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Evaluation of torrefaction condensates as phenol substitutes in the synthesis of phenol-formaldehyde adhesives suitable for plywood

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ABSTRACT

The last decades, investigators have been striving to find alternatives to materials and products from fossil sources in response to the need to get independent from petroleum. So far, the most attractive renewable source has been found to be biomass and especially wood that is easily accessible and offers a wide range of building blocks with diverse chemistries and structures that can then be used to build materials for the modern world. In this study, wood from Aspen, Pine and Birch as well as a mixture of Spruce and Pine was subjected to torrefaction and the fraction of the condensables with a dew point above 140 °C was used for the partial replacement of phenol (up to 40% wt) in the synthesis of resol phenol-formaldehyde resins suitable to be used as adhesives in the manufacturing of plywood panels. The condensables and the resins were subjected to typical lab analysis and thermal study with TGA and DSC while the plywood panels were tested and evaluated according to the European standards used by the relative industry. It was found that the studied torrefaction condensables may be successfully used in this application while the one from pine was the best performed overall.

1. Introduction

In recent years, the treatment of biomass has gained great importance, because it offers an outstanding solution to the need to replace products and energy derived from fossil resources. The most prevalent methods of biomass treatment today can be grouped in three categories: thermochemical (torrefaction, pyrolysis, gasification, combustion, etc.), chemical (organosolv process, alkaline hydrolysis, etc.) and biochemical (anaerobic digestion, fermentation, etc.) [1].

Especially the thermochemical treatment of torrefaction has been rapidly developed in the last about 10 years from the R&D stage to commercial operations [2]. Torrefaction of biomass takes place in an inert atmosphere at the temperature range of 250–300 °C [3] and results in a solid product (TSP)[1] with low moisture content, lower O/C ratio and higher calorific value or energy density than the initial biomass [4]. The heating value of wood torrefaction solid product is about 21–23 MJ/kg when wood biomass has a heating value of about 19 MJ/kg. Even more, if a torrefied wood is completely devitalized then it is turned into charcoal with a heating value of about 30 MJ/kg [2]. During the torrefaction process, about 70% of the treated biomass is retained as a solid product [5]. From the chemical point of view, the solid product consists of a chaotic structure of the original structures, reaction products, char and ash.

Next to the torrefied solid product, a gaseous by-product is formed, that can be combusted for the generation of process heat. Alternatively, the torrefaction gas can be (partially) condensed to recover the so-called torrefaction condensabales (TC).[2] The volatiles of the process (condensed and non-condensed products) include mostly moisture, acetic acid and other oxygens, CO_2, CO, small amounts of methane [6] and fragments of the chemicals found in the initial biomass [7].

The easy and durable production of torrefied products at large scale, still faces some problems related with the difficulty to compact (e.g. by pelletization) torrefied biomass and with the outdoor storage of torrefied material without weather protection, like coal [2]. In addition, the formation of condensable species in the torrefaction gas can pose problems in the downstream processing of the gas due to uncontrolled condensation that may cause clogging of gas pipes and the like. The controlled recovery of the condensable species will prevent these problems and offers an opportunity for by-product valorisation.

In this study, a new use of wood torrefaction condensables (TCs) has been explored within the scope to find added-value applications for this material. Although not all of its compounds have been characterized

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[1] TSP = Torrefaction solid product.
[2] TC = Torrefaction condensable.

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yet, various fragments of the initial biomass constituents have been identified, like lignin decomposition fractions (phenol, p-coumaryl alcohol, etc.) and their reaction products [7]. In the current work, TCs of different wood species have been evaluated as phenol substitutes in the synthesis of phenol-formaldehyde (PF) resins suitable to be used as bonding materials (adhesives) in the preparation of plywood panels. Although a lot of work has been carried out on the replacement of phenol in PF resins by phenolic-based chemicals resulted from other thermochemical treatments of biomass like fast pyrolysis [8–10], vacuum pyrolysis [11], liquefaction [12,13], as well as fractionated pyrolysis [14], there are no literature references for the use of TC in the preparation of such resins. Hence, this study promotes the state of the art in the field and the developed products may be considered as novel.

2. Materials and methods

2.1. Torrefaction process

Clean wood chips from softwood and hardwood were chosen to produce a substantial amount of TCs (more than 10 kg). The chips were screened to sizes lower than 40 × 40 × 15 mm and were dried to a moisture content below 10%wt. The TCs studied were from Aspen, Birch, Pine and a mixture of Spruce/Pine of unknown ratio.

