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Phenolic Resins

Condensation Reactions Between Phenol, Formaldehyde and 5-Hydroxymethylfurfural, Formed as Intermediate in the Acid Catalyzed Dehydration of Starchy Products

Helmut Koch and Joachim Pein

Maizena Gesellschaft mbH, Kalkarer Straße 81, D-4190 Kleve, Federal Republic of Germany

SUMMARY

The incorporation of starch hydrolysates in phenolic resins of the novolak and resol type via intermediate acid catalyzed dehydration to 5-hydroxymethylfurfural (HMF) has been investigated. The course of reaction was monitored by carbon-13-NMR and IR spectroscopy. Due to the formation of HMF/phenol condensates, savings of up to 40 % phenol and 50 % formaldehyde (by weight) are possible in comparison to commercial resins. Besides maintenance of essential property profiles, additional benefits may be achieved with respect to faster curing and lower amounts of free monomers.

INTRODUCTION

Increasing importance is being attached by the chemical industry to the use of renewable raw materials under the specific aspects of availability and environmental protection (1,2). The natural polymer starch may, through conversion and modification, be adapted in a most versatile way to the requirements imposed on a raw material or intermediate product for biotechnical or chemical syntheses (3-5).

The incorporation of starch hydrolysates in phenolic resins seems to be rather fascinating because the natural product is not used as a filler but as a chemical building block (6-9). Under the acid conditions prevailing in resin manufacture, 5-hydroxymethylfurfural (HMF) is formed as an intermediate, replacing not only part of the formaldehyde - which has recently come under heavy attack - but also phenol. It has been the aim of our investigations to better understand this incorporation of starchy products in phenolic resins and to find out how essential properties of phenolic resins are influenced.

FORMATION AND REACTIONS OF HMF

Figure 1 shows schematically how starch is hydrolyzed under acid conditions to reducing glucose units which, following the pattern of the browning reaction, are then dehydrated in a multi-stage reaction to 5-hydroxymethylfurfural (HMF), a starting compound for further reaction with phenol but also for selfcondensation and decomposition (10).

Very important for an incorporation of HMF in phenolic resins is that self condensation into water-insoluble, humin-like polymers and decomposition into levulinic acid and formic acid are largely avoided. This is achieved by letting the formation of HMF take place already in the presence of phenol. In this respect the use of starch hydrolysates with varying molecular weight distribution may offer an advantage over pure glucose because the dehydratable monosaccharide units are then formed successively. This allows another form of variation.

