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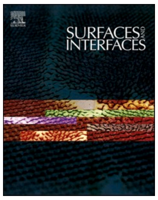

Surface characteristics of phenolic resin coatings

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ABSTRACT

Phenolic resins are commonly used as polymer binders for metal, paper and mineral wool substrates. For such applications, mechanical, adhesive and thermal properties are considered most important, and the effect of synthesis and structural parameters on such end-use characteristics are well-documented. However, surface characteristics of cured phenolic resins can be equally relevant and are often overlooked. Widely used resins are phenol-urea-formaldehyde (PUF) and phenol-formaldehyde (PF). It is believed that the inherent chemistry and curing procedure of these resins result in coatings with distinct surface properties and wettability. To gain more insight into surface characteristics such as morphology, chemical composition and wettability of cured PUF and PF resins, different binder formulations were applied on glass substrates and subsequently characterised by Scanning Electron Microscopy (SEM), Contact Angle Goniometry (CAG) and X-Ray Photoelectron Spectroscopy (XPS). The effect of catalyst, chemical composition and curing conditions on surface characteristics of various PUF and PF coatings were investigated. The curing temperature was found to have a strong influence on surface properties; curing at 200 °C yields a surface with varying degrees of oxidation, differences in linkages between phenolic and urea species, and a lower overall nitrogen content in case of urea-containing coatings, resulting in stronger fluctuations in water-wettability compared to surfaces hardened at lower temperatures.

1. Introduction

The term ‘phenolic resin’ (PR) refers to a versatile class of polymers with an equally versatile range of applications. PRs are used for instance as adhesives and coatings for wood and metal substrates, and their varied applicability is due to their favourable cost, a plethora of options for chemical modifications [1–4], and good mechanical and fire-retardant properties [5–7] after curing.

It is therefore no surprise that PRs are widely used as wood adhesives, applied to for instance fibre- and particleboards or exterior-grade plywood [1,8-16]. Without any prior chemical modification, PRs exhibit good chemical resistance and are known to enhance the adhesive strength of wood substrates [12,14,15]. Extensive research has also been carried out on the effect of chemical modification of PRs with for instance lignin, in order to increase mechanical and adhesive properties when applied on wood substrates [17–21].

The use of PRs however is not limited to just wood, and they can also be employed in ablative materials for air- and spacecraft [7,22], often in the form of a composite reinforced with carbon materials [23], and as binders for fibrous materials such as glass fibres and stone wool [2, 24-26].

One of the simplest phenolic resins are resoles, which are prepared by condensation of phenol (P) with formaldehyde (F) under basic conditions in water, typically with a molar ratio of $F/P \geq 1$. The Lederer-Manasse reaction between phenol and formaldehyde results in the addition of methylol groups at the *ortho* or *para* position of phenol, with the *para* position generally being the most favourable [27]. Upon exposure to heat, methylolated phenolic species condense and form a rigid thermoset network by formation of dimethylene ether (DMEb) and methylene (Mb) bridges between phenolic units (Fig. 1a).

The properties of phenolic resins are heavily dependent on reaction parameters such as the F/P molar ratio, catalyst, pH, and reaction time

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and temperature. The impact of these synthesis variables on structural properties of the resin, such as molecular weight and gel time, and end-use properties like the mechanical strength of the cured resin, are generally well-investigated [2,14,27-31]. Conversely, surface properties of such cured resins, like water-wettability, roughness, and surface morphology, are typically not researched. These characteristics are of considerable importance when the hardened resole is used in applications where it is in direct and near-continuous contact with water. This is for instance the case in coated hydrophilic stone wool used in horti- and floriculture. Here, the wettability of the stone wool substrates with coated fibres is vital to provide water and nutrients to plants at the right amount and rate during different stages of crop growth and development.

The effect of the amount and type of catalyst on the reaction kinetics of forming phenolic prepolymers has already been extensively studied [28,32-36]. It is generally found that organic catalysts, such as triethylamine (TEA), direct the addition reaction of formaldehyde to phenol to the *ortho* reactive sites, whereas for inorganic catalysts the *para* position is typically favoured [32,34,36].

Of interest is also to consider the structure of the prepolymers that are formed, as this can influence the properties of the cured resin. TEA-catalysed phenolic prepolymers are linked mainly by dimethylene ether bridges. Conversely, NaOH-catalysed phenolic prepolymers contain predominantly methylene bridges [34]. As dimethylene ether linkages increase the oxygen content of the final cured resin, it is thought that a PF-resin rich in these bridging groups exhibit a more polar character than PF-resins with predominantly methylene bridges. Furthermore, depending on the curing temperature and the F/P molar ratio, dimethylene ether bridges are converted to methylene linkages, liberating formaldehyde [34]. It is therefore reasonable to expect that not only catalyst type and F/P ratio but also curing temperature and time, influence the water wettability of phenol-formaldehyde films.

Resoles can easily be modified to form resins with improved properties for a vast range of applications [1,3,4,37-40]. As the free formaldehyde content increases with increasing F/P ratio for a given PF resin, it can become essential to modify the resin to limit possible formaldehyde emissions whilst simultaneously enhancing resin properties. In general, this is achieved by addition of melamine, resorcinol or urea (U) to the mixture. For instance, urea acts as a formaldehyde scavenger, yielding methylolated urea species like mono-, di- and trimethylol urea [2]. Co-condensation of methylol phenol with methylol urea yields a phenol-urea-formaldehyde (PUF; Fig. 1b) network with better mechanical and thermal characteristics compared to a PF network [2].

To allow for effective condensation of methylolated urea species with methylolated phenolic species, acidic conditions are required. However, resoles themselves are not stable under acidic conditions, where polycondensates can be formed and precipitate out of solution [2]. Therefore, latent acid hardeners such as $(NH_4)_2SO_4$ are usually employed, which at elevated temperatures neutralise the base. Additionally, through the reaction of ammonium sulphate with free and liberated formaldehyde, hexamethylenetetramine is formed, decreasing the pH [2].

An alternative for the use of inorganic catalysts for the synthesis and curing of phenolic resins is to use tertiary amines or tertiary alkanol amines [2,32,34,41]. Tertiary alkanol amines such as 2-dimethylamino-2-methyl-1-propanol ensure an initial basic pH of the resin. It is assumed that the incorporation of the catalyst in the thermoset network during curing results in acidification, ensuring proper co-condensation between UF- and PF-fractions [2,41]. Tertiary amines such as triethylamine (TEA) and dimethylethanolamine similarly allow for basic reaction conditions. During crosslinking of the resin at elevated temperatures, these catalysts evaporate and the resin is acidified by the methylolated phenolic species present in the system [2,41].

PUF resins can be synthesised from either co-condensing P, F and U in a single step, or via a multi-step procedure whereby PF fractions react with UF fractions [14,31,42-44]. As with PF resins, the molar ratio F/(P + U) has a pronounced influence on structural and thermal properties of PUF resins. Fan et al. [43] found that in presence of an MgO catalyst, upon increasing the formaldehyde content not only the methylolated phenolic species increased in amount, but also the phenolic species bridged to urea by a methylene linkage. Water resistance of PUF has been commonly tested by monitoring the adhesion of the resin to a substrate after immersion in boiling water for a set time [11,14], but chemical and physical changes of the cured resin are not often in the

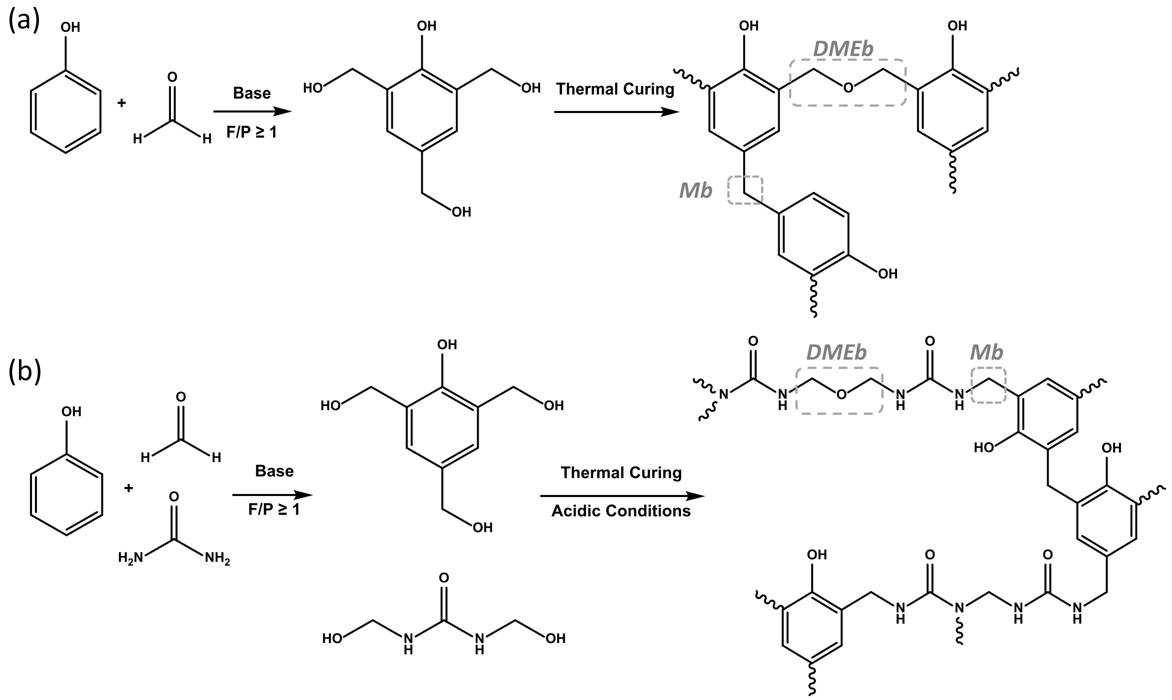

Fig. 1. Synthesis and curing of (a) phenol-formaldehyde (PF) and (b) phenol-urea-formaldehyde (PUF) resin. Different linkages can be formed during curing: dimethylene ether (DMEb) or methylene bridges (Mb).

scope of the research.