The fresh wood chips of each feedstock were torrefied in the torrefaction pilot plant of ECN, a slowly moving bed reactor with a counter-current flow of torrefaction gas. The biomass intake capacity is around 50 kg/hr. The torrefaction temperature was set at 280 °C. A throughput of approximately 44 kg/h was selected, giving a residence time in the torrefaction reactor of approx. 45 min. From every 1 m^3 box with chips fed to the unit, a sample was taken and the moisture content was determined by drying in an oven. The wood chips could be fed to the reactor continuously. During torrefaction, condensables were produced and the fraction of the condensables with a dew point above 140 °C was separated from the gas stream and collected in small bins. This was the TCs used in this study. All TCs were subjected to Thermogravimetric Analysis (TGA) using a Setaram Setsys TG-DTA-16/18 device. Samples (5.5 ± 0.2 mg) were placed in alumina crucibles, while an empty alumina crucible was used as the reference. Each sample was heated from ambient temperature until 800 °C in a flow of air, with a heating rate of 20 °C/min.

2.2. Resins

CHIMAR HELLAS S.A., a private research institute with core business the development of know-how for adhesives and chemicals for the production of wood-based panels and the provision of on-site services to the relative industry, used the TCs for the partial replacement of phenol in the synthesis of phenol-formaldehyde polymers (resins) suitable to be used as adhesives for the production of plywood panels. The resins in this study are named as PF-A when TC of Aspen was used, PF-B when TC of Birch was used, PF-P when TC of Pine was used and PF-SP when TC of a mixture of Spruce and Pine was used for their synthesis. The other raw materials used in the synthesis of the resins were commercial water-based solutions of phenol (90% w/w), formaldehyde (40% w/w) and sodium hydroxide (50% w/w).

The synthesis of the new polymers was based on CHIMAR proprietary technology for the production of phenol-formaldehyde (PF) resins. A typical PF resin was also included in the study as a control.

For the comparison of their performance, initially, all TCs were evaluated as phenol substitutes at the level of 20% during the synthesis of the resins. The code names of the resins prepared are PF-A20 for the one modified with TC from Aspen, PF-B20 for the one modified with TC from Birch, PF-P20 for the one modified with TC from Pine and PF-SP20 for the one modified with TC from a mixture of Spruce and Pine. The TCs from Birch and Pine wood, that were the best performed, were further tested as phenol substitutes at higher levels. In particularly, PF-B30 is the resin with 30% phenol replacement by TC from Birch while PF-P30 and PF-P40 are the resins with 30% and 40% phenol replacement accordingly by TC from Pine.

The physicochemical properties of the new resins were determined according to the lab analysis techniques followed for the typical PF resins. The properties of interest were viscosity, solid content, pH, gel

Table 1
Requirements of the standard EN314-2:1993.

Mean shear strength, f N/mm^2	Mean apparent cohesive wood failure, W%
$0.2 \le fv < 0.4$	≥80
$0.4 \le fv < 0.6$	≥60
$0.6 \le fv < 1.0$	≥40
$1.0 \le fv$	No requirement

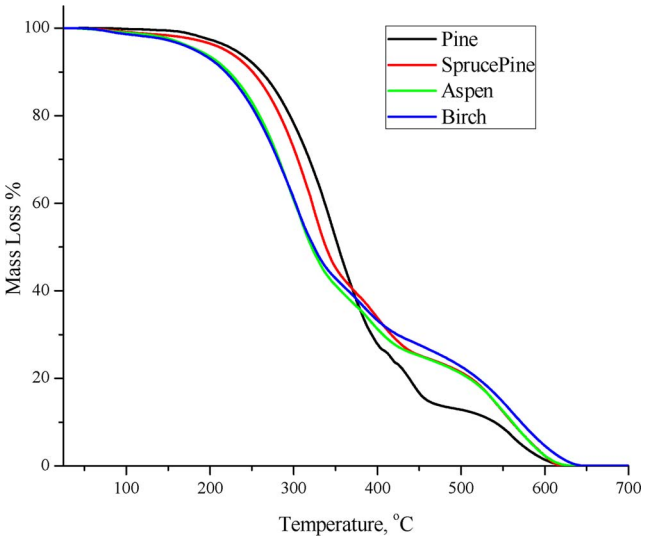

Fig. 1. TGA results of the studied TCs.

