

Characterization and Adhesive Performance of Phenol-Formaldehyde Resol Resin Reinforced with Carbon Nanotubes

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Chemical, physical, thermal properties and bonding quality of phenol-formaldehyde resol resin (PF) synthesized with single-walled carbon nanotubes (SWCNTs) was evaluated at varying ratios from 1 wt% to 5 wt%. The effect of the SWCNTs addition on thermal and chemical properties of the PF resins was characterized by thermal gravimetric analysis (TGA) and Fourier transform infrared (FT-IR) spectroscopy, respectively. FT-IR analysis revealed that the peaks of the modified PF resol resins were similar to those of the reference (laboratory-produced) PF resol resin. These similarities indicated that the synthesis of the resins with phenol, formaldehyde, and carbon nano tubes was successful. The PF resins modified using SWCNTs demonstrated higher thermal stability than the reference PF resin. It was found that the bonding strength of the PF resin containing 3 wt% SWCNTs could reach 12.45 N/mm² in dry conditions and 7.57 N/mm² in wet conditions. The bonding test results demonstrated that the SWCNTs were able to improve the bonding performance of the resin under dry and/or wet conditions. This work presents an effective method to improve PF resins with SWCNTs reinforcement for use in the wood and/or polymer composite industries.

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INTRODUCTION

Phenol is derived from various fossil fuels, *e.g.*, coal and petroleum. It can be produced from toluene and benzene. The cumene-to-phenol process for phenol-acetone (PA) manufacturing is the most widely used synthetic route. By this process, two products (phenol and acetone) are obtained simultaneously from one reactant (cumene). Cumene hydroperoxide is formed from the oxidation of cumene, and subsequently, phenol and acetone are produced from the decomposition of the peroxide *via* a catalyst of concentrated mineral acid (Ge and Jin 1996; Schmidt 2005; Zakoshansky 2007; Pilato 2010).

Phenolic resins represent one of the primary polymer forms and have a wide application range among industrial products including adhesives, coatings, and insulation materials. In the synthesis of oligomers, an aldehyde, *e.g.*, formaldehyde, reacts with a phenol in the presence of an acidic catalyst to produce a novolac, or in the presence of a basic catalyst to form a resole (Knop and Pilato 1985; Jensen *et al.* 1996). Phenol-formaldehyde (PF) resol resin exhibits a high degree of thermal and chemical resistance in

addition to superior mechanical properties and dimensional stability; all of these factors make it an excellent choice in the production of wood-based composite panels, including oriented strand board (OSB), fiberboard, and plywood (Park *et al.* 1999; Ayrilmis and Ozbay 2017).

Carbon nanotubes (CNTs) represent a new type of elemental carbon composed of long cylinders of carbon atoms, which are bonded covalently and exhibit exceptional mechanical and electronic characteristics. These CNTs can be found in two forms: single-walled carbon nanotubes (SWCNTs), which are produced as a single graphene layer, and multi-walled nanotubes (MWNTs), which are produced with additional graphene layers surrounding the core of the SWCNTs. Carbon nanotubes (CNTs) have recently been considered for use in polymer composites as reinforcing elements due to their superior mechanical and electrical features (Dresselhaus *et al.* 1996; Harris 2004; Antolín-Cerón *et al.* 2008).

There are many studies on strengthening different adhesives used in industry by means of various nanoparticle additives. Some of these studies focus on improving the thermal conductivity of the adhesives, as well as improving their resistance to external environmental conditions and their mechanical properties (Soltannia and Taheri 2014; Wehnert *et al.* 2015; Khoramishad *et al.* 2018; Wang *et al.* 2021). Studies have shown that the nanoparticles additives used in different proportions have achieved considerable improvements in the thermal conductivity, resistance to environmental conditions, and adhesion strength of the adhesives.