One of the few studies which are devoted to characterising the surface energy and water wetting of cured phenolic resins is that of Matsushita et al. [45], where phenol-formaldehyde resins were prepared, cured and subsequently analysed with contact angle goniometry (CAG) and inverse gas chromatography. Phenol-formaldehyde resins with an F/P molar ratio of 2.2 were synthesised using NaOH as catalyst. Coatings prepared thereof yielded water contact angles of 59.9° ± 1.6° after 50 measurements, indicating excellent reproducibility of the water wetting characteristics. Surface energy characterisation by contact angle measurements was determined from Lifshitz-van der Waals and acid-base components. The Lifshitz-van der Waals component was determined to be 31.6 mJ/m^2, which accurately reflects the relatively large non-polar content of the PF-coating. However, this is offset slightly by the contribution of the hydroxyl group of the phenolic species, as seen from the electron-donor part of the acid-base component (18.8 mJ/m^2).

Lee et al. [46] investigated curing parameters of phenol-formaldehyde resins by monitoring the curing behaviour of resins synthesised with F/P of 1.3, 1.9 and 2.5 and an NaOH catalyst. Moreover, surface energy of the resulting PF networks was assessed using CAG on coatings cured at 140 °C, 150 °C, 160 °C for times up to 60 min. It was observed that the water contact angle on PF surfaces increases steadily with increasing curing time. Expectedly, the surface energy of these coatings decreased with increasing curing time, mainly because of a decline in the polar component of the surface energy. The authors postulate that these results indicate a surface which is more deprived of polar hydroxyl groups for longer curing times but note that a surface re-orientation effect of certain groups is still likely to occur. Unfortunately, dynamic contact angle measurements were not performed to test if this was indeed the case.

In this research, surface characteristics and water-wettability properties of PF and PUF coatings were investigated. As evident from the overview given above, for PF and PUF resins, and coatings prepared thereof, there is already ample knowledge of their structural, mechanical and adhesive properties, but the relation between surface properties and wettability remains to be investigated. Therefore, in this work phenolic resins synthesised with either potassium hydroxide (KOH) or triethylamine (TEA) as catalyst, with and without a urea component, were applied as coatings on model glass substrates. The water-wettability of the different coatings was determined with CAG and the effect of water on the surface morphology was investigated by scanning electron microscopy (SEM) studies. Additionally, the response of the different coatings to repeated wetting and dewetting of the surface was studied through successive dynamic contact angle measurements. The influence of cure properties on static water contact angle measurements was investigated by determining the surface chemistry using X-ray photoelectron spectroscopy and correlating the composition to wettability. In this way, a greater understanding of the impact of catalyst, chemistry and curing conditions on surface properties of phenolic resin coatings is obtained.

2. Experimental

2.1. Materials

The commercial PUF resin was kindly provided by ROCKWOOL A/S (Hedehusene, Denmark). Ammonium sulphate ($\geq$ 99%), triethylamine ($>$99.5%), urea ($\geq$ 99%), and phenol ($>$ 99%) were obtained from Sigma-Aldrich. Ammonia 25 wt% in water and K_2SO_4 ($\geq$ 99%) were obtained from Merck. Formaldehyde 37 wt% solution in water (including 10–15% methanol stabiliser) was purchased from Thermo-Scientific. Before use phenol was stored at room temperature under P_2O_5 in a desiccator and commercial PUF resin was stored in a freezer at −19 °C; all other chemicals were used as received.

2.2. Methods

2.2.1. Syntheses

Salt-free PUF resin (PUF-TEA; F/P = 3.5) was synthesised as follows: phenol (20 g; 0.21 mol), formaldehyde (60 g; 54 mL; 0.74 mol) and triethylamine (5.8 mL; 0.04 mol) were charged into a three-neck flask equipped with a stirring bar, reflux condenser and thermometer. Next, the methylolation and oligomerisation of the phenolic species was carried out at 70 °C whilst stirring at 180 RPM. After 4 h a solution of urea (18.99 g, 0.32 mol) in water (30 g) was added to the flask and the reaction was continued for 2 h at 55 °C. Thereafter, the reaction was quenched by placing the reactor in an ice bath and the resin was stored in a fridge at 5 °C until further use.

Salt-free PF resin (PF-TEA; F/P = 2.6–3.4) was synthesised as follows: phenol (e.g., 20 g; 0.21 mol), formaldehyde (e.g., 44 g; 39 mL; 0.54 mol) and triethylamine (e.g., 5 mL; 0.04 mol) were charged into a three-neck flask equipped with a stirring bar, reflux condenser and thermometer. The reaction between phenol and formaldehyde was carried out for 1 hour at 85 °C whilst stirring at 180 RPM. Thereafter, the reaction was quenched by placing the reactor in an ice bath and the resin was stored in a fridge at 5 °C until further use.

2.2.2. Binder preparation

The commercial PUF binder (PUF-KOH; F/P = 3.3, P/U = 1.3, urea content approximately 45% based on solids; solids content approximately 50%) was prepared by addition of ammonia (0.03 g/g PUF-KOH resin) and ammonium sulphate (0.09 g/g PUF-KOH resin) to the commercial PUF resin and stirred for at least 1 hour with a magnetic bar before application on glass substrates.

2.2.3. Coatings preparation

The phenolic resin coatings were applied by means of dip coating using a Biolin Scientific KSV NIMA LayerBuilder with an immersion and withdrawal speed of 100 mm/min, using the three different binder formulations. Soda lime glass microscopy slides were used as substrates, which were cleaned by sonication for at least 30 min in acetone and in isopropyl alcohol, consecutively, after which they were wiped dry with lint-free paper and further blown dry with air. The applied binder layers were subsequently cured in either an oven for 10 or 20 min at 200 °C under air atmosphere, or in a closed chamber with a heating plate at 150 °C under an N_2 or air flow of approximately 150 L/h at 1 bar. Cure time for PUF-TEA and PUF-KOH inside the closed chamber was 20 min and for PF-TEA coatings 15 min. The resulting coating thicknesses were between 4 and 12 μm (estimated with SEM or contact profilometry).

2.2.4. ^{13}C-nuclear magnetic resonance measurements

Liquid resins were characterised by qualitative ^{13}C NMR on a Bruker Advance III HD 400 MHz spectrometer using DMSO-d6 as solvent. Spectra are the average of 160 spectra recorded with a recycle delay of 4 s.

2.2.5. Water contact angle measurements

Static and dynamic contact angle measurements were conducted on a Dataphysics OCA30 goniometer, using MilliQ water (resistivity of 18.2 MΩ · cm) as probe liquid. For static water contact angle measurements, droplet volumes were 2 μL and measurements were performed on at least three different spots per coating, recording the contact angle for at least 30 s using the OCA20 software. Values reported are the average of all individual left and right contact angle values after 30 s measurement time. Dynamic contact angle measurements were carried out by first placing a droplet of 2 μL on the coating surface. From there, the droplet volume was increased and decreased by 25 μL respectively at a rate of 0.25 μL/s. The advancing and receding contact angle were determined following the procedure of Korhonen et al., where the dynamic contact angles are taken from the data points where the contact angle remains more or less stable, but the droplet volume is still changing [47].

2.2.6. *Interfacial tension measurements*

The interfacial tension (IFT) of the water-air interface of water which had been in contact with a coating surface was measured on a Dataphysics OCA30 goniometer, using a pendant drop method preceded by dynamic contact angle measurements as shown schematically in Fig. 2. First, a droplet of MilliQ water of approximately 2 µL was deposited on the coating surface using a needle of 0.52 mm diameter. From there, the droplet volume was increased by 30 µL at a rate of 0.25 µL/s. Then, an empty needle of 1.65 mm in diameter was injected into the droplet after which 28 µL of the droplet was repeatedly withdrawn into and dispensed from the needle at least 2 times at a rate of 0.25 µL/s. Finally, the droplet was suspended in air from the needle to determine the interfacial tension using the OCA20 software. The IFT was recorded for at least 60 s at a frequency of 1 datapoint per second. Reported values are from the average of one IFT measurement on two different coatings.

2.2.6. *Scanning electron microscopy*

Coating surfaces were characterised using scanning electron microscopy (SEM; ThermoFisher Scientific Phenom Pro-X and ThermoFisher Scientific Quanta 200 3D-FEG) and energy-dispersive X-ray spectroscopy (EDX; ThermoFisher Scientific Phenom Pro-X). All surfaces were coated with a thin gold layer (approximately 5 nm) using a Quorum Technologies Q150TS sputter coater to minimise charging effects.

2.2.7. *Attenuated total reflection infra-red spectroscopy*

Bulk chemistry of coatings of PUF-TEA and PF-TEA was characterised with attenuated total reflection infra-red spectroscopy (ATR-FTIR) on a ThermoFisher Nicolet iS20 with diamond ATR crystal, scanning from 450 – 4000 cm^{-1} and averaging 8 scans per measurement.

2.2.8. *X-ray photoelectron spectroscopy*

Chemical composition of coating surfaces (approximately up to the first 10 nm) was obtained by means of X-ray photoelectron spectroscopy (XPS), using a ThermoFisher Scientific K-Alpha instrument with an aluminium anode (monochromated Al Kα radiation of 1486.6 eV) and a flood gun for charge compensation. Binding energy spectra of C_{1s} ($E_{b,C1s}$ = 284.8 eV), N_{1s} ($E_{b,N1s}$ = 399 eV) and $O1s$ ($E_{b,O1s}$ = 532 eV) electrons were recorded using ThermoFisher Scientific Avantage software, using 30 scans, a pass energy of 50 eV and a step size of 0.1 eV. Data was processed using CasaXPS software, where the binding energy spectra were used to obtain atomic concentrations for each coating, employing a Shirley background and relative sensitivity factors for each element ($RSF_{C1s} = 1$, $RSF_{O1s} = 2.881$, $RSF_{N1s} = 1.676$). The C_{1s} spectrum was charge corrected so that C—C bonds corresponded to a binding energy of 284.8 eV.

The C_{1s} binding energy spectrum was deconvoluted into C—C/C—H/C═C (284.8 eV), C—O/C—N (286.4 ± 0.2 eV), C═O/N—C═O (287.4 ± 0.3 eV) and NCON (289 ± 0.2 eV) [25] to determine the relative amount of different bonds or functionalities at the surface. Besides this, a CO/CC ratio was determined, defined as the fraction of oxygen-carbon to carbon-carbon bonds [48]:

$$\frac{CO}{CC} = \frac{C_{286.4} + C_{287.4} + C_{289}}{C_{284.8}} = \frac{(C-O) + (C=O) + (NCON)}{C-C} \qquad (1)$$

where $C_{284.8}$, $C_{286.4}$, $C_{287.4}$ and C_{289} refers to the atomic percentage of C—C/C—H/C═C, C—O/C—N, C═O/N—C═O and NCON contributions, respectively.