Table 2
Properties of resins with 20% phenol substitution level.

Resin Torrefied biomass	PF std –	PF-A20 Aspen	PF-B20 Birch	PF-P20 Pine	PF-SP20 Spruce/Pine
Solids, %	46	46	46	46	46
Viscosity, cP	330	580	670	580	450
pH	12.65	12.48	12.51	12.65	12.68
Gel time@ 130 °C, s	345	150	120	120	120
Alkalinity, %	7.30	7.55	7.55	7.80	7.50
Free Formaldehyde, %	0.285	0.313	0.292	0.312	0.302
Conductivity, mS/cm	22	23	23	24	24
Viscosity while stored at 5 °C, cP					
After 22 days	350	570	690	570	465

Table 3
Properties of resins with 30 and 40% phenol replacement by TCs from Birch & Pine.

Resin Torrefied biomass	PF-B30 Birch	PF-P30 Pine	PF-P40 Pine
Solids, %	46	46	46
Viscosity, cP	610	610	650
pH	12.38	12.37	11.72
Gel Time @ 130 °C,s	180	180	270
Alkalinity, %	6.42	6.27	6.18
Free Formaldehyde, %	0.260	0.270	0.220
Conductivity, mS/cm	20.00	19.10	19.83
Viscosity while stored at 5 °C, cP			
After 22 days	700	600	610