Previous studies have shown that PF resin can be successfully reinforced by different types of chemicals, *e.g.*, boron compounds (Gao *et al.* 1999; Liu *et al.* 2002; Wang *et al.* 2010; Bian *et al.* 2015), nano-particles (Lin *et al.* 2006; Liu *et al.* 2014; Strečková *et al.* 2014; Solyman *et al.* 2017; Kawalerczyk *et al.* 2020), and other chemicals (Park and Riedl 2000; Fan *et al.* 2009; Fan *et al.* 2010; Zhang *et al.* 2013; Guan *et al.* 2014; Özbay and Ayrilmis 2015; Guan *et al.* 2016).

The purpose of this study was to add different amounts of SWCNTs for use in phenol-formaldehyde (PF) synthesis and investigate the effect of SWCNTs addition on the chemical, physical, and thermal properties of the resin. Experiments were then conducted to investigate its bonding performance under indoor and outdoor exposure conditions.

EXPERIMENTAL

Materials

Commercially available (GENTAŞ Chemical Industries, Izmit, Turkey) phenol (liquid), and formaldehyde (aqueous solution, 37 wt%) were used in the study. The as-produced SWCNTs (Nanografi, Turkey) measuring approximately 1 to 2 nm for the external diameter and 0.8 to 1.6 nm for the inner diameter, with a 5 to 35 µm length, had a purity rating of greater than 65%. Other analytical chemicals, *e.g.*, sodium hydroxide pellets, ethanol, and acetone, were obtained from Sigma-Aldrich (St. Louis, MO).

Preparation of the Single-Walled Carbon Nanotubes (SWNTs) Solutions

The SWCNTs were subjected to sonication in 100% water for 2 h, at ambient temperature. After stirring, the nanotubes were then filtered and dispersed in 50 mL of water. They were then dried, and 2 mg of the dry nanotubes were placed in a vial with 20 g of water. The SWCNTs that dispersed in the water were transformed from agglomerated

bundles into individual ones after 2 h *via* an ultrasonic mixer (120 W). At the end of the dispersion process, the suspension was homogeneous and stable.

Synthesis of the Modified Phenol-Formaldehyde (PF) Resins

A glass reactor with a type K thermocouple, a reflux condenser, and a stirrer were used to prepare the modified PF resins. The temperature of the reaction was measured by placing the thermocouple inside the adhesive reactor. For the synthesis (2.0 = F/P molar ratio), 70 g of phenol, 110 g of formalin (in a 37 wt% water solution), and 6.25 g of NaOH solution (50 wt%; 1/3 of the total NaOH weight) were charged into the reactor. The phenol-formaldehyde reaction was carried out in the reactor at a temperature of 60 °C for 60 min under stirring, after which catalytic treatment with NaOH, was completed. The dispersed SWCNTs were slowly introduced into the reactor under vigorous stirring while maintaining the same temperature. The mixture was then heated to 90 °C, after which it was stirred for 60 min at 90 °C in order to polymerize. The temperature was lowered to 60 °C for the addition of the remaining NaOH (50 wt%) solution into the reactor. The mixture was then rapidly cooled to room temperature to obtain the SWCNTs-modified PF resol resin. The ratios (w/w%) selected for the dispersed SWCNTs and the PF resin were 1/100, 3/100, and 5/100, respectively. Pure PF resol resin (Lab. PF) was prepared, in the same way, which was used as a reference for comparison with the modified PF resin.

Characterization

The effects of the presence of SWNTs on the physical characteristics, including pH, dynamic viscosity, and the solid content of the PF resins, were examined and discussed. All the pH measurements were taken with a digital TES-1380 pH meter. The dynamic viscosity was determined *via* a Brookfield Dv-IPrime digital viscometer in compliance with ASTM standard D1084-08 (2008). ASTM standard D3529M-97 (2008) was used to calculate the solid contents. Three replicate measurements were taken, and the average was recorded as the value.

The formaldehyde content was measured using the perforator method according to EN standard 120 (1992). The formaldehyde was extracted from small wood samples using toluene and then transferred into water. The formaldehyde content of this solution was determined photometrically. The formaldehyde content was expressed in mg of formaldehyde per 100 g of the dry sample.