3. Results & discussion

3.1. *Resin definition and characterisation*

The present work focuses on characterising surface properties of coatings made from phenolic resins by varying curing conditions such as time, temperature and atmosphere. PF binders are already ubiquitously used and to some degree their water wettability has been studied before [45,46]. However, starting from this system, the chemical complexity was chosen to be increased by including coatings made from PUF binders in the scope of this research. Hereby, the influence of catalyst type, organic or inorganic (TEA versus KOH), was considered, allowing for a complete comparison of the chemistry (PF versus PUF), surface roughness and morphology, and effect of curing conditions (temperature, time, atmosphere) of the various phenolic resin coatings.

Henceforth, coatings prepared from commercial PUF binder are referred to as PUF-KOH, those prepared from salt-free, own-synthesised PUF binder will be referred to as PUF-TEA and coatings made from salt-free, own-synthesised PF binder are termed PF-TEA.

Fig. 3 shows the qualitative ^{13}C NMR spectra of PUF-KOH, PUF-TEA, and PF-TEA resins. For all resins, characteristic signals of substituted phenoxy and aromatic carbon atoms (151–158 ppm and 127–135 ppm respectively), as well as those of the methylol carbon bound to phenol (65 ppm and 61 ppm respectively), indicate that the methylolation of phenol was successful [14,40]. Moreover, oligomer formation was confirmed by the presence of peaks corresponding to methylene bridges at 36.1 ppm and 41.5 ppm. A multitude of signals can be observed in the phenoxy carbon and aromatic carbon region. This is due to the large variation in both the type of group (e.g., -H, -COH, -COC-, …) and degree of substitution of the phenyl ring. The most significant differences between the spectra are the peaks from 158 to 163 ppm. These peaks correspond the presence of free and methylolated urea. An additional contribution of the methylol urea group is seen at 65 ppm, which mostly coincides with the phenolic methylol group [40]. This indicates that the PUF resins are blends of UF and PF, with prior to curing still some degree of free urea. The ^{13}C NMR spectrum of PF-TEA shows a stronger

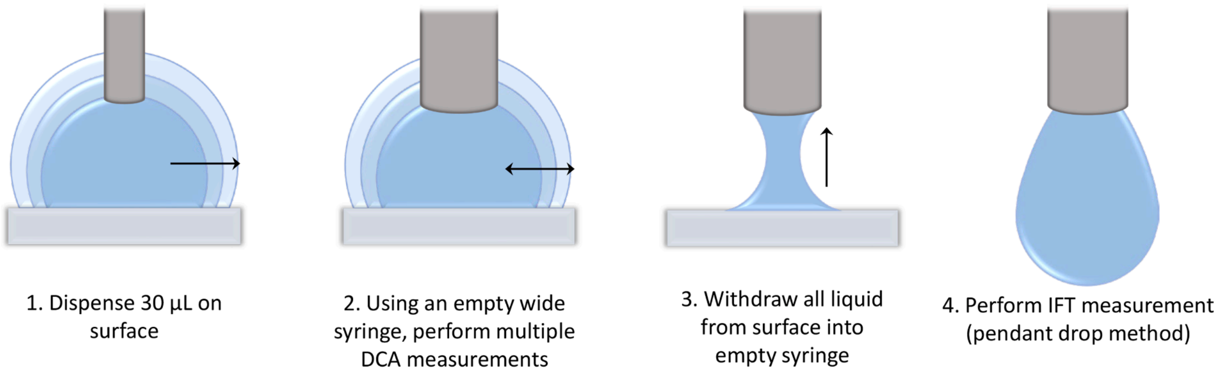

Fig. 2. Method for combining multiple dynamic contact angle measurements with measuring the interfacial tension of the water droplet used for probing the coating surface.

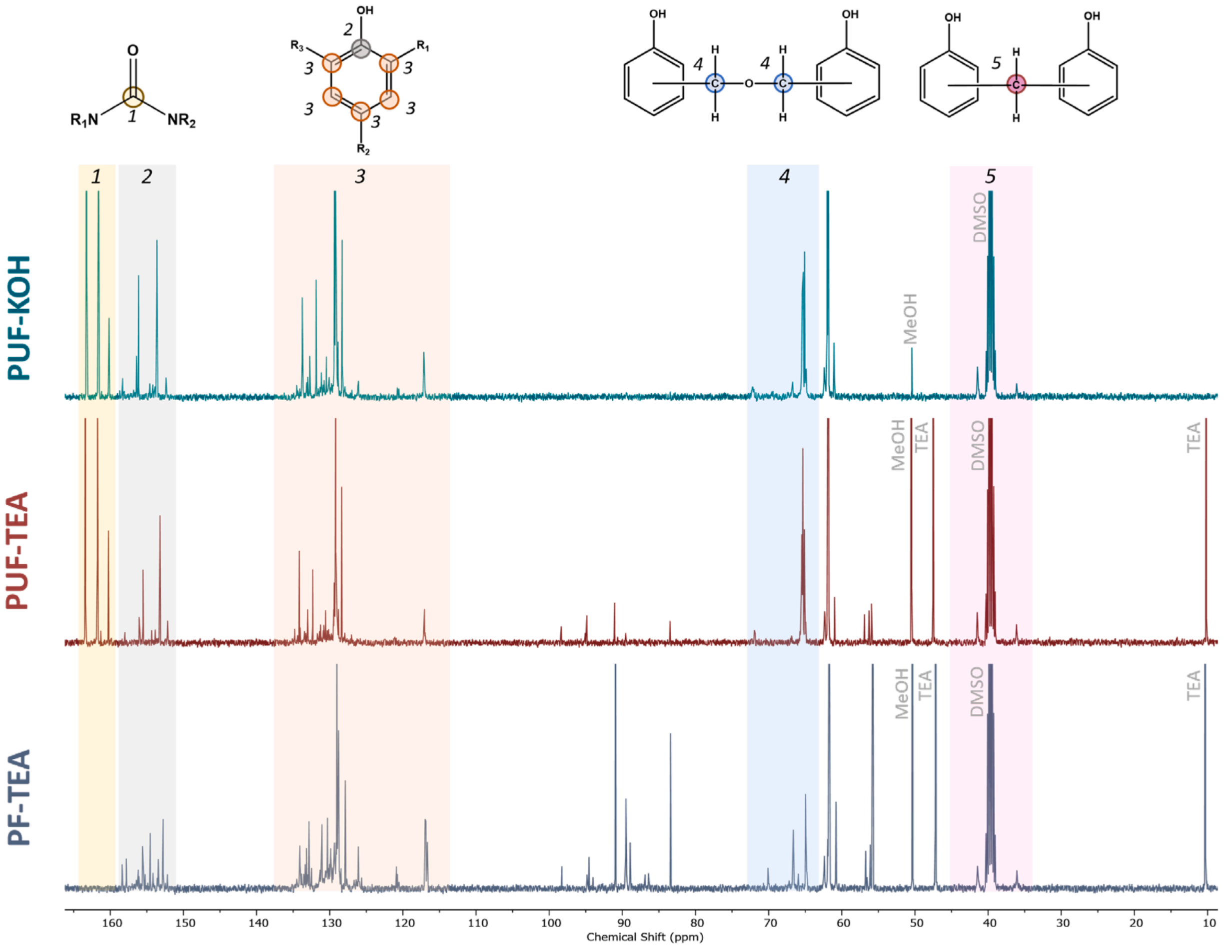

Fig. 3. ^{13}C NMR spectra of PUF-KOH, PUF-TEA and PF-TEA resin measured in DMSO-d6, which was used as internal reference at a chemical shift of 39.5 ppm. The presence of methanol in the spectra is from the formaldehyde solution, which contains methanol as stabiliser. Some characteristic areas and corresponding structures are indicated. R_1, R_2, and R_3 refer to either a methylol group, hydrogen atom, dimethylene ether or methylene bridge.

presence of reactive formaldehyde adducts (80–100 ppm) compared to PUF-TEA because of a shorter reaction time. Moreover, the shorter reaction time also means that the free phenolic content is larger than for the other resins, based on the intensity of the peak at 158 ppm which corresponds to the phenoxy carbon of unsubstituted phenol. Last, for the PF-TEA resin, there is a larger content of unsubstituted *para* phenolic species, indicated by the peak at 121 ppm.

Batch-to-batch, the own-synthesised PF-TEA and PUF-TEA resins showed only minute variations in their ^{13}C NMR spectra and solids content (approximately 38% for PF-TEA and 34% for PUF-TEA), indicating that the synthesis procedure allowed for obtaining reproducible resins that could be used for further studies.

Comparing the different resins with each other, main structural differences can be found in the formed species, with the PUF resins naturally containing methylolated) urea. The PF resins overall tended to be less further reacted as seen by the free and unsubstituted phenol.

3.2. *Surface morphology of phenolic coatings*

PUF-KOH, PUF-TEA and PF-TEA resins were applied on glass substrates by dip-coating, and subsequently cured at elevated temperatures inside an oven or a closed chamber equipped with a hot plate.

It is well-known that wetting of surfaces by water is governed not only by chemical, but also by physical (in)homogeneity. Therefore, surface characterization for the phenolic resin coatings before and after wetting with water was conducted by SEM. For PF-TEA and PUF-TEA surfaces, a scratch was made on the coating to allow for proper focussing on the surface. Both pristine PF-TEA and PUF-TEA surfaces are largely devoid of features, indicating that there is no initial surface roughness influencing water wettability (Fig. 4a and b). Deposits of particles could be seen near the edges of PUF-TEA and PUF-KOH coatings cured in the oven, possibly from unreacted urea or UF which precipitated out of solution during curing and drying of the coating (Figure S1). Lowering the curing temperature or increasing the coating thickness by increasing the withdrawal speed during dip coating was found to minimise the formation of these deposits near the film edges. This could be attributed to a lower difference between evaporation rates of the solvent at the edges versus the middle of the coatings, thereby preventing urea or UF fractions to precipitate out of solution.