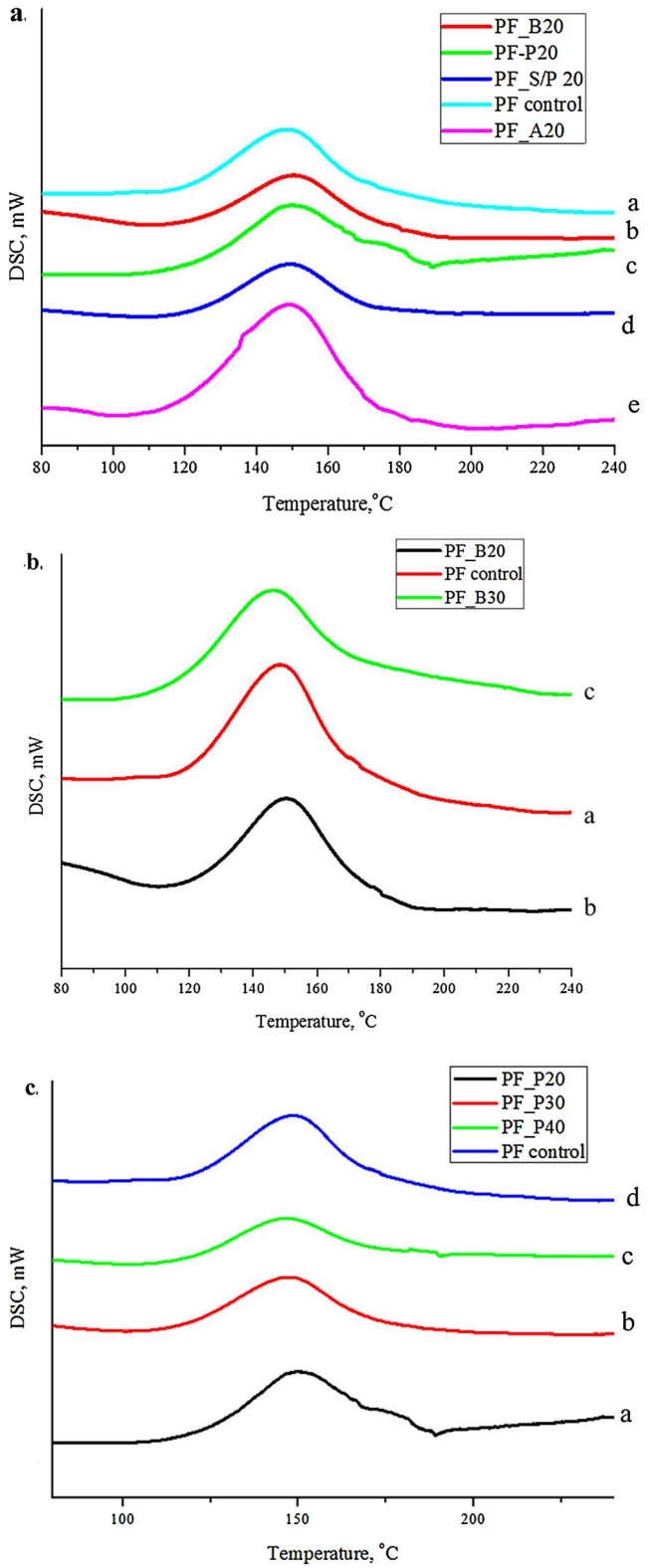

Fig. 2. (a) DSC of resins with 20% phenol replacement by the studied TCs a) PF control, b)PF-Birch, c)PF-Pine, d)PF-Spruce/Pine, e) PF-Aspen. (b) DSC graphs of resins modified with TC from Birch a) PF resin – control, b) PF-B20, c) PF-B30. (c) DSC graph of resins modified with TC from Pine a) PF-P20, b) PF-P30, c) PF-P40, d) PF resin–control.

time, alkalinity, free formaldehyde and conductivity. Moreover, the thermal properties of the resins were studied with Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements. In order to choose the optimum conditions for the TGA measurements, an experimental resin (the one with 20% phenol replacement of birch TC) was initially studied both in an inert atmosphere (N_2) and air. Also, the control PF resin was studied with TGA both liquid and after dried in an oven at 120 °C for 2 h.

Table 4
Details of DSC analysis of resins modified with TSPs from various wood species.

Resins	Tc, °C	ΔH, J/g
PF control	148.8	70.3
PF-A20	149.4	73.2
PF-B20	151.2	50.1
PF-B30	146.2	52.9
PF-P20	150.4	49.5
PF-P30	147.6	46.7
PF-P40	145.8	32.1
PF–S/P20	148.8	40.6

The TGA measurements were carried out with a Setaram Setsys TG-DTA-16/18 device. Samples of 5.5 ± 0.2 mg were placed in alumina crucibles. An empty alumina crucible was used as the reference. Each sample was heated from room temperature until 1000 °C in an air atmosphere, with a heating rate of 20°/min. The DSC measurements were conducted with a DSC141, Setaram calorimeter. The samples (14–16 mg) were placed in stainless steel sealed crucibles. Each sample was heated to 250 °C with a heating rate of 5°/min while nitrogen was used as carrier gas. For the DSC study, a steady baseline was established before each measurement using two empty pans with the same heating rates.

2.3. Plywood panels

The bonding ability of the resins was tested in the production of plywood panels of 3 layers. The face veneers were from Okoumé (that has a pinkish-brown colour) and the core veneer was from Poplar wood. Both types of veneers were from hardwood trees. The production of plywood panels was carried out with a process simulating the industrial practice.

For each polymer tested, an adhesive mixture was prepared, consisting of resin, extender (wheat) and water, and a certain quantity of it was manually spread on the veneers. The average assembly time was 20 min. The panels were initially subjected to cold pressing with a specific pressure of 10 kg/cm^2 for five minutes. After a close assembly time of about one hour, the panels were hot pressed for seven minutes at a temperature of 140 °C while a specific pressure of 12 kg/cm^2 was applied.

The panels were tested and evaluated for their bonding ability according to the European standards:

EN314-1:2004 Plywood – Bonding Quality – Part 1: Test methods

EN314-2:1993 Plywood – Bonding Quality – Part 2: Requirements

Although these standards apply to industrial productions, they give a good indication of the performance of lab-scale plywood panels too.

The standard EN314-1:2004 concerns the test method for the determination of the bonding quality in each glue line of the plywood panel. It describes the shape and dimensions of the samples, the equipment that has to be used and the methods of the treatments that the plywood panels have to be subjected to before their testing.

The standard EN314-2:1993 specifies requirements for bonding classes of veneer plywood according to their end use and correlates the treatments that have to be subjected to for each bonding classes (class1: dry conditions-interior use, class 2: covered panel-exterior use, class 3: non-covered panel-exterior use). For all bonding classes, each glue line shall satisfy two criteria: the mean shear strength and the mean apparent cohesive wood failure as shown in Table 1.