Fourier-transform infrared (FT-IR) spectroscopy *via* the Alpha FT-IR model was employed to determine the functional groups of the resin. The spectra were recorded within the range 400 to 4000 cm^{-1} in transmission mode.

The thermal stabilities of the PF resin samples were analyzed using a HITACHI STA 7300 thermogravimeter *via* heating from 20 to 700 °C at a rate of 10 °C/min under a N_2 gas stream at a rate of 30 mL/min.

Measurements of the Adhesive Performance

Beech (*Fagus orientalis* Lipsky) wood is generally used for testing the bonding performance of resins. Accordingly, beech wood specimens were prepared to evaluate the adhesive performance of the SWCNTs-reinforced PF resol resins. Beech wood planks were supplied by a commercial timber company in Düzce, Turkey. Prior to bonding, the lamellas with dimensions of 5 mm x 20 mm x 150 mm were prepared from beech planks using a planer saw. All the lamellas were planed in order to ensure smooth and flat surfaces prior to bonding. The lamellas were conditioned in a climate room at 20 ± 2 °C and $65 \pm$

5% relative humidity (RH) and allowed to reach a nominal equilibrium moisture content of 12%. The PF resol resin was applied on a single bonding surface of the lamellas at a treatment level of 180 g/m², and for all PF resol resins, a pressure of 2 kg/cm² was applied at a temperature of 130 °C for 15 min. After 10 weeks of conditioning at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 5%, the material was cut into samples. The dimensions of a typical sample are shown in Fig. 1. The bonded wood samples from the reference PF and each of the modified PF resol resin groups were separated into three different pre-treatment sub-groups before testing. The first sample groups (pre-treatment 1) was evaluated in the dry condition after conditioning for 7 days (65±5% relative humidity, 20±2 °C standard climate); the second group of the samples (pre-treatment 2) was soaked in cold water (20 °C) for 24 h; the third group of the samples (pre-treatment 3) was boiled for 3 h, then cooled in water (20 °C) for 2 h, in accordance with EN standard 12765 (2016) (as shown in Table 1). A Zwick/Roel Z50 universal testing machine was used to measure the adhesive performance as per BS EN 205 (2003).

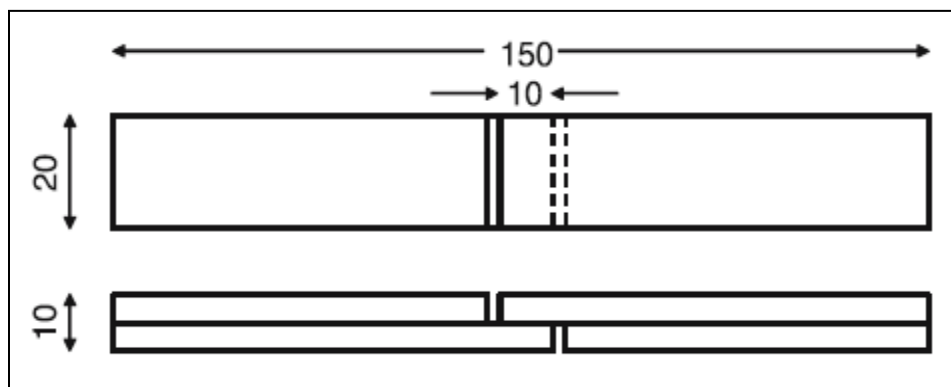


Fig. 1. Bonding strength test sample (size given in mm)

Table 1. Scale for Evaluating the Adhesive Line Quality Based on Strength and Durability

Test Number	Test Conditions	Scale Strength (N/mm ²)			
		C1	C2	C3	C4
Pre-treatment 1	7 days in standard conditions (dry condition)	≥ 10	≥ 10	≥ 10	≥ 10
Pre-treatment 2	7 days in standard conditions; 24 h in cold water at 20 °C ± 5 °C (wet condition)	-	≥ 7	≥ 7	≥ 7
Pre-treatment 3	7 days in standard conditions; 3 h in boiling water; 2 h in cold water at 20 °C ± 5 °C (boiling treatment)	-	-	-	≥ 4

