Synthesis of Novolac-Type Phenolic Resins Using Glucose as the Substitute for Formaldehyde

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ABSTRACT: Novel Novolac type phenolic resins were prepared using glucose as the substitute for toxic formaldehyde (a carcinogenic chemical). The resins were synthesized with varying molar ratios of phenol to glucose, catalyzed by strong acid (such as sulfuric acid) at 120–150°C. Analysis of the resins using gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H-NMR) showed that they were broadly distributed oligomers derived from the Fridel-Crafts condensation of phenol and glucose. Using hexamethylenetetramine (HMTA) as the curing agent, the phenol-glucose resins could be thermally cured and exhibited exothermic peaks at 130–180°C, typical of thermosetting phenolic resins. The cured resins showed satisfactory thermal stability, e.g., they started to decompose at >280°C with residual carbon yields of above 58% at 600°C. Based on the thermal properties, phenol-glucose resin with a molar ratio of 1 : 0.5 is promising as it could be cured at a lower temperature (147°C) and exhibited a satisfactorily good thermal stability: it started to decompose at >300°C with a residual carbon yield of >64% at 600°C. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1191–1197, 2010

Key words: renewable resources; resins; synthesis; curing of polymers; thermal properties

INTRODUCTION

As the first commercial synthetic resin, phenolic resins have been manufactured and extensively studied for over one century and still play an indispensable role in the production of many materials and products despite the emergence of more and more high performance polymers. However, the toxicity of phenol and formaldehyde (as a carcinogenic chemical),[1] together with the unrenewability of petroleum as the major resource for the production of these chemicals, has posed serious challenges to environmental and feedstock sustainability for the manufacture of phenol-formaldehyde resins. With an increasing world-wide resource shortage and growing environmental concerns, many researchers have been intensively investigating on substituting petroleum-based chemicals with bio-based chemicals derived from renewable resources (biomass).[2,3]

Considerable efforts have been made in phenolic resins production to replace the petroleum-based phenol totally or partially with lignocellulosic bio-mass, an abundant renewable resource. For instance, lignin was successfully used to replace phenol in production of Novolac-and Resol-type phenolic resins.[4–7] Nevertheless, almost all the efforts were in the replacement of petroleum phenol with lignin, the lignin-degraded bio-phenols or phenol-like tannins.[8] There were very few studies reported on substituting the carcinogenic formaldehyde (mainly produced from natural gas and coal through the route of syngas-methanol) with environmentally benign chemicals such as cellulose and its degraded products (carbohydrates and furfurals).

Carbohydrates (about 75 wt % of the total biomass composition) are the most abundant renewable resources, and can be transformed via chemical and enzymatic reactions to hundreds of chemicals,[9] many of which can be candidates of monomers for the synthesis of polymers. For example, hydroxymethylfurfural from glucose and furfural from xylose were used for the production of phenol-furfural resins.[10,11] However, it has been seldom reported on the application of sugar (glucose, xylose, starch, and cellulose) directly as the substitute for formaldehyde to synthesize phenolic resins.[12] Although glucose can be a potential candidate of aldehyde, the Friedel-Crafts reaction between phenol and glucose is more difficult than that between phenol and formaldehyde, indicating the far low reactivity of glucose as an electrophile due to the steric hindrance.
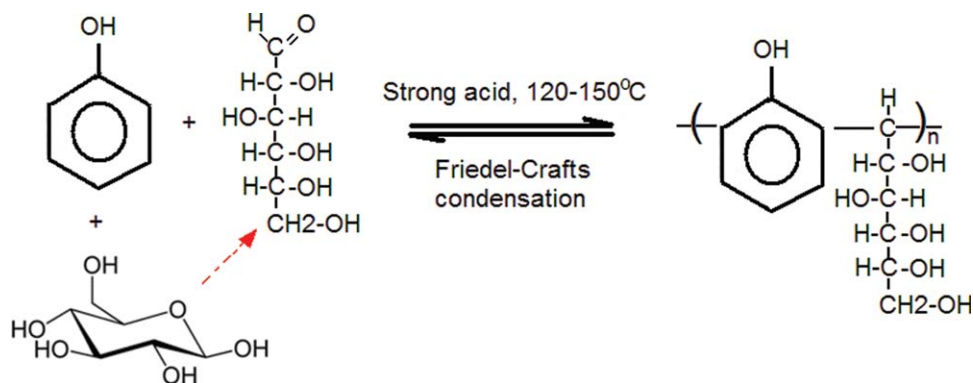
Scheme 1 Synthetic protocol of phenol-glucose resins through Friedel-Crafts condensation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In this work, we attempted to prepare Novolac-type phenolic resins employing glucose as the replacement of formaldehyde, and studied the structural and thermal curing characteristics of the resulted phenol-glucose resins. The thermal stability properties compared with a conventional phenol-formaldehyde resin were also investigated.