A vastly different surface morphology was observed for PUF-KOH coatings, where crystals and surface irregularities were visible (Fig. 4c and d). Based on EDX analyses, these crystals were determined to be K_2SO_4, the origin of which could be traced back to the catalysts used during the synthesis (KOH) and curing ($(NH_4)_2SO_4$) of the PUF-KOH resin. It was found that the K_2SO_4 crystals induce significant surface roughness (average roughness $R_a = 2.6 \pm 0.3$ μm; estimated with a laser scanning confocal microscopy measuring the top layer), with crystals also seen throughout the cross-section of the film, pushing the coating surface upwards.

Surface roughness is known to be able to affect the apparent contact angle, as described through wettability models such as those proposed by Wenzel [49], Cassie and Baxter [50], and Marmur [51]. However, in this specific case the surface roughness is bound to vary during the measurement, on account of dissolution of the salt crystals into the

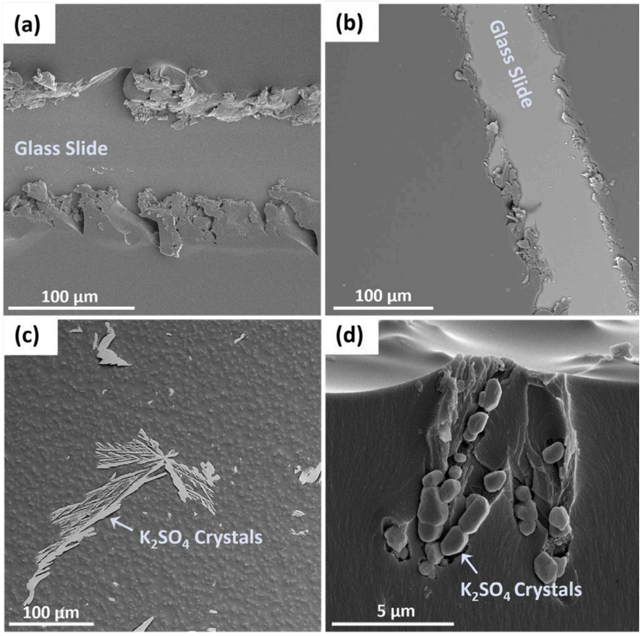

Fig. 4. Scanning electron micrographs of surfaces of (a) PF-TEA, (b) PUF-TEA and (c) PUF-KOH coatings. A cross-section of a PUF-KOH coating is shown in (d), where K_2SO_4 crystals are visible throughout the thickness of the coating.

water droplet, as well as after the measurement, due to the redeposition of crystals on the surface. This leads to a complex and dynamic influence of crystal-induced roughness on the wetting of PUF-KOH surfaces by water. This could be discerned from the individual wetting profiles of measurements carried out on PUF-KOH coatings, which were in general fluctuating more over measurement time than for instance wetting profiles for PUF-TEA coatings. This also has implications for applications where additives such as surfactants are included in the binder formulation, as interactions between crystals and additives are to be expected. For example, it is well-known that additives in the form of ions, small- or macromolecules influence nucleation, growth, aggregation, dissolution and growth habit of crystals [52–56]. As a result, the distribution of additives throughout the coating can also be affected, and hence surface properties such as water wettability can vary.

Modifying PF resins to PUF is expected to increase the hydrophilicity of coatings on account of a larger content of hydrophilic moieties. Somewhat surprisingly, the transient water contact angle values of the coatings prepared from the phenolic resins are quite similar (Fig. 5a). The tested F/P molar ratios were found to not have an influence on the average water contact angle value. For the probed coatings, within the first 10 to 15 s of measuring, there is typically a non-linear decrease in the water contact angle value which is a result of spreading of the droplet on the surface, irrespective of the phenolic resin type. Spreading can be seen as an increase in the base diameter of the droplet in the first stages of the measurement (Fig. S2). The subsequent, often linear, decrease is due to water penetration into the surface layers and (water droplet) evaporation [57,58]. In case the contact line of the water droplet is pinned, the radius or base diameter remains constant during evaporation, but the volume and contact angle decrease [59]. It is important to note that in case of surface effects such as rearrangements due to a change in interface (i.e., from coating-air to coating-water), after a few tens of seconds it can be assumed that this response has occurred and its influence on the contact angle value is exerted [60]. For fair comparison and to account for possible surface responses of the coatings to water, henceforth water contact angles measured after 30 s are used for comparison.

Interestingly, for some of the phenolic coating surfaces a macroscopically visible drying mark could be discerned after water contact angle measurements at the position where water droplets had previously been deposited. For PUF-KOH, SEM imaging of these spots show a significant change in the amount of K_2SO_4 crystals on the surface, which initially dissolved from the surface layers into the water droplet and were then redeposited upon droplet evaporation (Fig. 5b). For PF-TEA and PUF-TEA, wetting and allowing the droplet to evaporate from the surface typically yielded wrinkles and cracks, likely a result of stress release and dissolution of unreacted moieties (Fig. 5c and d). On top of that, the surface of phenol-urea-formaldehyde coatings contained new urea deposits after wetting and drying the surface. No matter the phenolic resin coating, contact with water results in changes in the surface morphology. In all cases mentioned above, subsequent wetting of these surfaces is expected to be affected by these changes on the surface on account of introduction of chemical and physical heterogeneity.

3.3. *Influence of surface changes on wettability*

It is clear that for PUF-KOH, PUF-TEA, and PF-TEA the coating surface is affected by water, especially if water is allowed to evaporate from the surface. Besides surface roughness, also chemical heterogeneity is introduced. To investigate the effect of leachables (such as K_2SO_4 and urea) on the water wettability, coatings were subjected to repeated dynamic water contact angle measurements, after which the interfacial tension of the water droplet was determined. Combined with scanning electron microscopy characterisation of the measured spots, this allows to elucidate possible factors affecting the water contact angle measurements.

Fig. 6 shows the advancing water contact angle (ACA) when repeatedly measuring on a PUF-KOH, PUF-TEA, and PF-TEA surface. The first measurement for these experiments always occurs on a pristine coating surface. For all probed coatings, it was observed that the first determined ACA is higher than the subsequently measured advancing contact angle values, although for PF-TEA this effect appeared to be less strong. While the actual values of the advancing contact angles with successive measurements were found to vary between coatings made from the same resin, as well as for coatings of the various phenolic resins, the trend of an initial change and the subsequent slower increase in wettability of the surfaces was seen for all the phenolic resin coatings measured this way. In principle, these changes in wettability can be the result of four different effects: 1) leaching of surface-active species into the water used for measurements, 2) plasticisation of surface layers, 3) introduction of surface roughness due to and during the measurement and 4) reorientation of surface groups either into the bulk or towards the coating-air interface in between measurements, or the coating-water interface during measurements.

To account for the possible influence of surface active leachables from the coating surface into the water droplet during contact angle measurements, the water-air interfacial tension of the probe liquid was determined after repeated dynamic contact angle measurements. Interestingly, the interfacial tension of water droplets used for the successive dynamic water contact angle measurements on PUF-KOH, PUF-TEA, and PF-TEA surfaces show similar values, which is approximately that of pure water (72.1 ± 0.4 mN/m), see Table 1. Additionally, refreshing the water in between successive dynamic contact angle measurements was found to have little influence on the obtained ACA value (Fig. S3). This implies either that there is no leaching of surface-active components into the water droplet, or that the concentration of such species is too low to have an impact on the interfacial tension and therefore cannot influence the results. Similar results were obtained for cured PUF-TEA and PUF-KOH resin powders (particles size range 180–425 µm) which were in contact with water for an extended period (Table 1). After filtrating the powders, the water-air interfacial tension of the used water was evaluated, and again yielded values close to that of pure water.