RESULTS AND DISCUSSION

Characteristics of the Modified Phenol-Formaldehyde (PF) Resol Resin

The dynamic viscosity, solids content, and pH of the PF resol resins modified using different amounts of SWCNTs are given in Table 2. The dynamic viscosity slightly increased as the addition rate of SWCNTs to the PF resol resin was increased. The lowest

viscosity (345 cPs) was found in the Lab. PF resol resin, whereas the highest viscosity (445 cPs) was obtained from the 5 wt% SWCNTs-modified PF resol resin. The modified PF resol resin pH values were similar because the pH values were continuously adjusted during the resin synthesis. Although the PF resin solids content decreased as the SWCNTs content decreased, it increased when the SWCNTs content was higher. The base solid content (41.46 wt%) of the PF resin increased to 52.71 wt% with the addition of 5 wt% SWCNTs.

The wood samples bonded with 5 wt% SWCNTs modified PF resol resin had the lowest formaldehyde emission value (0.156 mg/100 g), followed by 3 wt% SWCNTs modified PF resol resin (0.188 mg/100 g), 1 wt% SWCNTs modified PF resol resin (0.218 mg/100 g), and the Lab. PF resol resin (0.264 mg/100 g), respectively. The formaldehyde emission level of the PF resol resin sharply decreased with an increased SWCNTs. As such, SWCNTs could be used as an adsorbent for the removal of formaldehyde.

Table 2. Physical Properties of the Resin Sample Types

Resin Type	SWCNTs (wt%)	Viscosity (25 °C, cPs)	pH (20 °C)	Solid Content (wt%)	Free Formaldehyde Contents (mg/100 g)
Lab. PF	0	345	11,74	41.46	0.264
1 wt% SWCNT/ PF	1	375	11.78	46.87	0.218
3 wt% SWCNT/ PF	3	406	11.85	50.14	0.188
5 wt% SWCNT /PF	5	445	11.91	52.71	0.156

The PF resol resins modified with SWCNTs and the Lab. PF resol resin were analyzed using the FT-IR spectrum (as shown in Fig. 2) to investigate the PF resol resin chemical structure. The peaks distributed *via* the FT-IR spectra of the PF resol resins were clearly similar to those of the Lab. PF resol resin. Nevertheless, differences were noted among the different types of SWCNTs-modified PF resol resins. These included differences in the intensity of the peaks assigned to characteristic functional groups because of the different addition rates of carbon nanotubes.

