrogen bonds with UF resins. This was also verified from DSC analysis where peak curing temperatures obtained from UF – carbonaceous material hybrids were found to be slightly higher than those of the pure resin, which implies the formation of bonds between the carbonaceous materials and the UF resin. Crystallinity values (CrI) have indicated that carbonaceous material incorporation

increased the crystallinity of the UF resin, which was verified by SEM analysis. The mechanical properties of the particle boards were improved due to the strong interfacial bonding between the wood particles and the UF/Carbonaceous materials. The addition of carbonaceous materials improved the Internal Bonding (IB), Modulus of Rupture (MOR) and Thickness Swelling (TS). The results provide an in-depth understanding of the carbonaceous materials that affect formaldehyde emissions from panels during the manufacturing process, which allow formaldehyde emissions to reduce as compared to panels with pure UF resin. From this work, it has been shown that carbonaceous materials can be used as fillers for the improvement of UF resin properties.

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