To investigate the possible effects of plasticization and reorientation,

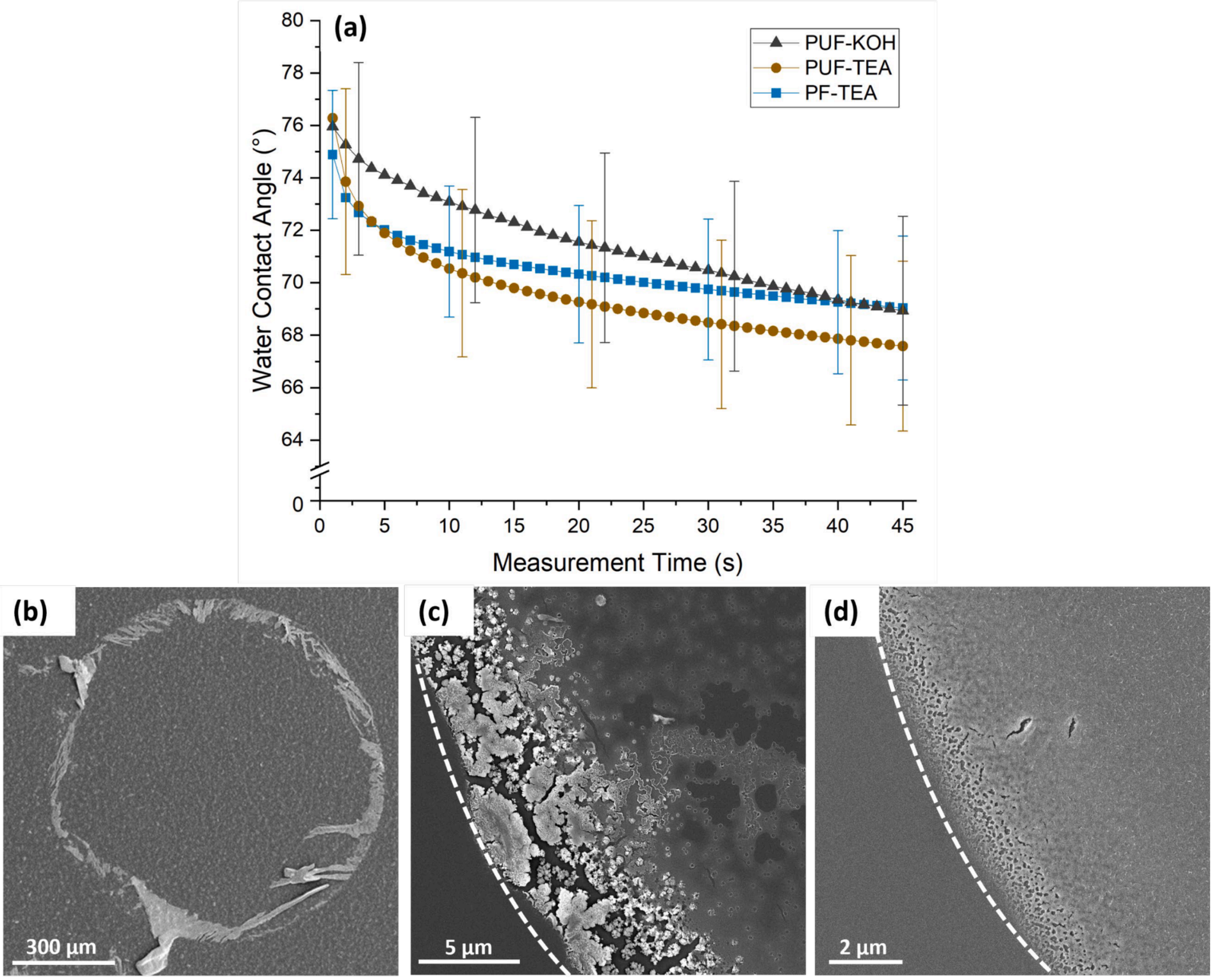

Fig. 5. Average water contact angle as function of measurement time (a) on PUF-KOH, PUF-TEA, and PF-TEA coatings. PUF-KOH was cured in an oven at 200 °C for 10 min, PUF-TEA was cured in a closed chamber at 150 °C for 20 min and PF-TEA was cured in a closed chamber at 150 °C for 15 min. Scanning electron micrographs of (b) PUF-KOH, (c) PUF-TEA and (d) PF-TEA coating surfaces after locally wetting with water and drying in air, allowing the water droplet to evaporate from the coating surface. Dotted lines were added to the micrographs (c) and (d) to indicate the boundary between pristine and wetted parts of the coatings.

drying times of 1 h and 2 h under room conditions were included in between some of the measurements, as shown in Fig. 6. For the three different coatings, a slight increase in the advancing water contact angle value is seen where the obtained values approximate that of the second measurement upon drying the surface in air. This indicates a possible reversal of surface plasticisation or the occurrence of a reorientation of surface groups, which for polymers are known to occur as a result of a change in interface conditions (e.g., due to a change in the interface from coating-water to coating-air) [61–64].

It is also noticeable that the initial water ACA measurements in Fig. 6 appear to permanently alter the surface. After this initial surface change, drying the surface yields a reproducible increase to approximately the ACA value of measurement 2. To some degree, the reason that the ACA value does not increase to above this value is likely due to too short drying times but might also be attributed to a change in surface morphology and roughness. However, typically only significant morphology changes were observed upon evaporating water directly from the coating surface, as shown in Fig. 7. The SEM micrographs in Fig. 7 show that the surface contains cracks and (urea) deposits, which was not observed as a direct result of the dynamic measurements, but rather as a result of water evaporation from the surface. Additionally, even if roughness was induced by the successive dynamic contact angle measurements, the decrease in surface wettability upon drying would imply that roughness changes cannot solely explain the observed behaviours of the phenolic resin coating surfaces.

Presumably, the presence of water can induce plasticisation and/or surface rearrangement effects. This is supported by the work of Zhao et al. [65] who studied the effects of moisture on the relaxation mechanisms of cross-linked PF-resins and found that water acts as a plasticiser by breaking hydrogen bonds between the hydroxyl groups of the network. Additionally, Zaldivar et al. [7] observed a decrease in glass transition temperature (T_g) for carbon fibre-phenolic resin composites with increasing moisture content, where the strength of the decrease was influenced by the state of cure.

While the T_g at varying relative humidity has not been determined within this research, it was found that free-standing thin PUF-TEA films (approximately 40–80 µm) exhibit a dimensional change at elevated relative humidity, indicating the possibility of such a cured system to swell (Fig. S4). Moreover, to some extent the cracks in the surface of the PUF-TEA coating shown in Fig. 7 can be a result of swelling and tension forces due to water uptake and evaporation, respectively. Thus, continued plasticisation of the surface during successive contact angle measurements can be expected and would allow for the observed reversibility of the advancing contact angle values upon drying, as shown in Fig. 6.

The possibility of surface rearrangements has not been explicitly investigated in this research. However, it is known that reorganisation at the surface as a result of a change in environment can occur even for glassy polymers, as such restructuring typically readily occurs over a distance of only 1–2 nm [66]. Furthermore, Lu et al. [61] have shown in

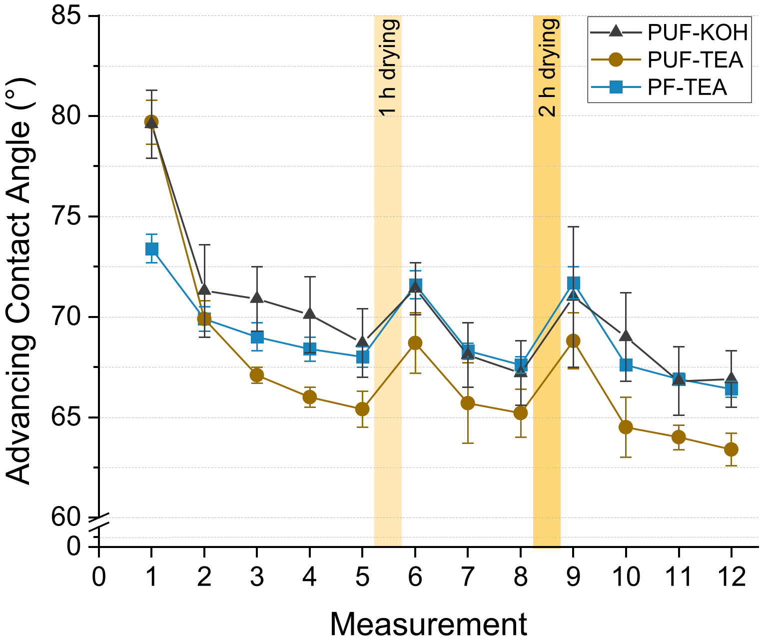

Fig. 6. Successive advancing contact angle measurements on a PUF-KOH, PUF-TEA, and PF-TEA coating surface. In between measurement 5–6, coatings were dried in air under room conditions for 1 h before continuing. In between measurements 8–9, coatings were dried in air under room conditions for 2 h before continuing. Standard deviations are obtained from the plateau where the advancing contact angle is more or less constant whilst the droplet volume is increasing.

Table 1
Water-air interfacial tension (IFT) values for water used for repeated dynamic water contact angle measurements on and immersion of PUF-KOH, PUF-TEA, and PF-TEA coatings, respectively.

Sampleet	$IFT_{coating}$ [a] (mN/m)	IFT_{powder} [b] (mN/m)
PUF-KOH	72.3 ± 0.3	72.3 ± 0.2
PUF-TEA	72.1 ± 0.2	71.9 ± 0.2
PF-TEA	72.2 ± 0.2	–

[a] IFT measurement of water used for at least 3 successive dynamic contact angle measurements.

[b] IFT measurement of water which contained cured, powdered resin for 1 day (0.5 g resin in 15 mL water).

their research that for a bisphenol type phenolic resin the orientation of surface phenyl groups depends on the relative humidity of the environment, and that changes in the surface structure are reversible. Because this could imply that measurement conditions will strongly affect the obtained results, coatings of PUF-TEA were stored at elevated relative humidity (approximately 92% RH) for up to 23 days and their wettability was probed at various intervals (Fig. S5). No discernible changes in water contact angle were found. It should be noted that this does not exclude the possibility of rearrangements or reorientations on the surface. However, for the coatings investigated in this work effects of humidity on the wettability appeared to be minimal. It should be noted that the effect of relative humidity on the dynamic contact angles was not assessed but given the unaffected static contact angle this influence is believed to be minimal as well.

Overall, the observed effects of repeated wetting on the phenolic

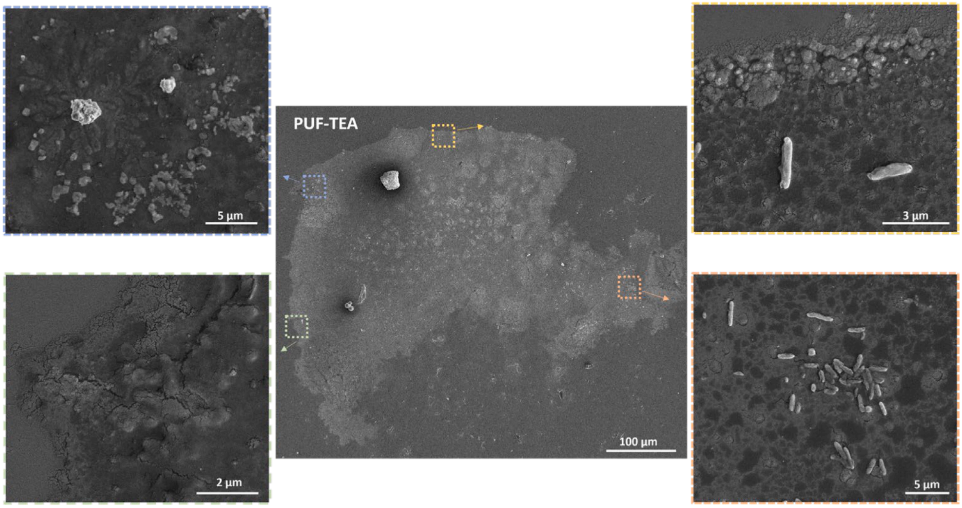

Fig. 7. Scanning electron micrographs of a PUF-TEA coating surface after repeated dynamic contact angle measurements on the same spot, after allowing water to evaporate from the surface, after the very last measurement. The identified regions in show different effects and features on the surface such as crystallisation and deposition of urea-species, and cracks in and dissolution of surface layers.

coatings indicate that first wetting of the surface greatly alters its surface characteristics. An interplay between locally induced morphology changes, compositional drift, and plasticisation effects are suspected to be at the basis of these surface changes.

3.3. *Influence of cure conditions on surface composition and wettability*

For the different phenolic coatings, special attention was paid to the coating surface composition, determined by X-ray photoelectron spectroscopy, whilst varying curing parameters such as temperature and time (Table 2). Representative XPS spectra of the coatings can be found in the Supporting Information. As it was found that for PUF-KOH surfaces the S:C ratio was typically smaller than 0.002, it is assumed that the contribution from K_2SO_4 crystals to the oxygen content is minimal and can therefore be neglected.