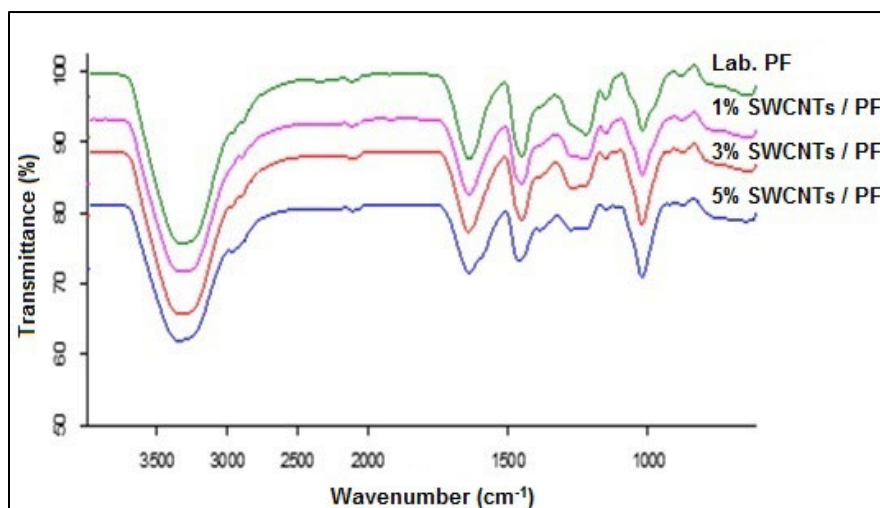


Fig. 2. FT-IR spectra of the resins

In the FT-IR spectra of all the PF resol resins, the broad peak between 3600 and 3200 cm^{-1} was attributed to the hydroxyl stretching vibration. The functional groups of aliphatic CH, CH₂, and CH₃ stretching were observed at 2950 and 2850 cm^{-1} . The aliphatic -CH₂ bending vibration was seen at approximately 1450 cm^{-1} and -CH₃ at approximately 1385 cm^{-1} . The peaks seen at 1600 cm^{-1} and 1500 cm^{-1} corresponded to the C=C aromatic ring vibrations. Furthermore, the peak at approximately 1370 cm^{-1} , which corresponded to the phenol O-H in-plane bend, was also observed in the modified PF resins. The intensity of the aliphatic C-H, -CH₂, and -CH₃ peaks in the modified 5 wt% SWCNTs PF resol resin were relatively strong when compared with the Lab. PF resol resin findings. The FT-IR spectra of the SWCNTs-modified PF resol resins demonstrated that extended hydrocarbon chains could be produced by the carbon nanotubes, thus enabling an improvement in the degree of crosslinking. Moreover, increasing the SWCNTs ratio enabled additional hydrocarbon chains to be formed during the synthesis, which helped in modifying the brittleness. However, the aforementioned modified 5 wt% SWCNTs PF resol resin peaks became weaker, which indicated that excess additions of SWCNTs could seriously affect the basic molecular structure of the modified PF resol resin. These results were consistent with previous FT-IR studies of PF resins (Gao *et al.* 2005; Poljansek and Krajnc 2005; Chen *et al.* 2008; Alshawi *et al.* 2019).

Thermogravimetric analysis (TGA) experiments were conducted to investigate the thermal stability of the Lab. PF and SWCNTs-modified PF resol resins. As shown in Fig. 3, in all PF resol resins, thermal degradation occurred in three temperature regions.