The plywood panels of this study were subjected to the severest pretreatments prescribed for panels of class 3. In particularly, the plywood panels before tested for their shear strength and wood failure

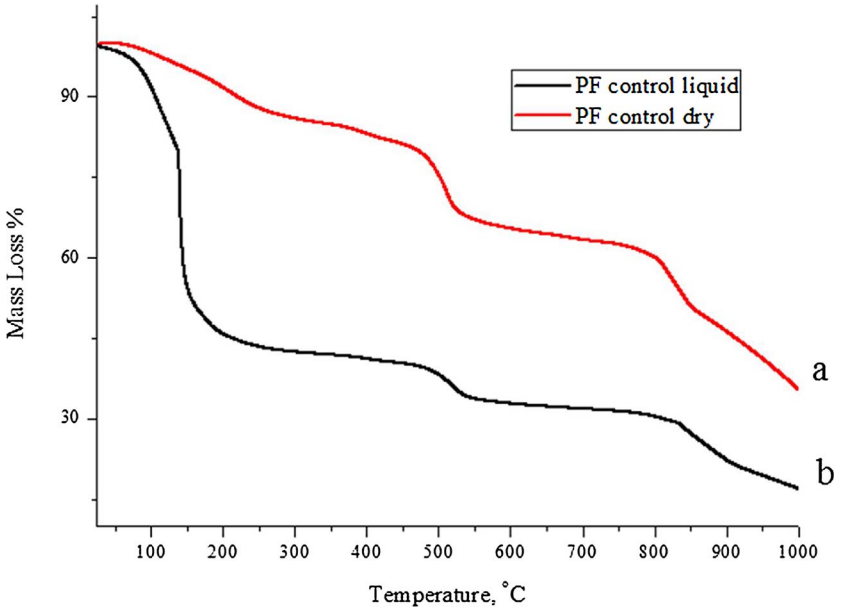

Fig. 3. TGA of dried (a) and liquid (b) PF resin.

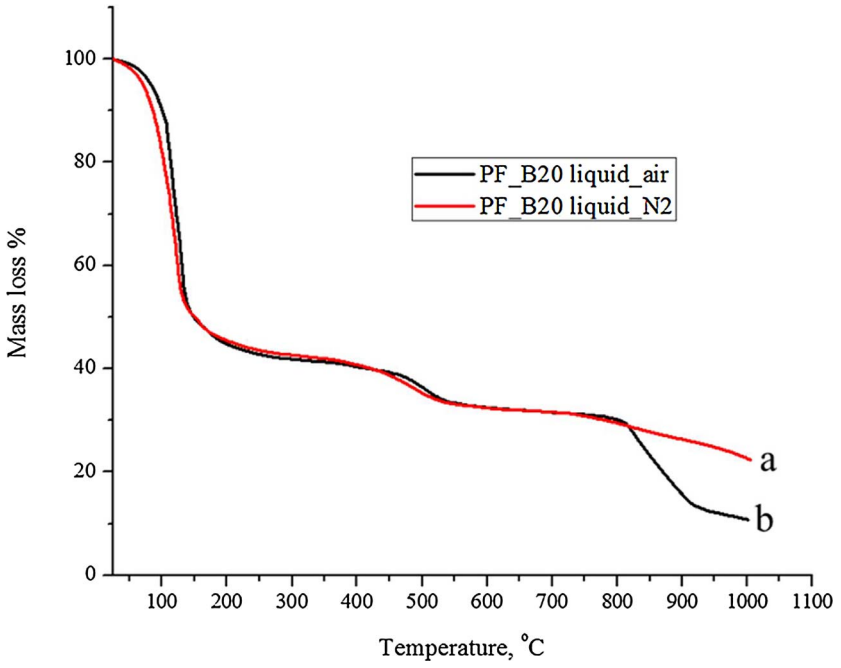

Fig. 4. TGA results of PF-B20 resin measured in air (b) and inert atmosphere (a).

performance were firstly immersed in water of 20 °C for 24 h (according to the pre-treatment 5.1.1 of the EN314-1:2004). Next they were subjected to a cycle test consisting of 4 h in boiling water16 h drying at 60 °C–4 h in boiling water and 1 h immersion in cool water (according to the pre-treatment 5.1.3 of the EN314-1:2004).

The formaldehyde emissions of the plywood panels were determined according to the Desiccator method (as per the Japanese standard JIS A 1460).

3. Results and discussion

3.1. Properties of torrefied condensates

The mass loss results of the TG analysis of the TCs are depicted in Fig. 1.