The main influence on chemical composition was found to be the curing temperature rather than the time, as coatings cured in an air convection oven at 200 °C have a similar surface composition for 10 and 20 min of hardening time (see Table 2). It is likely that processes that influence and define the final surface composition and state of cure occur relatively rapidly, and do not vary significantly within the studied variations of curing time. Additionally, for PUF-TEA the amount of nitrogen in the surface layers is consistently lower when curing at 200 °C, showing to be considerably decreased compared to 150 °C. The results for PUF-KOH cured at 200 °C match well with the ones of PUF-TEA cured at the same temperature. In these cases, thermal degradation of UF species could have occurred at the elevated hardening temperature, leading to a surface which is less enriched by UF fractions.

The CO/CC ratio as determined by XPS can be used a measure of the polarity of the surface, as it relates to the state of cure of the phenolic resin and for PUF-TEA and PUF-KOH takes into account the urea carbonyl content. Also, for PF-TEA coatings cured at 200 °C, this CO/CC ratio is lower than for coatings hardened at lower temperatures.

Overall, there appear to be two causes for the decrease in CO/CC ratio with increasing curing temperature. First, in line with the corresponding N:C ratios, the curing conditions dictate the actual urea content at the surface of PUF-KOH and PUF-TEA, which then affects the polarity of the surface. Next, oxidation can occur, which is offset by the selective evaporation of formaldehyde from dimethylene ether bridges, converting these into methylene linkages between PF and UF species. Examination of the deconvoluted O 1 s spectra of the different phenolic resin coatings showed an increase in the full width at half maximum (FWHM) when curing at 200 °C, with the peak broadening towards lower binding energies. This could correspond to the presence of additional C=O bonds (see Figs. S6–S8 in the SI) [67]. Peak broadening was best seen for PF-TEA coatings, where the FWHM of the O 1 s spectra increased on average from 1.6 eV to 2.0 eV.

Table 2
Overview of chemical composition, estimated with XPS, of phenolic resin coatings cured in an air convection oven varying the curing temperature and time.

Sample		Cure conditions	O:C	N:C	CO/CC
PUF-KOH	Oven	200 °C 10 min	0.29 ± 0.02	0.15 ± 0.01	0.70 ± 0.03
PUF-TEA	Oven	200 °C 10 min	0.29 ± 0.01	0.14 ± 0.01	0.64 ± 0.05
		200 °C 20 min	0.28 ± 0.02	0.15 ± 0.01	0.62 ± 0.03
		150 °C 20 min	0.31 ± 0	0.22 ± 0.01	0.83 ± 0.02
PF-TEA	Oven	200 °C 10 min	0.29 ± 0.01	–	0.39 ± 0.01
		200 °C 20 min	0.31 ± 0.01	–	0.37 ± 0.01
		150 °C 20 min	0.28 ± 0.01	–	0.49 ± 0.03

Besides XPS data showing oxidation in the first few surface layers (a few nm deep), ATR-FTIR analyses (up to 1 μm deep) also indicate that the "bulk" chemistry of the cured resins is affected by curing temperature (Fig. S9). For instance, for PUF-TEA hardened at 200 °C the presence of carboxylic acid or aldehyde groups was observed (C=O stretch at 1720 cm^{-1} and C=O overtone at 3620 cm^{-1}). The FTIR spectra of PF-TEA coatings cured at 200 °C are also markedly different from the spectra of PF-TEA hardened at 150 °C, with an increased signal at 1680 cm^{-1} and 1650 cm^{-1} which could indicate a larger number of C=O moieties [68]. Conley and Bieron [68] similarly observed chemical changes for phenolic resins when heated, albeit only after heating cured resins in air for several hours. Their observed changes included decreases in the number of methylene bridges between phenolic species, and an increase in for instance the -COOH and C=O content.

The effect of curing atmosphere was also investigated by curing the different phenolic resins inside a closed chamber under controlled nitrogen or air conditions. The curing temperature was held at 150 °C, which was the upper limit of the heating element inside the closed chamber. The elemental composition of surfaces obtained this way is shown in Table 3. As discussed above, the cure time has little impact on the surface composition. Hence, it can reasonably be assumed that the composition of PF-TEA cured for 15 min is similar to that after curing for 20 min.

In general, there appears to be no direct influence of atmosphere on the chemical composition of the different coatings. Still, it should be noted that only for PUF-TEA coatings cured in an air-rich atmosphere the spread in CO/CC ratio was found to be larger than all other coatings. From the ATR-FTIR data follows that the bulk structure, however, shows no signs of oxidation at 150 °C of the PUF-TEA and PF-TEA coatings (Fig. S9). Most likely, the absence of chemical changes with curing atmosphere is the result of the relatively low curing temperature, which limits both oxidation and selective evaporation of formaldehyde from dimethylene ether bridges. This is in line with results previously reported by Hu et al. [69], where only for curing resoles at temperatures above 160 °C the formation of carbonyl groups and breaking down of ether bridges was observed.

These results can now be connected with the results of the water-wettability study of, for instance, PUF-TEA coatings in which unstable results were observed, demonstrated by a significant spread in water contact angle values (Fig. S10). Disparities in water contact angle values were predominantly observed for coatings cured inside the oven, where variations where seen: 1) between coatings made from the same batch of PUF-TEA resin, 2) between coatings made from different batches of PUF-TEA resin, and 3) even within a PUF-TEA coating itself. These variations between batches of the same type occurred even though chemically the liquid resins showed only minute differences in their composition (based on ^{13}C NMR analyses, Fig. 3). Although it is hypothesised that there is little control over the co-condensation between PF and UF fractions during curing when using TEA as catalyst (resulting in surfaces which are then either PF- or UF-rich; see also CO/CC ratio of PUF-TEA cured in air in Table 3), the variation in wettability between PUF-TEA coatings

Table 3
Overview of chemical composition, estimated with XPS, of phenolic resin coatings cured inside a closed chamber under an air or nitrogen flow.

Sample	Cure atmosphere	O: C	N: C	CO/CC
PUF-KOH 150 °C 20 min	Air	0.33 ± 0.01	0.21 ± 0.01	0.80 ± 0.06
	N_2	0.33 ± 0.02	0.19 ± 0.01	0.76 ± 0.03
PUF-TEA 150 °C 20 min	Air	0.33 ± 0.01	0.21 ± 0.02	0.72 ± 0.12
	N_2	0.34 ± 0.01	0.22 ± 0.01	0.80 ± 0.04
PF-TEA 150 °C 15 min	Air	0.28 ± 0	–	0.48 ± 0.01
	N_2	0.28 ± 0.01	–	0.48 ± 0.02

cured inside the closed chamber was typically found to be small. For instance, comparing water-wettability of PUF-TEA coatings that were cured in an oven with those cured in a closed chamber, the average water contact angle for a set of 9 coatings produced from one batch, cured in the oven, was 69.8° ± 12.5°, whilst that of 18 coatings cured in the closed chamber was 68.1° ± 3.2°

The aforementioned observation was, to varying degrees, valid for all studied coatings. Table 4 shows an overview of the wettability and CO/CC ratio of some of the samples (for an overview of all samples, the reader is referred to Table S1 in the SI). For PUF-KOH surfaces, variations in the water contact angle values appear to be less strongly fluctuating compared to PUF-TEA and PF-TEA. Typically, the largest differences in surface wettability of the studied coatings were always found for PUF-TEA. The major difference between the PF-TEA and PUF-TEA, and the PUF-KOH resin is the catalysts used for synthesis and hardening, and as a result the pH during curing varies. For instance, compared with PUF-TEA, for PUF-KOH a lower pH during curing is attained due to the use of the latent acid hardener $(NH_4)_2SO_4$, which then facilitates a better co-condensation between UF and PF fractions. Thus, the fluctuations in chemical composition due to variations in cure parameters are less strong, which in turn yields a more homogeneous surface, regardless of hardening conditions.

For PUF-KOH, despite the average water contact angle value was found to change the least with varying curing conditions, it was seen that curing temperature did have an impact on surface morphology: at 150 °C, the crystal size appeared to be larger and the number density smaller compared to crystals on the surface of coatings cured at 200 °C (Fig. S11).

Although statistically the wettability of most coating surfaces presented in Table 4 can be considered similar, it is evident that the spread in water contact angle values is affected by the curing temperature, which influences the degree of oxidation as well as the state of cure. As shown, curing TEA-containing phenolic resins appears to lead to coating surfaces with a larger spread in wettability compared to KOH-containing coatings and phenolic resin coatings cured at lower temperatures. The curing atmosphere was found to not have an apparent influence on either the absolute value or the standard deviation. Still, it is important to take the curing conditions into account when a reliable wettability of phenolic resin coatings is required.

4. Conclusions

Several factors that influence the surface properties of phenolic resin coatings were investigated. Coatings were prepared from three different resin formulations, where both the chemistry (PUF or PF) and catalyst (KOH or TEA) were varied. It was found that the surface wettability of the prepared coatings was similar, despite coatings exhibiting both chemical and morphological differences. The use of inorganic catalysts for curing and hardening the PUF-KOH resin leads to coating surfaces containing water-soluble K_2SO_4 crystals, which create a rough surface before wetting, and which readily dissolve in water during wetting. Although this yields a dynamic surface, such coatings were found to exhibit similar behaviour as PUF-TEA and PF-TEA surfaces upon repeated wetting. Contact with water affects every coating surface by changing the surface morphology, predominantly when the water is allowed to evaporate from the coating surface. Changes occur either through dissolution and redistribution of components or by tensile forces exerted due to the evaporation of water from the surface. However, no influence of leachables on the interfacial tension of the water in contact with the surfaces was found. Water also has a plasticising effect on all the coating surfaces, as successive dynamic contact angle measurements show a gradual, reversible decrease in wettability after a first wetting.