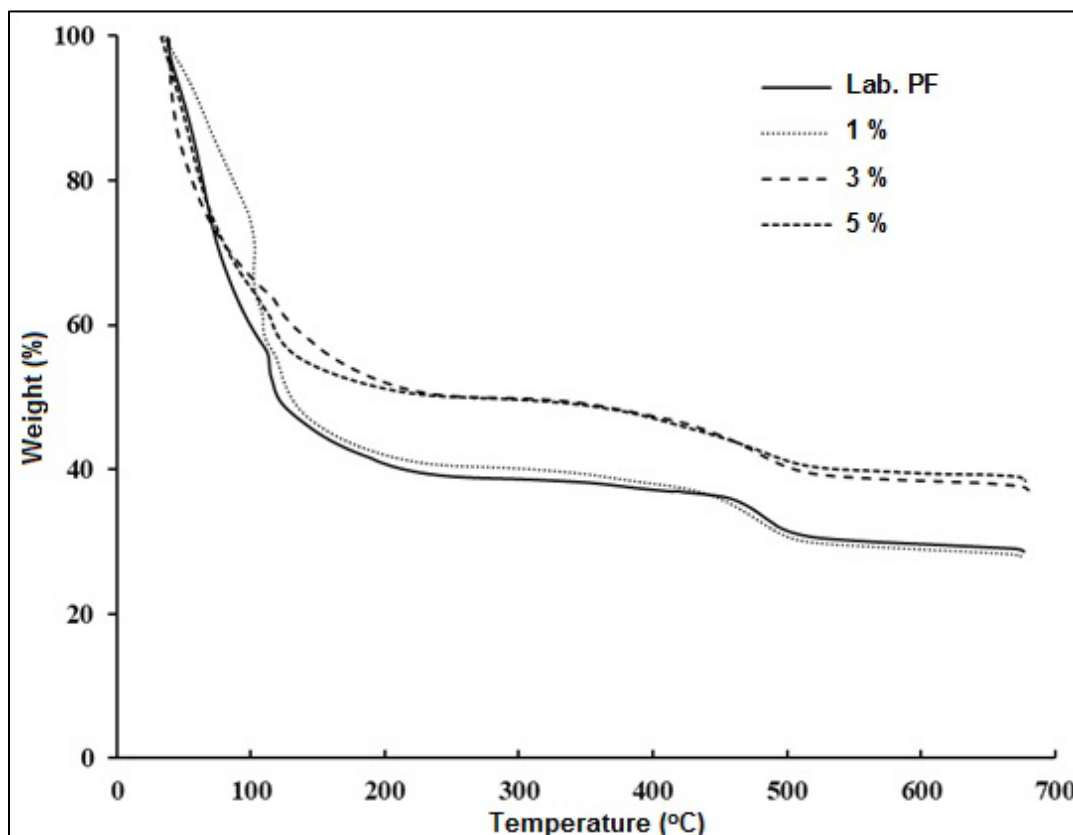


Fig. 3. The TGA curves of the resins under nitrogen atmosphere of the resins

In the first temperature region, up to approximately 180 °C, all the PF resol resins were stable. In the second region, 180 to 400 °C, a major weight loss took place. Wang *et al.* (2009) stated that in the range of 200 to 350 °C, this weight loss was likely because of cross-linking/condensation reactions as well as the removal of terminal groups due to decomposition. However, it is difficult to separate the decomposition range completely. For the last range, it seemed, however, that the weight loss at a temperature greater than 550 °C was primarily caused by decomposition of methylene bridges. The ratio of the additional degradation of phenols to carbonaceous structures was low until 600 °C, compared to that in the region between 180 and 400 °C. The rise in the amount of mass residues from the modified PF resins with the increase in the carbon nanotube ratio was likely caused by the loss of numerous SWCNTs chains. Another possible explanation is that the weight loss of this region was mostly linked to the dehydrogenation of benzene rings (Lee *et al.* 2012).

Adhesive Performance of the Modified Phenol-Formaldehyde (PF) Resol Resins

The adhesive performances of the Lab. PF-bonded wood samples and those bonded with PF resol resins modified with SWCNTs are summarized in Fig. 4.