It can be seen that the TCs from Aspen, Birch, Pine and the mixture Spruce/Pine initially lose mass in a similar manner. After the temperature of 380 °C, the sample from Pine decomposes with a faster rate in a process of two steps that signalizes a less stable material than the other TCs studied.

3.2. Properties of resins

The synthesis process of the resins was evolved smoothly for the majority of TCs and phenol substitution levels. An exception is the case of Birch, where some insoluble material was observed at the end of the synthesis in the case of 30% phenol replacement. This is the cause that no higher phenol substitution levels were tested for this sample.

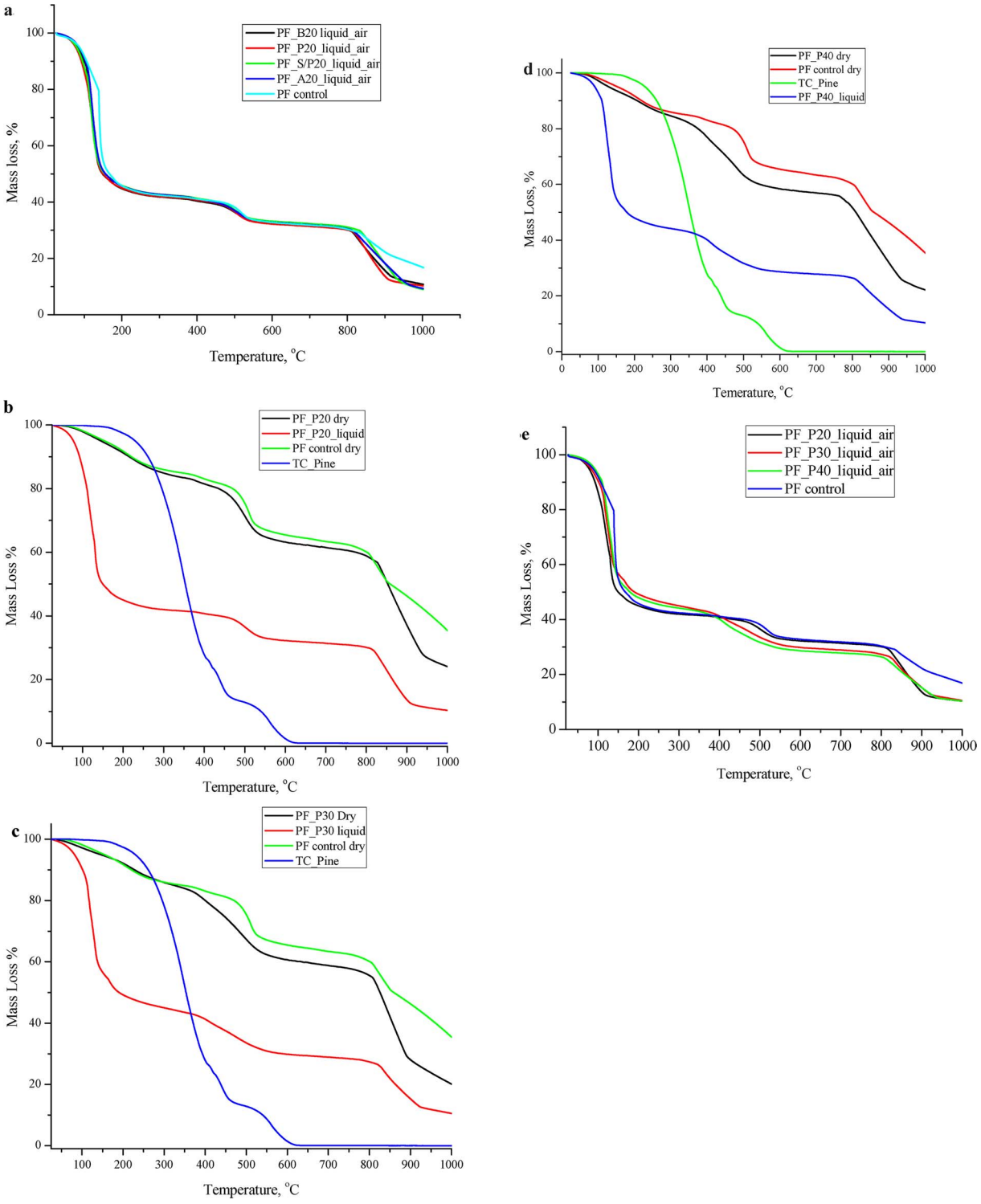

Fig. 5. (a) TGA graphs of resins with 20% phenol substitution by the studied TCs. (b) TGA graph of TC from Pine and PF control resin (in dry form) in comparison with PF-P20 resin in dry and liquid form. (c) TGA graph of TC from Pine and PF control resin (in dry form) in comparison with PF-P30 resin in dry and liquid form. (d) TGA graph of TC from Pine and PF control resin (in dry form) in comparison with PF-P40 resin in dry and liquid form. (e) TGA measurements of PF resin modified at various levels (20, 30 and 40%) with TC from Pine.