Surface chemistry of the phenolic resin coatings cured at various conditions largely followed the same trend. For a temperature of 200 °C, the state of cure for all coatings was markedly different compared to lower curing temperatures, which was reflected in the amount of dimethylene ether bridges being lower than for coatings cured at 150 °C, as seen by a change in CO/CC ratio. For urea-containing coatings, the nitrogen content exhibited the same behaviour, indicating that surface chemistry and polarity is largely governed by the distribution of UF fractions in the coating matrix and potential degradation of urea. Yet, oxidation at elevated temperatures was also found to occur. Major contributions to the surface chemistry and wettability variations of PUF-KOH and PUF-TEA stem from the distribution and co-condensation of urea species within and with the PF species. For applications in which a reliable wettability of phenolic resin coatings is required, a careful consideration of the cure conditions is advised.

Table 4
Influence of curing conditions of phenolic resin coatings on their water-wettability.

Conditions	Sample	CO/CC	WCA (°)
Oven	PUF-KOH[a]	0.70 ± 0.03	70.5 ± 3.6
200 °C	PUF-TEA[b]	0.62 ± 0.03	73.8 ± 5.6
Air	PF-TEA[b]	0.37 ± 0.01	76.4 ± 7.7
Closed chamber	PUF-KOH[b]	0.76 ± 0.03	70.0 ± 1.5
150 °C	PUF-TEA[b]	0.80 ± 0.04	70.8 ± 2.5
N_2	PF-TEA[c]	0.48 ± 0.02	69.7 ± 2.7

[a] Curing time 10 min.
[b] Curing time 20 min.
[c] Curing time 15 min.

CRediT authorship contribution statement

L. Moone: Conceptualization, Investigation, Methodology, Writing – original draft. **M.P.J. Donners:** Conceptualization, Writing – review & editing, Resources. **K. van Durme:** Conceptualization, Resources, Writing – review & editing. **D.V. Okhrimenko:** Conceptualization, Resources, Writing – review & editing. **R.A.T.M. van Benthem:** Supervision, Writing – review & editing. **R. Tuinier:** Supervision, Writing – review & editing. **A.C.C. Esteves:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2023.103840.

References

[1] L. Pilato, Phenolic resins: 100 Years and still going strong, React. Funct. Polym. 73 (2) (2013) 2, https://doi.org/10.1016/j.reactfunctpolym.2012.07.008. Art. no.

[2] S. Kowatsch, Mineral Wool Insulation Binders, in: L. Pilato (Ed.), Phenolic Resins: A Century of Progress, Springer, Berlin, Heidelberg, 2010, pp. 209–242, https://doi.org/10.1007/978-3-642-04714-5_10.

[3] C.P.R. Nair, Advances in addition-cure phenolic resins, Prog. Polym. Sci. 29 (5) (2004) 401–498, https://doi.org/10.1016/j.progpolymsci.2004.01.004.

[4] K. Tang, A. Zhang, T. Ge, X. Liu, X. Tang, Y. Li, Research progress on modification of phenolic resin, Mater. Today Commun. 26 (2021) 101879, https://doi.org/10.1016/j.mtcomm.2020.101879.

[5] C. Morterra, M. J. D, Low, "I.R. studies of carbons—VII. The pyrolysis of a phenol-formaldehyde resin, Carbon N Y 23 (5) (1985) 525–530, https://doi.org/10.1016/0008-6223(85)90088-0.

[6] B.K. Kandola, A.R. Horrocks, P. Myler, D. Blair, "Thermal characterization of thermoset matrix resins," in *Fire and Polymers*, in: ACS Symposium Series 797, American Chemical Society, 2001, pp. 344–360, https://doi.org/10.1021/bk-2001-0797.ch027.

[7] R.J. Zaldivar, G.L. Ferrelli, V. Arredondo, H.I. Kim, Effect of cure temperature on the thermal degradation, mechanical, microstructural and moisture absorption behavior of vacuum-only, carbon-fiber reinforced phenolic composites, J. Appl. Polym. Sci. 139 (34) (2022) e52819, https://doi.org/10.1002/app.52819.

[8] A. Trosa, A. Pizzi, Industrial hardboard and other panels binder from waste lignocellulosic liquors/phenol-formaldehyde resins, Eur. J. Wood Wood Prod. 56 (4) (1998) 229–233, https://doi.org/10.1007/s001070050307.

[9] A. Pizzi, A.N. Papadopoulos, F. Policardi, Wood composites and their polymer binders, Polymers (Basel) 12 (5) (2020), https://doi.org/10.3390/polym12051115.

[10] J.L. Paris, F.A. Kamke, R. Mbachu, S.K. Gibson, Phenol formaldehyde adhesives formulated for advanced X-ray imaging in wood-composite bondlines, J. Mater. Sci. 49 (2) (2014) 580–591, https://doi.org/10.1007/s10853-013-7738-2.

[11] D.-B. Fan, J.-M. Chang, J.-Z. Li, B.-H. Xia, Z.-T. Sang, Cure properties and adhesive performances of cure-accelerated phenol-urea-formaldehyde resins, Eur. J. Wood Wood Prod. 69 (2) (2011) 213–220, https://doi.org/10.1007/s00107-010-0414-1.

[12] H. Kajita, Y. Imamura, Improvement of physical and biological properties of particleboards by impregnation with phenolic resin, Wood Sci. Technol. 26 (1) (1991) 63–70, https://doi.org/10.1007/BF00225692.

[13] M. Dunky, A. Pizzi, Chapter 23 - Wood adhesives, in: D.A. Dillard, A.V. Pocius, M. Chaudhury (Eds.), Adhesion Science and Engineering, Elsevier Science B.V., Amsterdam, 2002, pp. 1039–1103, https://doi.org/10.1016/B978-044451140-9/50023-8.

[14] B. Tomita, C.-Y. Hse, Phenol–urea–formaldehyde (PUF) co-condensed wood adhesives, Int. J. Adhes. Adhes. 18 (2) (1998) 69–79, https://doi.org/10.1016/S0143-7496(97)00047-X.

[15] W.N. Ahamad, et al., Effects of compression ratio and phenolic resin concentration on the properties of laminated compreg inner oil palm and Sesenduk Wood composites, Forests 14 (1) (2023), https://doi.org/10.3390/f14010083.

[16] Z. Yang, G. Xian, H. Li, Effects of alternating temperatures and humidity on the moisture absorption and mechanical properties of ramie fiber reinforced phenolic plates, Polym. Compos. 36 (9) (2015) 1590–1596, https://doi.org/10.1002/pc.23067.

[17] H. Younesi-Kordkheili, A. Pizzi, A comparison among lignin modification methods on the properties of lignin–phenol–formaldehyde resin as wood adhesive, Polymers (Basel) 13 (20) (2021), https://doi.org/10.3390/polym13203502.

[18] S. Yang, Y. Zhang, T.-Q. Yuan, R.-C. Sun, Lignin–phenol–formaldehyde resin adhesives prepared with biorefinery technical lignins, J. Appl. Polym. Sci. 132 (36) (2015), https://doi.org/10.1002/app.42493.

[19] W. Yang, et al., Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: a comparative study, Mater. Des. 161 (2019) 55–63, https://doi.org/10.1016/j.matdes.2018.11.032.

[20] N.S. Çetin, N. Özmen, Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: II. Particleboard production and properties, Int. J. Adhes. Adhes. 22 (6) (2002) 481–486, https://doi.org/10.1016/S0143-7496(02)00059-3.

[21] S. Sarkar, B. Adhikari, Lignin-modified phenolic resin: synthesis optimization, adhesive strength, and thermal stability, J. Adhes. Sci. Technol. 14 (9) (2000) 1179–1193, https://doi.org/10.1163/156856100743167.

[22] H. Kollek, H. Brockmann, H. Muller von der Haegen, Chemistry of curing and adhesion properties of phenolic resins, Int. J. Adhes. Adhes. 6 (1) (1986) 37–41, https://doi.org/10.1016/0143-7496(86)90070-9.

[23] J. Si, J. Li, S. Wang, Y. Li, X. Jing, Enhanced thermal resistance of phenolic resin composites at low loading of graphene oxide, Compos. Part Appl. Sci. Manuf. 54 (2013) 166–172, https://doi.org/10.1016/j.compositesa.2013.07.019.

[24] Phenolic Resin Adhesives, in: A. Pizzi (Ed.), Handbook of Adhesive Technology, 3rd ed, CRC Press, 2017.

[25] A. Zafar, J. Schjødt-Thomsen, R. Sodhi, R. Goacher, D. de Kubber, Investigation of the ageing effects on phenol-urea-formaldehyde binder and alkanol amine-acid anhydride binder coated mineral fibres, Polym. Degrad. Stab. 98 (1) (2013) 339–347, https://doi.org/10.1016/j.polymdegradstab.2012.09.007.

[26] D.V. Okhrimenko, et al., Impact of curing time on ageing and degradation of phenol-urea-formaldehyde binder, Polym. Degrad. Stab. 152 (2018) 86–94, https://doi.org/10.1016/j.polymdegradstab.2018.04.001.

[27] M.-F. Grenier-Loustalot, S. Larroque, P. Grenier, J.-P. Leca, D. Bedel, Phenolic resins: 1. Mechanisms and kinetics of phenol and of the first polycondensates towards formaldehyde in solution, Polymer (Guildf) 35 (14) (1994) 3046–3054, https://doi.org/10.1016/0032-3861(94)90418-9.

[28] M.-F. Grenier-Loustalot, S. Larroque, D. Grande, P. Grenier, D. Bedel, Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics, Polymer (Guildf) 37 (8) (1996) 1363–1369, https://doi.org/10.1016/0032-3861(96)81133-5.

[29] M.-F. Grenier-Loustalot, S. Larroque, P. Grenier, Phenolic resins: 5. Solid-state physicochemical study of resoles with variable FP ratios, Polymer (Guildf) 37 (4) (1996) 639–650, https://doi.org/10.1016/0032-3861(96)83151-X.

[30] The Correlation Between Preparation and Properties in Phenolic Resins, in: L. Gollob, A.(Ed.) Pizzi (Eds.), Wood Adhesives. Chemistry and Technology, 1st ed, CRC Press, Boca Raton, 1989, pp. 121–153, https://doi.org/10.1201/9780203733721-5.

[31] G. He, B. Riedl, Phenol-urea-formaldehyde cocondensed resol resins: their synthesis, curing kinetics, and network properties, J. Polym. Sci. Part B Polym. Phys. 41 (16) (2003) 1929–1938, https://doi.org/10.1002/polb.10558.