EXPERIMENTAL

Materials

Phenol (ACS reagent, 99.7 wt %, Mallinckrodt Baker), D-glucose (ACS reagent, Fisher Scientific) and hexamethylenetetramine (ACS reagent, 99+ wt %, Sigma-Aldrich) were used as received. ACS reagent-grade or HPLC-grade sulfuric acid (concentration 96 wt %), acetone, tetrahydrofuran (THF) and ethanol were from Canadawide Scientific and used as received.

Synthesis of phenol-glucose novolac resins

Quite different from the easy reaction of phenol and formaldehyde at 80–90°C under mildly acidic catalysis, the synthesis of phenol-glucose resin requires much higher temperatures of 120–150°C, catalyzed by strong acids such as sulfuric acid, hydrochloric acid, and K10 montmorillonite, etc. The synthetic protocol may be illustrated in Scheme 1.

As shown in the proposed Scheme, phenol and glucose can be polymerized into a resin via Friedel-Crafts reactions at the temperatures of 120–150°C with a strong acidic catalyst such as sulfuric acid, hydrochloric acid, and K10 montmorillonite, etc. A number of preliminary tests have been conducted for the phenol-glucose resin synthesis at temperatures varying from 120 to 150°C with different acids (including HCl, and K10 montmorillonite and H_2SO_4). The results of these preliminary tests showed that the resulting resins at a higher temperature were inferior in terms of color (darker) likely

due to enhanced side reactions of glucose (e.g., dehydration reactions). As such, the resin synthesis was conducted mainly at a low temperature of 120°C, a temperature proved to be enough for the polymerization of phenol and glucose. The polymerization reaction could proceed in the presence of each strong acid tested (i.e., HCl, K10 montmorillonite or H_2SO_4), but our preliminary tests showed that sulfuric acid was the most effective acid for catalyzing the reaction, so in this study sulfuric acid was chosen as the main catalyst. In a typical run of the synthesis, phenol (9.4 g, 0.1 mol) and glucose (9 g, 0.05 mol) were charged into a 100 mL flask. After heated to 120°C in an oil bath, 0.09 g sulfuric acid (96 wt % concentration) was added. The reaction was kept for 3 h at 120°C, and a dark viscous liquid was obtained. After cooling down to 60°C, 1.7 mL sodium hydroxide solution (1.0 M) was added to neutralize the product solution. Water was removed by rotary evaporation under reduced pressure at 60°C. The resulted product was a brown viscous resin.

The above procedure was applied for the synthesis of a series of phenol-glucose resins with various molar ratios of phenol-to-glucose (1 : 0.4, 1 : 0.5, 1 : 0.75, and 1 : 0.9). All the resins obtained were brown viscous liquids at room temperature. For reference, a conventional phenol-formaldehyde Novolac resin was also prepared (85°C, 2 h, phenol-to-formaldehyde molar ratio of 1 : 0.85, HCl catalyst at 0.5 wt % of phenol).

