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C-13 NMR IDENTIFICATION OF UREA-FORMALDEHYDE RESINS

Beat Meyer and Rudi Nunlist

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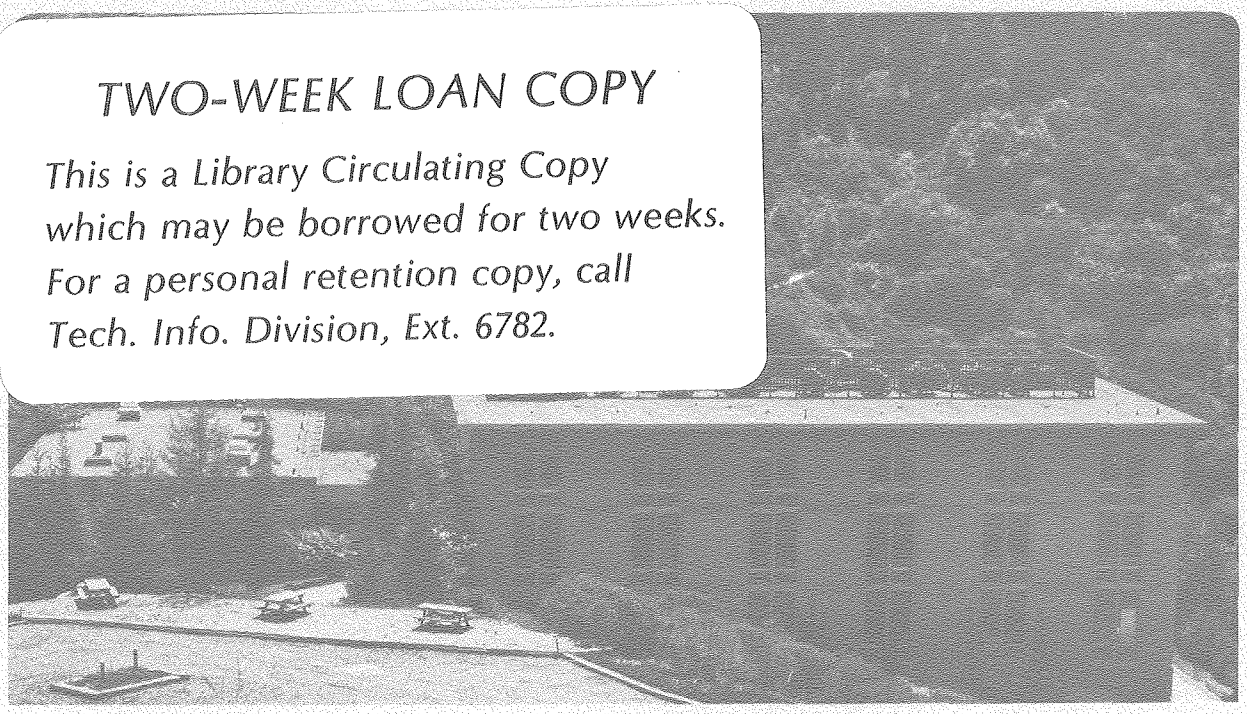

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Beat Meyer and Rudi Nunlist

Chemistry Department, and Molecular and Materials Research Division

Lawrence Berkeley Laboratory

University of California, Berkeley, California 94720

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by
Beat Meyer and Rudi Nunlist
Chemistry Department, Molecular & Materials Research Division
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

The art of urea-formaldehyde resin formulation was developed around 1930 for the purpose of manufacturing cast objects. Recently, these resins have been increasingly used as adhesives in the forest products industry and for the production of foamed in-place urea-formaldehyde insulation, which has found a large, new market in the thermal insulation of residential and commercial building shells, and in the fire protection of structural steel in high rise buildings. About 500,000 tons of formaldehyde are annually converted into urea-formaldehyde resins, half of which goes into wood adhesives for particleboard. These resins have mechanical, chemical and other properties not matched by any other adhesive at a comparable price. Furthermore, they are biodegradable. However, in some of the new, large volume uses, problems have arisen from the slow release of formaldehyde. Currently, chemists, forest products specialists, manufacturers, regulators, lawyers, and even consumers are debating whether these problems are due to unreacted formaldehyde left in the finished product, or to hydrolytic or other degradation of the resin, and whether these effects are caused by intrinsic problems in the resin chemistry (1,2), by the large surface area and uneven film thickness of cured resins in these applications, by improperly cured resin, improperly formulated resin, over-age resin, improper application, product design or other shortcomings in quality control.