The physicochemical properties of resins with 20% phenol replacement are shown in Table 2 while the physicochemical properties of resins prepared with TCs from Birch and Pine, having higher phenol substitution are cited in Table 3.

The results show that the experimental resins have a higher viscosity than the control, although prepared under the same conditions. Also, their gel time is increased as the substitution level of phenol increases.

The results of the study of these resins with DSC are presented in Fig. 2(a,b,c) while the respective curing temperatures (Tc) and ΔHs are shown in Table 4.

The results show that all experimental resins cure at close temperatures, while as the phenol substitution level is increased the curing temperature and enthalpy values are decreased.

Regarding the TGA measurements, in order to choose the optimum testing conditions, two preparatory measurements were carried out.

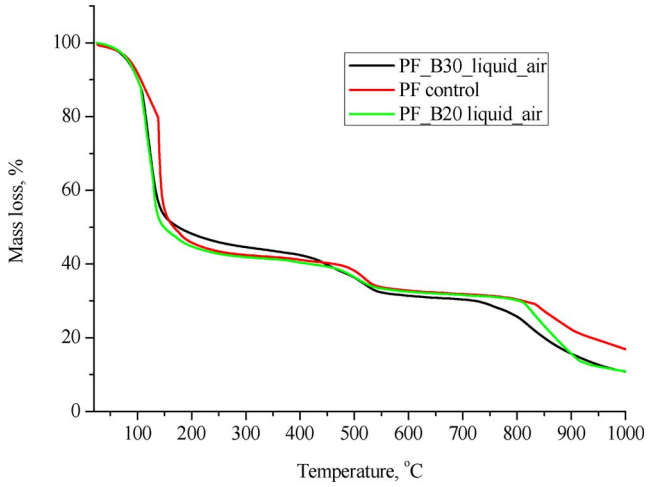

Fig. 6. TGA measurements of PF resins modified with TC from Birch at the levels of 20 and 30%.

Table 5
Testing results of plywood produced with resins having 20% phenol replacement by the studied TCs.

Formula	1	2	3	4	5
Resin	PF std	PF-A20	PF-B20	PF-P20	PF-SP20
TSP	–	Aspen	Birch	Pine	Spruce/Pine
EN314.1					
Pre-treatment 5.1.1:	*Immersion in water of 20 °C for 24 h*				
Shear strength, N/mm^2	1.53	1.50	1.64	1.67	1.55
Wood failure, %	65	65	50	60	45
Pre-treatment 5.1.3:	*4 h boiling water–16 h drying at 60 °C–4 h boiling water–1 h cool water*				
Shear strength, N/mm^2	1.36	1.18	1.37	1.43	1.31
Wood failure, %	65	45	55	50	15
Desiccator results, mg/L	0.041	0.015	0.037	0.035	0.040

Table 6
Testing results of plywood produced with resins containing the best performed TCs.

Formula	1	2	3	5	6	7
Resin	PF std	PF-B20	PF-B30	PF-P20	PF-P30	PF-P40
TSP	–	Birch	Birch	Pine	Pine	Pine
EN314.1						
Pre-treatment 5.1.1:	*Immersion in water of 20 °C for 24h*					
Shear strength, N/mm^2	1.54	1.42	1.52	1.42	1.56	1.57
Wood failure, %	45	35	40	35	45	15
Pre-treatment 5.1.3:	*4 h boiling water–16 h drying at 60 °C–4 h boiling water–1 h cool water*					
Shear strength, N/mm^2	1.24	1.13	1.13	1.18	1.20	1.12
Wood failure, %	60	55	35	45	25	20
Desiccator results, mg/L	0.056	0.033	0.063	0.057	0.048	0.060

First, the control resin (PF) was studied both in liquid and dry form, in order to monitor if there is any difference in their decomposition performance. Secondly, the experimental resin with 20% phenol replacement by Birch TC (PF-B20) in liquid form was studied both in an inert atmosphere (N_2) and air.