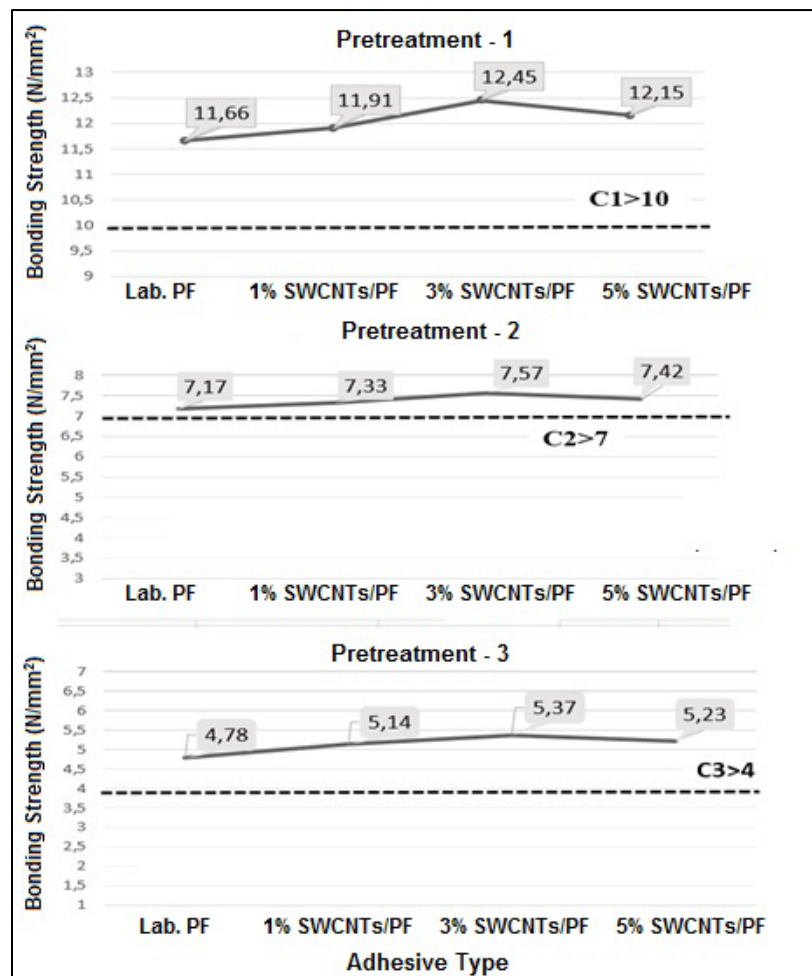


Fig. 4. Adhesive performance of the resins (C1, C2 and C3 durability classes: minimum requirements according to EN standard 12765).

Under dry conditions (Pre-treatment-1), it was found that the bonding performances of all the PF resol resins were highly satisfactory. For instance, the highest shear strength was exhibited by the PF resol resin modified with 3 wt% SWCNTs. The shear strength of the wood samples slightly decreased from 12.45 to 12.15 N/mm² as the carbon nanotube content increased up to 5 wt%. According to EN standard 12765 (2016), under dry conditions, the minimum value of bonding strength must be 10 N/mm². It was determined that all the wood samples bonded with the modified PF resins met the requirements of the standard.

Moreover, the adhesive performance of the modified PF resins for wood bonding matched the performance of the Lab. PF resin, especially under wet conditions (Pre-treatment-2). For Pre-treatment-2, a higher adhesive strength was seen in the wood bonded with the modified PF resins compared to the wood bonded with Lab. PF resin. However, as the amount of SWCNTs in the PF resin was increased by 5 wt%, the bonding strength of the wood samples after Pre-treatment-2 decreased from 7.57 to 7.42 N/mm². The modified PF resins containing 1 wt% to 5 wt% SWCNTs met the requirements for the C2 durability class, according to EN standard 12765 (2016) (as shown in Fig. 4).

The PF resins modified with 1 wt% to 3 wt% SWCNTs rather consistently revealed a favorable adhesive performance compared with the Lab. PF resin under the boiling water treatment (Pre-treatment-3). The bonding strength values decreased drastically after the boiling water treatment, with the highest adhesive performance found in the 3 wt% SWCNTs-modified PF resin, whereas the lowest strength was seen in the Lab. PF resin. The PF resins modified with up to 5 wt% SWCNTs met the requirements for the C3 durability class, according to EN standard 12765 (2016) (4 N/mm²). It can be concluded that the SWCNTs concentration and different exposure conditions were effective on the bonding performance of the SWCNTs-modified PF resol resins. Moreover, previous studies have also reported that it was possible to reinforce polymers with SWCNTs to improve their physical, mechanical, and thermal properties (O'Connell *et al.* 2001; Star *et al.* 2001; Kymakis *et al.* 2002; Kashiwagi *et al.* 2005; Jackson *et al.* 2016).

CONCLUSIONS

1. The thermal stability of the phenol formaldehyde (PF) resins modified with single-wall carbon nanotubes (SWCNTs) was higher than the thermal stability of the reference PF resin.
2. The thermal stability of the PF resins with 3 wt% and 5 wt% SWCNTs content was higher than the thermal stability of the PF resin with 1 wt% SWCNTs. It can be concluded that the adhesive performance of PF resol resins modified with SWCNTs was affected by the SWCNTs concentration and the different exposure conditions.
3. The modified PF resol resins were more effective than the Lab. PF resol resin because of their good adhesive performance under dry and/or wet conditions.
4. The results of the Fourier transform infrared (FT-IR) analysis showed that the peaks of the modified PF resol resins were highly similar to the peaks of the reference PF resin. This similarity demonstrated that the synthesis of the modified PF resins using phenol, formaldehyde, and carbon nanotubes had been successful.

5. The formaldehyde emission level of the PF resol resin sharply decreased with increasing SWCNTs. As such, SWCNTs could be used as an adsorbent for the removal of formaldehyde.
6. This work presents an easy and effective technique for developing novel PF resins with carbon nanotube reinforcement for use in the wood and/or polymer composite industries.

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