Product characterization

The molecular weights and their distributions of the obtained phenol-glucose resins were analyzed (three samples for each resin) on a Waters Breeze GPC (1525 binary HPLC pump; UV detector at 270 nm; Waters Styrange HR1 column at 40°C) using THF as eluant at a flowing rate of 1 mL/min, and polystyrene standards were used for calibration. The
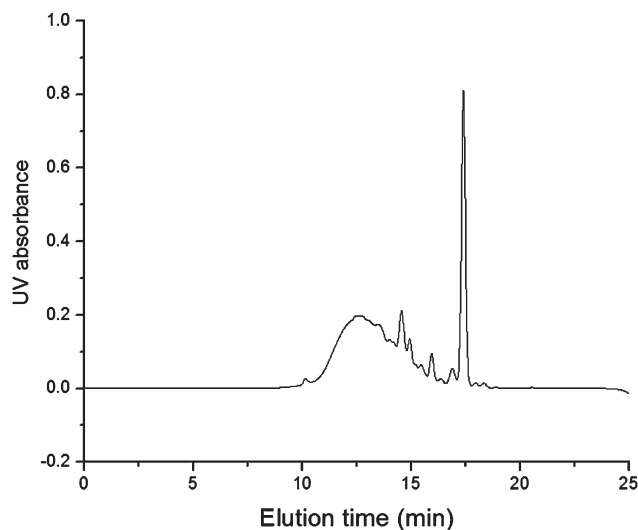
Figure 1 Representative GPC profile of the phenol-glucose resin (phenol-to-glucose molar ratio of 1 : 0.5) (THF as eluent at 1 mL/min, UV detector at 270 nm, polystyrene standards).

chemical structures of the phenol-glucose resins were characterized by solution ^{1}H-NMR (400 MHz, Bruker) in DMSO (0.3% tetramethylsilane as internal standard) at room temperature, and by FTIR (IR2000, Perkin–Elmer, US) in the range of 500 – 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The thermal cure of the resins was studied by differential scanning calorimetry (DSC) technique (DSC 1, Mettler-Toledo, Switzerland) at a heating rate of 10°C/min under 50 mL/min N$_2$. To prepare the samples for the DSC tests, the obtained Novolac resins were crashed and milled to fine powders, and the fine powder was then mixed with 15 wt % hexamethylenetetramine (HMTA, curing agent) sufficiently. The results were calculated based on three replicate samples. In addition, the well mixed powders of resin and HMTA were thermally cured as per the following schedule: 1 h at 120°C, 1 h at 150°C, and 2 h at 180°C. The cured resins (brown solid materials) were subject to thermal stability tests using thermogravimetric technique on a TGA (TGA 1000i, Instrument Specialists) at a heating rate of 10°C/min under 30 mL/min N$_2$. Again, averages results from three replicate tests were reported.

RESULTS AND DISCUSSION

Characterizations of the phenol-glucose novolac-type resins

The prepared phenol-glucose resins were brown viscous fluids, and have excellent solubility in organic solvents such as acetone, ethanol and THF. Although physical mixing glucose and phenol at above 100°C could form a brown viscous blend too, the blend could not be dissolved in organic solvents

(due to the poor solubility of glucose). The change of the solubility might imply the occurrence of polymerization between phenol and glucose.

The molecular weight distributions of the obtained resins were characterized by GPC, and a representative GPC profile was showed in Figure 1. A sharp peak of phenol was detectable at the retention time of 17.5 min in all the as-synthesized resin products, suggesting the presence of unreacted phenol in the products, as expected due to the large amount of phenol added in the synthesis. The GPC analysis results for all the obtained resins (with a phenol-to-glucose molar ratio ranging from 1 : 0.4 to 1 : 0.9) are summarized in Table I. The results revealed that the M_n for the obtained resin was in the range of 322–512, and the M_w in the range of 974–1500 and with a polydispersity (M_w/M_n) between 2.5 and 3.5, similar to the GPC results for conventional phenol-formaldehyde resins.[11] As such, the as-prepared resins are broadly dispersed oligomers with some contents (about 20 mol %) of free phenol. It should be noted however the key purpose of the GPC analysis in this study was to evidence the occurrence of the condensation reactions between phenol and glucose. The GPC results reported in Table I are the average values from three replicate samples, and the relative standard deviations were found to be small (mostly <5–10%). As such, the standard deviations are not shown in the Table for simplicity. As showed in Table I, the resins with the phenol-to-glucose molar ratios of 1 : 0.4 to 1 : 0.75 have essentially no apparent difference in M_n or M_w (considering the 5–10% relative stand deviation of the data), while there was an unexpected increases in molecular weights at the high molar ratio of 1 : 0.9. This trend is not fully understood so far, possibly owing to the self condensation of glucose. More research on this is thus needed.