HMF, unlike formaldehyde, shows a methylol function in addition to the

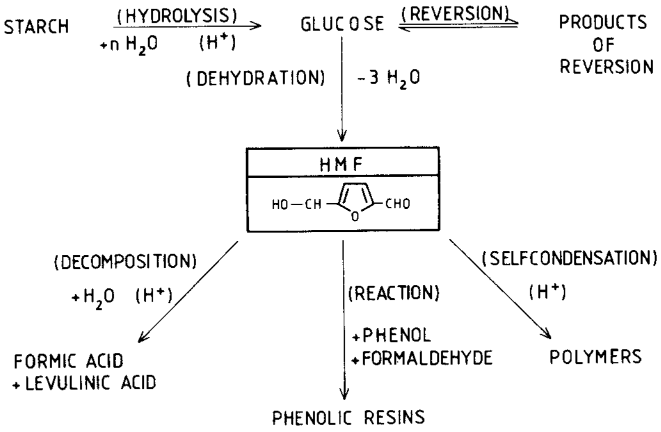

Fig. 1: Formation and reactions of HMF

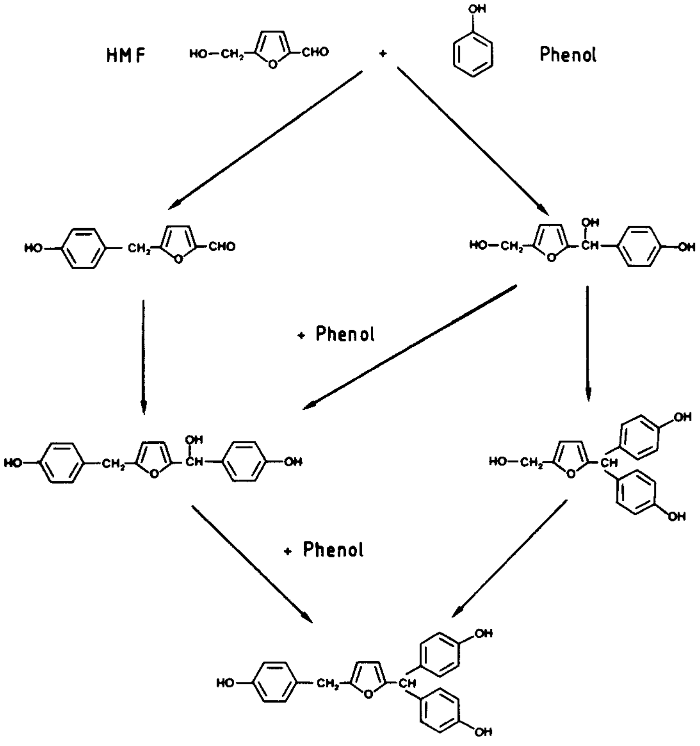

Fig. 2: Possible reactions between phenol and HMF

aldehyde function so that condensation reactions with the phenol may take place via the aldehyde as well as the methylol group. Mudde (6,7) claims that condensation with as much as three phenol nuclei is possible, but from the findings so far made this seems fairly improbable.

When studying phenol conversion in relation to time, it is noted that, when starch hydrolysates are included, mainly phenol and formaldehyde tend to condensate first before further condensation with HMF derived from the hydrolysate takes place.

SPECTROSCOPIC INVESTIGATIONS

Carbon-13-NMR Valuable clues to the hydrolysis of oligomeric starch hydrolysates and the incorporation of furan units in phenolic resins are provided by carbon-13-NMR spectra (Figure 3). Starch hydrolysates show characteristic signals of the C-1 within a range from 92 to 103 ppm. The signals of the bridged C-1 and of the C-1 featuring free OH groups in the α- and ß-form are clearly visible, and so maltooligomers may be shown in addition to glucose (11).

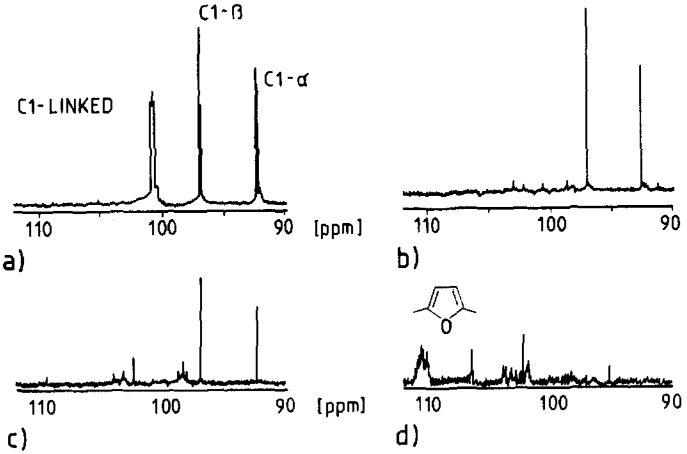

Fig. 3: C-1 signals of carbohydrates in carbon-13-NMR spectra of starch hydrolysate-modified novolak; a) pure hydrolysate; b) 110 °C reaction temperature; c) 130 °C; d) end product (150 °C).

In the end product the signals of the anomeric C-1 have disappeared, which means that there is no free glucose present any more (confirmed by GPC). At the same time new signals appear, with those at 107-111 ppm being attributable to the CH groups of furan structures that have developed (12).