In our attempt to sort out these factors and correlate resin chemistry with product properties (3), we have found it difficult to obtain well characterized commercial resins suitable for basic research. Manufacturers in the U.S. and abroad frequently provide only information about solid resin content, viscosity and gel times of adhesives. Furthermore, we found that, contrary to the assumption of many resin users, the urea-formaldehyde resins supplied by different manufacturers had different chemical properties. In fact, in some cases we found that some resin suppliers did not provide us with reproducible materials, and that the U:F ratio, if given, differed from that which we obtained by elemental analysis. We therefore found a need to identify resins. As a method of analysis, we selected C-13 NMR spectroscopy, because it has established itself as the most reliable method for analyzing laboratory and commercial carbon containing chemicals, including such complex materials as coal (4). It provides a comprehensive inventory of all functional carbon groups, and thus eliminates the guessing whether some additives or intermediates might have been omitted or overlooked. The test can be conducted <u>in situ</u>, without shifting the labile equilibria among species, which makes chromatographic methods questionable. The method is quick, and thus allows identification of intermediates during reaction and kinetic studies. The tests cost only a fraction of wet analysis. Unlike proton NMR, used in the pioneering studies of Chiavarini (5), C-13 NMR yields excellent resolution, as shown by Tomita (6) and Slonim (7) using laboratory resins. Furthermore, gated decoupling (8) has made it possible to overcome the nuclear Offenhauser effect (NOE) which previously prevented quantitative work with carbon 13. Finally, NMR machines are integrated with computers, and it is easy to store a large number of spectra for future reference and comparison. Such comparison can be conducted directly on the NMR computer, and chemical analysis can be deduced in final, numerical form.

<u>Experimental</u>: Commercial urea-formaldehyde resins were used as supplied by manufacturers. 5 ml D_2O was added to 25 ml resin in a 25 mm diameter NMR glass tube. Measurements were made at 20°C. 400 to 2,000 scans were used to accumulate spectra on an NMR instrument consisting of a Brucker magnet, a Nicolet computer combined with laboratory assembled electronics. Spectra were recorded at 4.3T corresponding to 45MHz carbon frequency. Dioxane was used as an internal

standard.

Results and Discussion: Figure 1 shows the 40 to 100 ppm region of the C-13 NMR spectrum of five commercial resins obtained from four manufacturers. Figures 1a and 1b are particleboard resins. Resins 1c-1e are foam resins. Both particleboard resins contain six dominant functional groups in the aliphatic range, while the foam resins contain up to 22 functional groups in significant concentrations. Peaks are identified with the help of model compounds, and by comparison with the spectra of synthetic laboratory resins published by Tomita (6) and Slonim (7). Only the most important peaks are discussed here.

Chemically the most important reactive component of the liquid resin is the aldehyde group. Some excess formaldehyde is necessary to ensure crosslinking. In aqueous resins, free formaldehyde appears in its hydrated form, as methylene glycol, $CH_2(OH)_2$, which appears at 83.1 ppm, and as polyoxymethylene glycol, $HO(CH_2O)_nH$, at 86.6, 87.7 and 90.0 to 91.5 ppm. Only in resin 1e is methylene glycol clearly noticeable in the figure. But even in this resin, the concentration is far below 1.0 wt%. In contrast, until 5 years ago, resins contained at least 1.5 wt% or more methylene glycol (1). Latent formaldehyde can also be incorporated into resins as methylol. In all resins the $-NH-\underline{C}H_2OH$ methylol group at 65 ppm is the predominant species. The peak at 71.7 ppm, due to $=N-\underline{C}H_2OH$ methylol is also present in all resins, but it is more prominent in the adhesive resins than in the foam resins. The total methylol concentration ranges anywhere from 5 to 25 wt%. The optimum concentration of methylol in a resin depends on other resin components, but the observed levels are obviously higher than was common in the past. Thus, we conclude that manufacturers currently favor methylol which is formed by reacting methylene glycol with urea, either at the beginning of the resin synthesis, or at the end by "second addition".