The ^{1}H-NMR spectra of phenol-glucose resin (at phenol-to-glucose molar ratio of 1 : 0.5) and the pure D-glucose are comparatively shown in Figure 2. The ^{1}H-NMR results clearly show that there were signals at 6.6–7.3 ppm (aromatic H), 4.3–5.0 ppm (—OH), 3.4–3.6 ppm (—CH$_2$—), and 3.0–3.2 ppm (—CH) originating from protons in glucose in the final phenol-glucose resin, without clear signals from protons on

TABLE I
The Molecular Weight Characteristics of the Phenol-Glucose Resins by GPC

Phenol-glucose resins	M_n	M_w	Polydispersity
Phenol-glucose (1 : 0.4)^a	362	990	2.73
Phenol-glucose (1 : 0.5)	360	985	2.74
Phenol-glucose (1 : 0.75)	322	974	3.02
Phenol-glucose (1 : 0.9)	512	1307	2.55

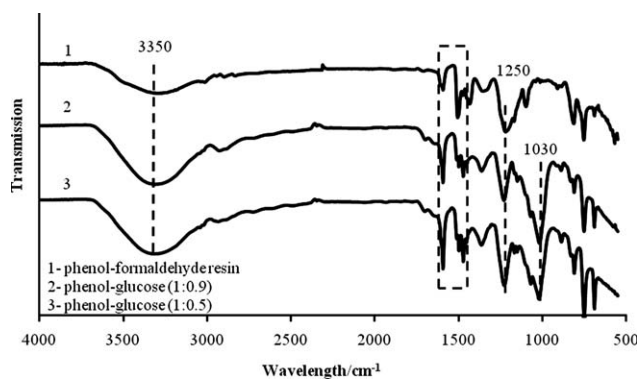^{a} Phenol-to-glucose molar ratio of 1 : 0.4.
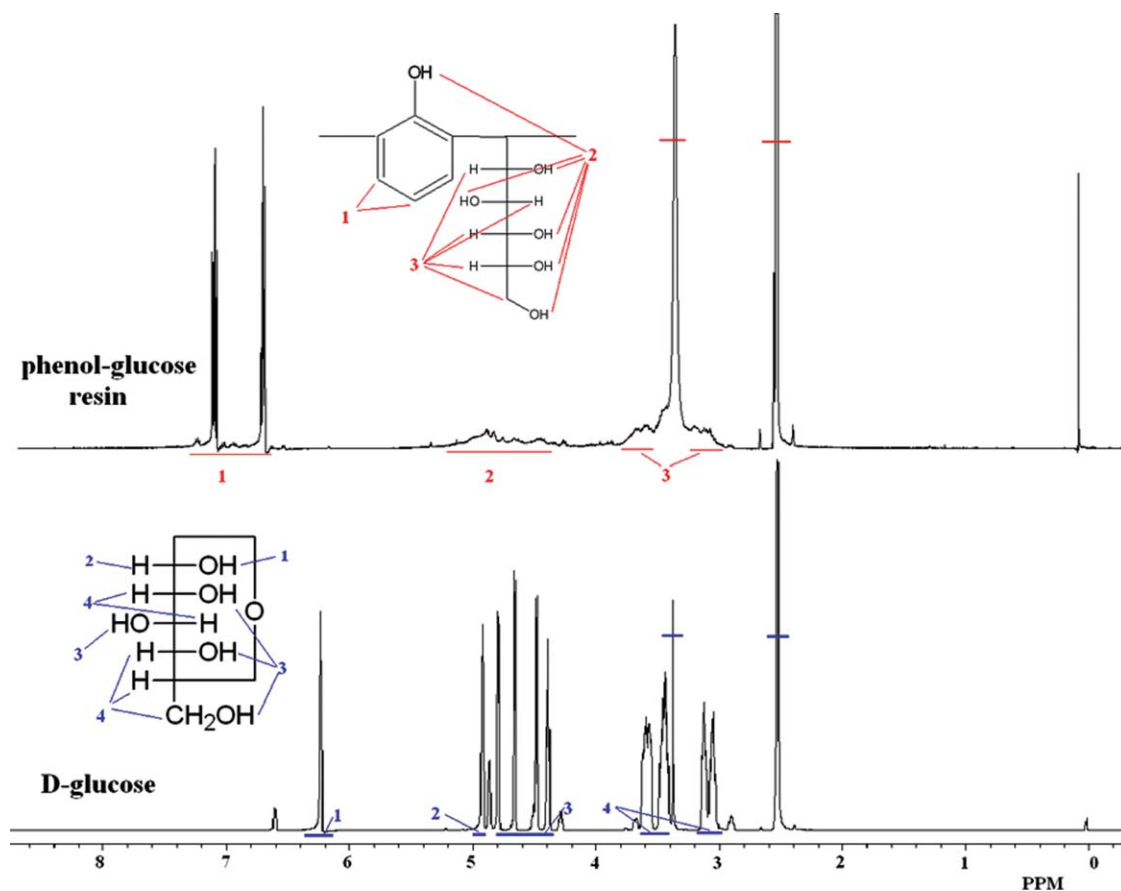
Figure 2 ^{1}H-NMR spectrum of phenol-glucose resin (at phenol-to-glucose molar ratio of 1 : 0.5) in comparison with that of D-glucose (DMSO with TMS as internal standard). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