Another circumstance favourable to the use of carbon-13-NMR spectra was that in the range from 149 to 158 ppm the substitution patterns of phenol nuclei are visible without interference from carbohydrate signals. Using the C-1 of the phenol nuclei it is possible to clearly distinguish between o-and p-substitution as well as between double and triple substitution (13).

In Figure 4 the spectra of two novolaks, made without and with starch hydrolysate, are compared.

If hydrolysate is included, p-substitution is observed more frequently and double and triple substitutions less frequently than with conventional novolaks. If condensation takes place solely between phenol and hydrolysate,

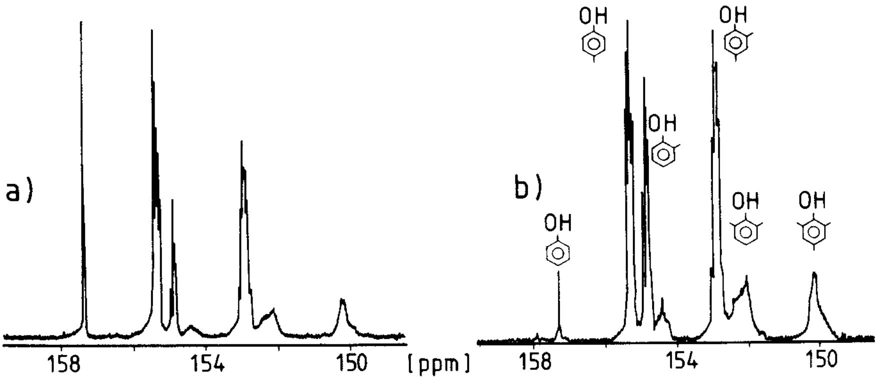

Fig. 4: C-1 signals of phenolic rings in carbon-13-NMR spectra of conventional and of starch hydrolysate-modified novolaks; a) with hydrolysate; b) without hydrolysate.

p-substitution and the absence of multiple substitutions are observed almost exclusively.

IR spectra When monitoring the reaction between phenol and starch hydrolysates by means of IR spectra, there are no hints obtained that would point to cross-linkages being produced by 3 HMF molecules combining with one phenol nucleus. Where condensation takes place exclusively between phenol and starch hydrolysate, IR bands in the 900 cm^{-1} range are lacking. This coincides with the absence of C-1 signals at 150.2 ppm in the carbon-13-NMR spectra, which are characteristic of triple substituted phenol nuclei.

The relevant IR spectra (Figure 5) also furnish clues to the intermediary occurrence and disappearance of HMF. At a reaction temperature of 125 ^{o}C one may already discern what is clearly visible at 140 ^{o}C as a band at 1645 cm^{-1}. This band is to be attributed to the furfural structure, which means that condensation with phenol takes place at least partly via the methylol group. In the end product this band at 1645 cm^{-1} has disappeared again, as may be expected considering the high reactivity of the aldehyde group.

The additional band in the end product at 1710 cm^{-1} points to the presence of levulinic acid, a HMF consecutive product.

APPLICABILITY ASPECTS

The change in resin composition and degree of condensation leads to a number of functional properties among which free phenol and formaldehyde contents , rheological behaviour and reactivity are the most important ones. The rheological properties of novolaks are determined by melt viscosities and flow times while the reactivity is determined by cross-linking time (B-time) and flow distances.

On aqueous resols, viscosity is measured and reactivity determined by means of B-time. Other characterizing criteria are water-dilutability and water-resistance.

By suitable selecting reaction conditions, the molar ratio of starch hydrolysates, and their molecular composition, it is possible to produce resins which in their essential properties are identical to nonmodified resins. Moreover, starch hydrolysates permit individual properties of phenolic resins to be changed selectively.