[32] G. Astarloa-Aierbe, J.M. Echeverría, A. Vázquez, I. Mondragon, Influence of the amount of catalyst and initial pH on the phenolic resol resin formation, Polymer (Guildf) 41 (9) (2000) 3311–3315, https://doi.org/10.1016/S0032-3861(99)00519-4.

[33] J. Bouajila, G. Raffin, H. Waton, C. Sanglar, J.O. Païsse, M.F. Grenier-Loustalot, Phenolic resins – characterizations and kinetic studies of different resols prepared with different catalysts and formaldehyde/phenol ratios (I), Polym. Polym. Compos. 10 (5) (2002) 341–360, https://doi.org/10.1177/096739110201000502.

[34] N. Gabilondo, M. Larrañaga, C. Peña, M.A. Corcuera, J.M. Echeverría, I. Mondragon, Polymerization of resole resins with several formaldehyde/phenol molar ratios: amine catalysts against sodium hydroxide catalysts, J. Appl. Polym. Sci. 102 (3) (2006) 2623–2631, https://doi.org/10.1002/app.24017.

[35] D. Fan, F. Chu, T. Qin, J. Li, Effect of synthesis conditions on the structure and curing characteristics of high-urea content PUF resin, J. Adhes. 87 (12) (2011) 1191–1203, https://doi.org/10.1080/00218464.2011.628871.

[36] B. Kałędkowski, J. Hetper, Synthesis of phenol–formaldehyde resole resins in the presence of tetraalkylammonium hydroxides as catalysts, Polym. (Guildf) 41 (5) (2000) 1679–1684, https://doi.org/10.1016/S0032-3861(99)00345-6.

[37] J. Grinins, M. Iesalnieks, V. Biziks, I. Gritane, G. Sosins, Birch wood surface characterization after treatment with modified phenol-formaldehyde oligomers, Polym. (Basel) 14 (4) (2022), https://doi.org/10.3390/polym14040671.

[38] Y. Li, et al., High-efficiency surfactant prepared from phenolic resin for multi-walled carbon nanotube aqueous suspension, J. Nanopart. Res. 20 (6) (2018) 162, https://doi.org/10.1007/s11051-018-4264-9.

[39] D. Wang, J. Ding, B. Wang, Y. Zhuang, Z. Huang, Synthesis and Thermal Degradation Study of Polyhedral Oligomeric Silsesquioxane (POSS) Modified Phenolic Resin, Polymers (Basel) 13 (8) (2021), https://doi.org/10.3390/polym13081182.

[40] G. Vázquez, F. López-Suevos, A. Villar-Garea, J. González-Alvarez, G. Antorrena, 13C-NMR analysis of phenol-urea-formaldehyde prepolymers and phenol-urea-formaldehyde-tannin adhesives, J. Adhes. Sci. Technol. 18 (13) (2004) 1529–1543, https://doi.org/10.1163/1568561042411231.

[41] G. Wu, "Strongly basic tertiary amino alcohols as catalyst," WO1997000900A1, 09, 1997 Accessed: 05, 2022. [Online]. Available: https://patents.google.com/patent/WO1997000900A1/en?oq=WO+1997%2f000900.

[42] B. Tomita, C.-Y. Hse, Cocondensation of urea with methylolphenols in acidic conditions, J. Polym. Sci. Part Polym. Chem. 30 (8) (1992) 1615–1624, https://doi.org/10.1002/pola.1992.080300814.

[43] D.-B. Fan, G.-Y. Li, T.-F. Qin, F.-X. Chu, Synthesis and structure characterization of phenol-urea-formaldehyde resins in the presence of magnesium oxide as catalyst, Polym. (Basel) 6 (8) (2014), https://doi.org/10.3390/polym6082221.

[44] B. Pang, M.-K. Li, S. Yang, T.-Q. Yuan, G.-B. Du, R.-C. Sun, Eco-friendly phenol–urea–formaldehyde co-condensed resin adhesives accelerated by resorcinol for plywood manufacturing, ACS Omega 3 (8) (2018) 8521–8528, https://doi.org/10.1021/acsomega.8b01286.

[45] Y. Matsushita, S. Wada, K. Fukushima, S. Yasuda, Surface characteristics of phenol–formaldehyde–lignin resin determined by contact angle measurement and inverse gas chromatography, Ind. Crops Prod. 23 (2) (2006) 115–121, https://doi.org/10.1016/j.indcrop.2005.04.004.

[46] Y.-K. Lee, H.-J. Kim, M. Rafailovich, J. Sokolov, Curing monitoring of phenolic resol resins via atomic force microscope and contact angle, Int. J. Adhes. Adhes. 22 (5) (2002) 375–384, https://doi.org/10.1016/S0143-7496(02)00017-9.

[47] J.T. Korhonen, T. Huhtamäki, O. Ikkala, R.H.A. Ras, Reliable measurement of the receding contact angle, Langmuir 29 (12) (2013) 3858–3863, https://doi.org/10.1021/la400009m.

[48] L.M. Matuana, D.P. Kamdem, Accelerated ultraviolet weathering of PVC/wood-flour composites, Polym. Eng. Sci. 42 (8) (2002) 1657–1666, https://doi.org/10.1002/pen.11060.

[49] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Ind. Eng. Chem. 28 (8) (1936) 988–994, https://doi.org/10.1021/ie50320a024.

[50] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, Trans. Faraday Soc. 40 (1944) 546–551, https://doi.org/10.1039/TF9444000546.

[51] A. Marmur, Wetting on hydrophobic rough surfaces: to be heterogeneous or not to be? Langmuir 19 (20) (2003) 8343–8348, https://doi.org/10.1021/la0344682.

[52] F. Kuschel, An. König, S. Herold, Crystallization of potassium sulfate from pure aqueous solution and in presence of surfactants, Cryst. Res. Technol. 18 (4) (1983) 427–434, https://doi.org/10.1002/crat.2170180402.

[53] J.P. Canselier, The effects of surfactants on crystallization phenomena, J. Dispers. Sci. Technol. 14 (6) (1993) 625–644, https://doi.org/10.1080/01932699308943435.

[54] H. Füredi-Milhofer, S. Sarig, Interactions between polyelectrolytes and sparingly soluble salts, Prog. Cryst. Grow. Charact. Mater. 32 (1) (1996) 45–74, https://doi.org/10.1016/0960-8974(96)00006-X.

[55] M. Bujan, M. Sikirić, N. Filipović-Vinceković, N. Vdović, N. Garti, H. Füredi-Milhofer, Effect of anionic surfactants on crystal growth of calcium hydrogen

phosphate dihydrate, Langmuir 17 (21) (2001) 6461–6470, https://doi.org/10.1021/la0107190.

[56] H. Füredi-Milhofer, D. Škrtić, M. Marković, Lj. Komunjer, Kinetic analysis of the influence of additives on spontaneous precipitation from electrolytic solutions, Dispers. Syst. (1988) 195–200, https://doi.org/10.1007/BFb0116783.

[57] C. Bourges-Monnier, M.E.R. Shanahan, Influence of evaporation on contact angle, Langmuir 11 (7) (1995) 2820–2829, https://doi.org/10.1021/la00007a076.

[58] A.K. Panwar, S.K. Barthwal, S. Ray, Effect of evaporation on the contact angle of a sessile drop on solid substrates, J. Adhes. Sci. Technol. 17 (10) (2003) 1321–1329, https://doi.org/10.1163/156856103769172760.

[59] A.J.D. Shaikeea, S. Basu, A. Tyagi, S. Sharma, R. Hans, L. Bansal, Universal representations of evaporation modes in sessile droplets, PLoS ONE 12 (9) (2017) e0184997, https://doi.org/10.1371/journal.pone.0184997.

[60] D.Y. Kwok, A.W. Neumann, Contact angle measurement and contact angle interpretation, Adv. Colloid Interface Sci. 81 (3) (1999) 167–249, https://doi.org/10.1016/S0001-8686(98)00087-6.

[61] X. Lu, J. Han, N. Shephard, S. Rhodes, A.D. Martin, D. Li, Z. Chen, Phenolic resin surface restructuring upon exposure to humid air: a sum frequency generation vibrational spectroscopic study, J. Phys. Chem. B 113 (39) (2009) 12944–12951, https://doi.org/10.1021/jp9058092.

[62] K.B. Lewis, B.D. Ratner, Observation of surface rearrangement of polymers using ESCA, J. Colloid Interface Sci. 159 (1) (1993) 77–85, https://doi.org/10.1006/jcis.1993.1299.

[63] J.K. Pike, T. Ho, K.J. Wynne, Water-induced surface rearrangements of poly (dimethylsiloxane-urea-urethane) segmented block copolymers, Chem. Mater. 8 (4) (1996) 860–865, https://doi.org/10.1021/cm9504596.

[64] A.C.C. Esteves, I.D. Günbas, J.M. van Riel, B.A.J. Noordover, G. de With, R.A.T. M. van Benthem, Time-resolved surface rearrangements of polymer films monitored by dynamic recovery contact angle (DRCA), RSC Adv. 4 (39) (2014) 20094–20101, https://doi.org/10.1039/C4RA01329H.

[65] W. Zhao, S.L. Hsu, S. Ravichandran, A.M. Bonner, Moisture effects on the physical properties of cross-linked phenolic resins, Macromolecules 52 (9) (2019) 3367–3375, https://doi.org/10.1021/acs.macromol.9b00385.

[66] J.T. Koberstein, Molecular design of functional polymer surfaces, J. Polym. Sci. Part B Polym. Phys. 42 (16) (2004) 2942–2956, https://doi.org/10.1002/polb.20157.

[67] L. Liang, et al., Surfactant-induced reconfiguration of urea-formaldehyde resins enables improved surface properties and gluability of bamboo, Polymers (Basel) 13 (20) (2021), https://doi.org/10.1007/s11051-018-4264-9.

[68] R.T. Conley, J.F. Bieron, A study of the oxidative degradation of phenol-formaldehyde polycondensates using infrared spectroscopy, J. Appl. Polym. Sci. 7 (1) (1963) 103–117, https://doi.org/10.1002/app.1963.070070110.

[69] H. Hu, W. Wang, L. Jiang, Y. Zhang, Y. Yang, J. Wang, Curing mechanism of resole phenolic resin based on variable temperature FTIR spectra and thermogravimetry-mass spectrometry, Polym. Polym. Compos. 30 (2022), https://doi.org/10.1177/09673911221102114, 09673911221102114.