furan ring.[13] The disappearance of hemiacetal proton in glucose at 6.25 ppm proved the condensation reaction between phenolic ring and glucosic hemiacetal. Figure 3 presents the FTIR spectra of the as-synthesized phenol-glucose resins (at phenol-to-glucose molar ratios of 1 : 0.5 and 1 : 0.9) in comparison with that of the phenol-formaldehyde control resin. The FTIR spectra of the as-synthesized phenol-glucose resins were very similar to the characteristic profile of the phenol-formaldehyde control resin. For example, the FTIR spectra of phenol-glucose resins and the control resin all showed the absorption at 3350 cm^{-1} (—OH stretching), 3020 cm^{-1} (aromatic C—H stretching), 2970 cm^{-1} (aliphatic C—H stretching), 1600/1500/1450 cm^{-1} (phenyl ring C—C stretching), and 697/752/850 cm^{-1} (phenyl ring C—H bending). As shown in Figure 3, the main difference between the IR spectra from the phenol-glucose resins from that from the phenol-formaldehyde control resin might be: there was strong absorption at 1130 cm^{-1} (C—O stretching) in the phenol-glucose resins (ascribable to the presence of glucose), while this absorption was absent in the control resin. The absorption peak at 1130 cm^{-1} (C—O stretching) was

stronger in the phenol-glucose resin at a larger molar ratio of phenol-to-glucose as anticipated. It is also clear that no apparent signals ascribable to furan ring were observable in the FTIR spectra of all the as-synthesized phenol-glucose resins.