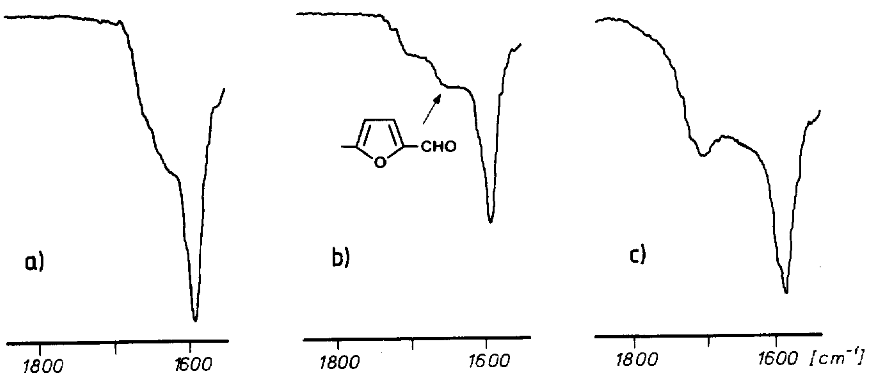

Fig. 5: IR spectra of starch hydrolysate-modified novolak (course of reaction); a) 125 °C; b) 140 °C; c) end product.

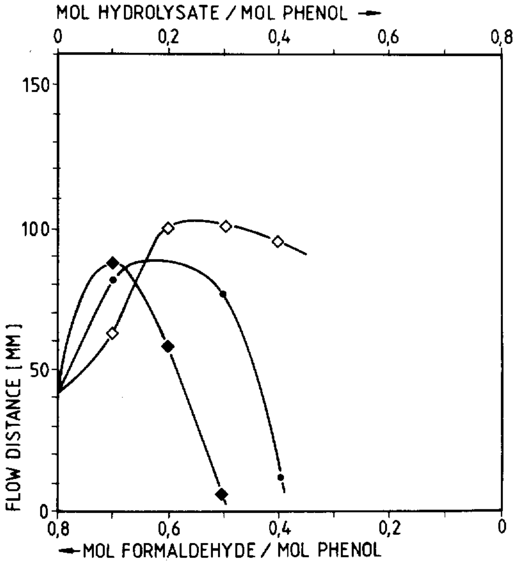

Fig. 6: Influence of nature and amount of starch hydrolysate on flow distances of novolaks; (◆) 44 DE hydrolysate; (●) 73 DE hydrolysate; (◇) 94 DE hydrolysate with more than 20 % fructose

Reactivity of phenolic resins In Figure 6 the flow distances of novolaks are plotted to show the influence of varying formaldehyde replacement levels and of hydrolysate composition. While low molar proportions of hydrolysate initially lead to larger flow distances, there are lower flow times and higher reactivities of the modified novolaks observed when certain hydrolysate levels are exceeded. The maximum of flow distance coincides with the maximum measured for B-time. As flow distances become shorter, B-times become shorter, too. The same analogy applies to the minima for flow times and melting points.

As may be seen from Figure 7, the distinctly higher reactivity of resols may very simply be illustrated by their curing behaviour as related to time. For this purpose paper tubes impregnated with resol are heated for different periods whereupon the cured resin portion is determined by extraction with acetone. Starch hydrolysates lead to much shorter curing times at equal temperature. This effect is even greater than the increase in reactivity which in nonmodified resols can be brought about by higher reaction temperatures. The sequence of curing speeds corresponds to the B-times of the resols.

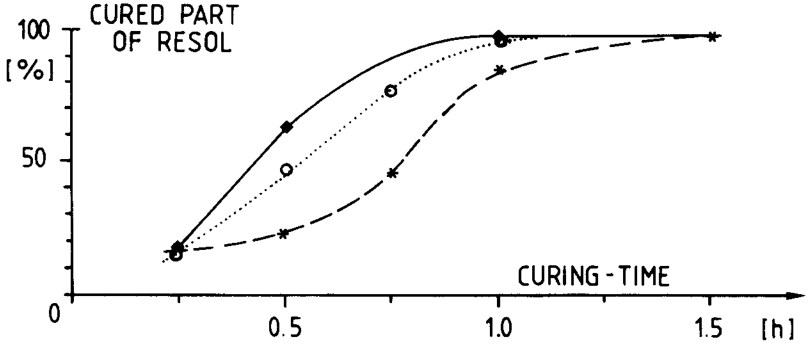

Fig. 7: Influence of starch hydrolysate on curing behaviour of resols;
(✱) P:F:H = 1:2.5:0; 65 °C. (○) P:F:H = 1:2.5:0; 80 °C.
(◆) P.F.H = 1:2:0.5; 65 °C.