The TGA study of the control PF resin (Fig. 3) illustrates that the water affects only the mass loss at the beginning of the heating, while in general, the decomposition performance of the resin is not dependent on its physical state during the measurement.

The TGA study of the PF-B20 resin in liquid form in an inert atmosphere (N_2) and air (Fig. 4) shows that the decomposition performance of the resin is practically independent of the measurement conditions until 800 °C. Beyond this temperature, the sample in air loses mass more rapidly.

Based on the above observations and considering the fact that practically the resins are used in liquid form and at air conditions, all further TGA measurements were carried out with liquid resin in air atmosphere. An exception is the resins modified with TC from Pine that gave the best performance in panels and they were studied in comparison with the control both in dry and liquid form.

The TGA graphs of the liquid resins with 20% phenol replacement by the studied TCs are presented in Fig. 5a.

They show that all resins have similar decomposition performance until about 800 °C. After that, the experimental resins lose mass more rapidly than the control PF resin. The thermal decomposition performance of resins modified with TC from Pine at various levels is illustrated in Fig. 5b–e.

It was found that their thermal decomposition tendency is not affected by the physical state of the resin. The water affects only the mass loss at the beginning of the heating. Moreover, it was observed that the lower the phenol substitution level, the closer the decomposition performance of the resin to the control PF (Fig. 5e).

The graphs in Fig. 5e make evident that until 200 °C all resins lose mass due to the evaporation of water and other chemicals of low molecular weight (e.g. formaldehyde). The typical PF resin (control) has two clear decomposition steps and seems to be more stable at the temperatures of 300–490 °C, while the experimental resins lose progressively mass during this temperature range. Between 490–550 °C, the standard PF loses weight faster contrary to the experimental resins that continue their more gradual mass loss. After about 550 °C all resins are relatively stable until about 800 °C where clearly the experimental resins lose mass at a faster rate. At the end of the experiment (1000 °C), the control resin has higher remaining mass (ash) compared with the experimental ones.

The TGA results of resins prepared with phenol substitution by TC from Birch at the levels of 20 and 30% are shown in Fig. 6.

These graphs show that also these experimental resins have very similar decomposition performance to the control. As in the case of resins modified with TC from Pine, the lower the phenol substitution level, the closer the mass loss performance of the resins modified with TC from Birch to the control PF resin. At high temperatures (above appx. 800 °C) the control resin seems to be more stable than the experimental ones.

3.3. Properties of plywood panels

The properties of panels prepared with resins having 20% phenol replacement by the studied TCs are presented in Table 5.

The results show that although all experimental resins meet the requirements of the standard EN 314-2:1993 (Table 1), the resins produced with TCs from Pine and Birch have better performance, especially regarding the wood failure.

The testing results of plywood panels manufactured with resins containing the best performed TCs at phenol substitution levels of 20, 30 and 40% are shown in Table 6.

From these results, it becomes evident that at the mild testing conditions (pre-treatment 5.1.1) the resins with up to 30% phenol replacement have performance comparable to the typical PF resin. When the testing conditions become severer (pre-treatment 5.1.3), then the higher the phenol replacement level, the lower the performance of the resin regarding mostly the wood failure values. Especially in the case of panels prepared with the resin having 40% phenol substitution by Pine TC, a significant drop in the properties is observed.

Concerning the free formaldehyde emissions of panels, they are at

very low levels no matter of the experimental resin used for their manufacturing. Hence, all panels may be considered as of F**** class (F**** upper value is 0.3 mg/L) according to the JIS A1460 standard.

4. Conclusion

All TCs tested in this study can be used for partial replacement of phenol during the synthesis of phenol-formaldehyde resins. Such resins have physicochemical and thermal properties close to a typical PF resin and may be used as adhesives for the manufacturing of plywood panels suitable for exterior applications. Among the TCs tested, the one from Pine followed by the one from Birch had the best performance. This study proves the potential of using a waste of the torrefaction process in added-value applications. For future work, it is interesting to further characterise physicochemically the feedstocks and their TCs in order to gain more insight into the relation between feedstock type, torrefaction conditions and properties of resins.

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