The reaction mechanism between phenol and glucose in the presence a strong acid might be complex

Figure 3 FTIR spectra of the as-synthesized phenol-glucose resins (at phenol-to-glucose molar ratios of 1 : 0.5 and 1 : 0.9) in comparison with that of the phenol-formaldehyde control resin.
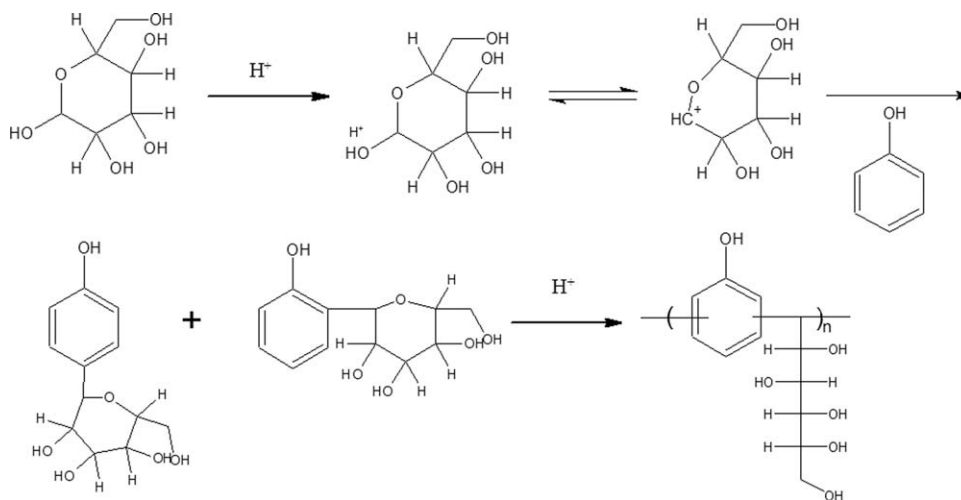
Scheme 2 Friedel-Crafts reaction mechanism in the synthesis of phenol-glucose resins.

as there are many possible degradation pathways for the hydrolysis degradation of glucose in an acidic aqueous solution, producing hydroxymethyl-furfural and carboxylic acids as the main degraded products.[14–18] Based on the results of NMR and FTIR as discussed earlier, the Friedel-Crafts condensation reactions between glucose and phenol under acidic catalysis were likely the dominant pathway resulting in the formation of oligomeric resins. It was thus believed that the existence of phenol as solvent and reactant at a large amount would govern the reactions of Friedel-Crafts condensation.[19,20] Accordingly, a reaction mechanism was proposed and depicted in Scheme 2 to elucidate the possible reactions in the synthesis of phenol-glucose resins.

Thermal cure of phenol-glucose resins with HMTA

As well known, Novolac phenol-formaldehyde resin can be thermally cured with a curing agent such as HMTA. The thermal cure behaviors of the obtained phenol-glucose resins were studied using HMTA by DSC, and the results are shown in Figure 4. Irrespective of the phenol-to-glucose molar ratio, all the phenol-glucose resins exhibited exothermic peaks covering the similar range of 130–180°C peaking at around 152°C. As shown in the Figure, the DSC curves of all the phenol-glucose resins are comparable with that of a typical phenol-formaldehyde Novolac resin.[21,22] However, the phenol-glucose resins exhibited a slightly broader exothermic peak than that of the typical phenol-formaldehyde Novolac resin, and the peak temperatures of our phenol-glucose resins (except the one at the phenol-to-glucose molar ratio of 1 : 0.5) were about 5°C higher than that of the phenol-formaldehyde Novolac resin. This may suggest the retarding influence of side sugar chains on the curing reactions. Among the