This means that starch products allow faster curing of both novolaks and resols and so are apt to accelerate technical processing.

Residual amounts of free monomers The residual contents of free phenol and especially of free formaldehyde are very important criteria in phenolic resins. In carbohydrate-modified novolaks the free phenol content is comparable to that of conventional products while the free formaldehyde level was always found to be on the detection limit.

Resols modified with starch hydrolysates present an even more favorable picture. At a 20 % molar formaldehyde replacement level and a condensation temperature of 65 °C, residual monomer contents are, under otherwise identical reaction conditions, lowered by the factor 2-3, which is more than what would be proportionate to the replacement level (Figure 8). For phenol the effect is similar to the one that would be achieved with higher condensation temperatures (80 °C). For formaldehye it is much greater, which means that a higher molar proportion of starch hydrolysates is much more suited for lowering the free formaldehyde content than a increase of temperature. This is a very important finding considering the potential hazard connected with formaldehyde.

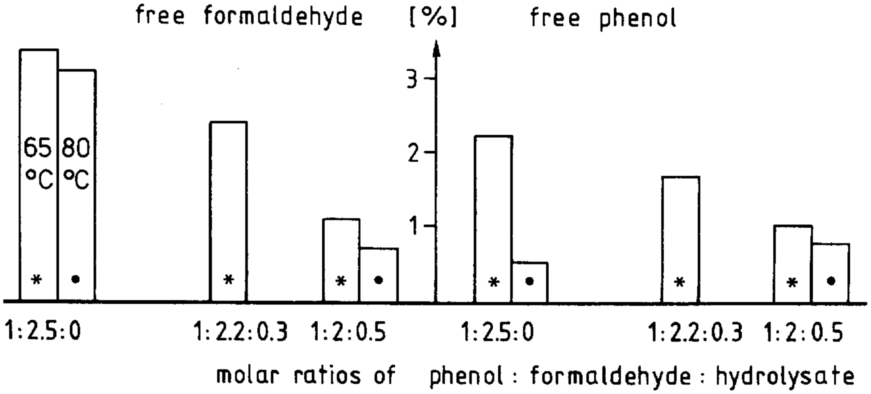

Fig. 8: Influence of starch hydrolysate on the free monomer content of modified resols; alkaline catalyst: 3 % NaOH.

By lowering condensation temperatures and at the same time reducing the content of free formaldehyde it is also possible to improve water-dilutability.

ECONOMIC ASPECTS

The investigations so far undertaken and reported here have shown that it is possible to replace up to 35 % of the formaldehyde commonly used in the manufacture of phenolic resins. This limit is set by the very high viscosities and cross-linking speeds that occur at replacement levels above 35 %.

Since HMF has a much higher molecular weight (M = 126) than formaldehyde (M = 30), savings up to 50 % (by weight) formaldehyde are possible for novolaks and resols as well as savings of 25 % phenol for novolaks and 40 % for resols.

Another advantage in connection with novolaks is derived from the fact that smaller amounts of water have to be evaporated because starch hydrolysates show a higher solids content than formaldehyde solutions.

While the use of starch hydrolysates in novolaks does not call for a change in process conditions, carbohydrate-modified resols require a two-step process. First a HMF phenol precondensate is produced in acid catalysis, which after alkalization is then reacted in the usual manner with formaldehyde. It is assumed that the precondensate is methylolated as it happens in conventional resol manufacture.

RESUME

The investigations described here offer the chance of making broader use of nonfossil, renewable resources. It should be noted, however, that a wide use of this potential is impeded presently by the agropolitical environment which today still governs the manufacture and use of starch products in the EEC.

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