phenol-glucose resins, although their temperature ranges of the thermal cure were very similar the peak temperature drifted to a slightly higher value with increasing the glucose molar ratio in the resin formula, implying again the retarding effect of sugar on the curing reactions between phenol-rings and HMTA. It shall be noted that the exothermic peak values (or enthalpy) were not quantitatively analyzed in this study since the heat flow were not normalized (by dividing the sample mass). In addition, as shown in Figure 4, the phenol-glucose resin (1 : 0.5) showed the lowest exothermic peak temperature (147°C) than the others including the phenol-formaldehyde control resin, suggesting that the molar ratio of 1 : 0.5 seemed to be the optimal condition for the synthesis of phenol-glucose Novolac resins. This is
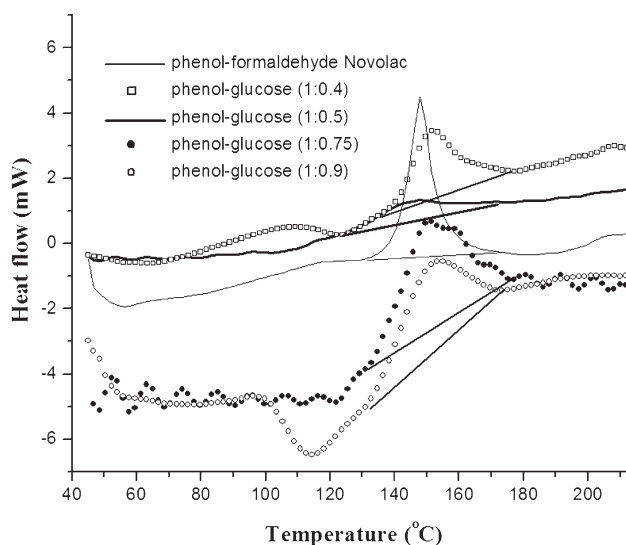
Figure 4 DSC curves of phenol-glucose resins with 15 wt % HMTA as the curing agent (heating rate of 10°C/min, N_2 50 mL/min).

TABLE II
The Thermal Stability Characteristics of the Cured Phenol-Glucose Resins by TGA

Cured phenolic resins[a]	T_{onset}[b] (°C)	T_5[c] (°C)	T_p[d] (°C)	Solid residue at 600°C (wt %)
Phenol-formaldehyde	298	316	562	72
Phenol-glucose (1 : 0.4)[e]	318	318	385	65
Phenol-glucose (1 : 0.5)	280	303	351	64
Phenol-glucose (1 : 0.75)	276	285	346	58
Phenol-glucose (1 : 0.9)	262	285	333	58

[a] All the green phenol-glucose resins were cured with 15 wt % HMTA.
[b] T_{onset} is the temperature where the resin starts obvious mass loss.
[c] T_5 is the temperature at which the mass loss is 5%.
[d] T_p is the peak temperature at which the thermal decomposition proceeds fastest.
[e] Phenol-glucose (1 : 0.4) is the resin from phenol and glucose in the molar ratio of 1 : 0.4.

however difficult to be accounted for by the retarding influence of side sugar chains on the curing reactions. More research work is needed.

Thermogravimetric analysis (TGA) has been widely used to characterize the thermal stability of phenolic resins.[23,16] The results of TGA measurements for the cured phenol-glucose resins are summarized in Table II. As expected, due to the presence of a large amount of side sugar chains, the cured phenol-glucose resins showed inferior thermal stability in terms of the initial decomposition temperature (T_{onset}) and the carbon residue yield at elevated temperatures, compared with the phenol-formaldehyde resin. With the increase of the content of glucose in the phenol-glucose resin, the resin's thermal stability monotonously decreased resulting from the degradation of sugar chains, leading to a lower decomposition onset temperature and a smaller carbon residue yield. However, even for the phenol-glucose (1 : 0.9) resin, the thermal stability is satisfactorily good with the T_{onset} at 262°C and the carbon yield of around 60 wt % at 600°C.

Although the aim of this article is to produce formaldehyde-free novolacs by replacing the formaldehyde in the resin synthesis with glucose, HMTA (which might decompose to formaldehyde in an acid environment) is however needed as a cross-linking agent or a hardener (normally at 10–15 wt % of the resin) for any novolacs (including our phenol-glucose resins). Justification seems to be needed for the benefits of such new formulation or process for resin production. Firstly, the obvious benefit of replacing formaldehyde with glucose at the stage of resin synthesis may be that the hazard emission of formaldehyde in the resin synthesis process could be avoided. To better elucidate the benefits of replacing formaldehyde with glucose, the consumption of raw materials was calculated and is compared in Table III, taking 100 kg of HMTA-cured novolac as the basis, and assuming that the phenol-formaldehyde (or glucose) molar ratio in the resin synthesis was 1 : 0.5, and 15 wt % HMTA was added for curing of the resin. As clearly shown from the above Table, replacing formaldehyde with glucose in the resin synthesis could reduce ∼ 12 kg formaldehyde and displace around 30 kg of phenol by renewable and inexpensive resource (glucose) in the manufacture of 100 kg cured final novolac product. This would thus yield very significant economic and environmental benefits to the resin production.

It is also worthy to note that the as-prepared phenol-glucose resins are abundant in hydroxyl groups from the sugar side chains. Accordingly, the resins are expected to show good wetting and adhesion capability to many substitutes, and they can be mixed well with sawdust, sand and clay, etc. Employing a curing agent, the mixtures will form hard solidified materials upon heating. Thus, these phenolic-glucose resins are promising for a variety of applications as adhesive, paint, coating, and composite materials.[24] At the current stage, the motivation of replacing petroleum-based phenol with

TABLE III
Comparison of the Raw Materials Consumption for the Production of 100 Kg of HMTA-Cured Novolac of Phenol-Formaldehyde Resin or Phenol-Glucose Resin[a,b]

Cured resin product (100 kg)	Raw materials (kg)				
	Phenol	Formaldehyde	Glucose	HMTA	(Formaldehyde + HMTA)
Phenol-formaldehyde	74.99	11.97	0	13.04	25.01
Phenol-glucose	44.43	0	42.53	13.04	13.04

[a] Assuming the phenol-formaldehyde (or glucose) molar ratio in the resin synthesis was 1 : 0.5.
[b] Assuming 15 wt % HMTA was added for curing of the Novolac-type resin.

renewable biomass-derived feedstocks in resin synthesis is mainly related to the concerns over environment and resource availability. Most of the works reported in literature were focused on the feasibility studies, consistently demonstrating that the biomass-based resins show inferior properties (including the mechanical properties) compared with the commercial phenol-formaldehyde resins, due to the inherent low reactivity of the biomass-derived feedstock resulting partly from the steric hindrance of the bio-based chemicals. As such, our phenol-glucose resins would not be an exception, although mechanical tests (e.g., bond strength) of the resins cured with hexamethylenetetramine as adhesives for plywood production was not performed in this work. This work was primarily focused on the synthesis and physical/thermal characterizations of the glucose-based resins. In the next stage of the research, the adhesion tests will be conducted using plywood samples in accordance with the ASTM standard of D 906-98.

CONCLUSIONS

In this work, glucose was successfully applied to replace the toxic formaldehyde to synthesize novel Novolac type phenolic resins, catalyzed by strong acid at a high temperature (120–150°C). The condensation polymerization could proceed readily with solutions of phenol and glucose at varying molar ratios (1 : 0.4 to 1 : 0.9) through the Friedel-Crafts reaction mechanism. Evidenced by the thermal cure behaviors and the thermal decomposition properties, the obtained phenol-glucose resins showed satisfactory characteristics, as compared to the conventional phenol-formaldehyde resins. For instance, the cured resins showed excellent thermal stability, e.g., they started to decompose at >280°C with residual carbon yields of >58% at 600°C. Based on the thermal properties, phenol-glucose resin with a molar ratio of 1 : 0.5 is promising as it could be cured at a lower temperature (147°C) and exhibited a satisfactorily good thermal stability: it started to decompose at >300°C with a residual carbon yield of >64% at 600°C. Replacing formaldehyde with glucose in the resin synthesis could reduce a significant amount of formaldehyde and displace a marked portion (to about 50 wt %) of phenol by renewable and inexpensive resource (glucose) in the novolac manufacture process. This would thus yield very significant economic and environmental benefits to the resin production.

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