Since methylol has a lower formaldehyde vapor pressure than methylene glycol, the use of methylol reduces the odor of resins and reduces the formaldehyde level in the air at the work place where the liquid resin is used. Furthermore, such resins readily meet regulatory requirements for low methylene glycol analysis of liquid resins (9). Unfortunately, however, methylol readily hydrolyzes. Thus, excess methylol in finished products exposed to moisture will slowly release formaldehyde.

From figure 1 one would expect that all of the five resins emit very little formaldehyde at the work place, but that products made with these resins might be capable of readily releasing formaldehyde if excess methylol is not protected by other built-in functional groups which can act as formaldehyde scavengers.

Urea and its derivatives have peaks around 160 ppm which are not shown in figure 1. Among the product peaks, the most prominent low-shift peaks are the methylene linkages at 47.7 ppm and 53.8 ppm. The first peak is due to linkage among secondary amines; the latter connects one secondary nitrogen to a tertiary nitrogen. The methylene linkages are very stable and resist hydrolysis. In contrast, almost all other bonds are vulnerable to hydrolysis. The peak at 55.6 ppm is due to the methoxy group which is present whenever resins are made from formalin. Formalin contains 10-15 wt% methanol, which solubilizes formaldehyde polymers via the formation of low molecular weight ethers. Thus, the methoxy groups stabilize liquid resins, and prevent aging (1), but the bond remains susceptible to hydrolysis. The particleboard resins, fig. 1a and 1b, contain very little methoxy, while the foam resins are rich in methoxy. The peak at 69 ppm is due to dimethylene ether. This type of linkage adds elasticity to the cured resin and helps prevent shrinkage. Thus, this functional group is desirable for foam resins.

Resin fig. 1e contains two additional strong peaks at 61.5 and 72.5 ppm not present in any other resin. These peaks are due to ethylene glycol, which was apparently added to the resin 1d to modify product properties. All of the foam resins show a variety of other chemical functions which are not present in the adhesive resins. These functions differ in the shown and other foam resin formulations and impart to the resin individual properties which account for

the proprietary and customized properties which foam resin suppliers usually claim for their products.

Conclusions: The current work shows that adhesive and foam resins differ significantly in qualitative and quantitative composition, and that the differences in the C-13 NMR spectra can be readily recognized, even by an untrained person. In fact, the "finger prints" of resins are so characteristic that our NMR operators, who were not familiar with urea-formaldehyde resin chemistry, rapidly learned how to distinguish between particleboard or plywood adhesives and foam resins, as well as between different manufacturers and individual batches. Thus, we believe that the NMR method lends itself extremely well to quality control. Furthermore, NMR machines are connected with computers, and a large number of spectra can be conveniently stored and recalled if the necessity should arise for comparison. Such comparison can be conducted on-line, and if properly programmed, the full chemical analysis can be printed out.

Since spectra recorded during aging of resins and during curing change substantially, and since spectra can be recorded rapidly and *in situ*, the C-13 NMR method makes possible quality control during resin manufacture. In fact, the NMR method makes it possible to modify resins during synthesis. Thus, chemical knowledge can be used to supplement the art and intuition of manufacturers. Furthermore, a full chemical analysis of the reaction products of the resin and of additives provides the potential for improving resins far beyond current standards.

Finally, such chemical analysis will make it possible to correlate basic resin chemistry with properties of the finished products. Preliminary work indicates that such a correlation might be more readily achieved than formerly anticipated. For example, there seems to be a direct correlation between the concentration of methoxy groups and formaldehyde release from hardwood-plywood. This correlation has been confirmed by the observation of methanol in the off-gas of such products (2).

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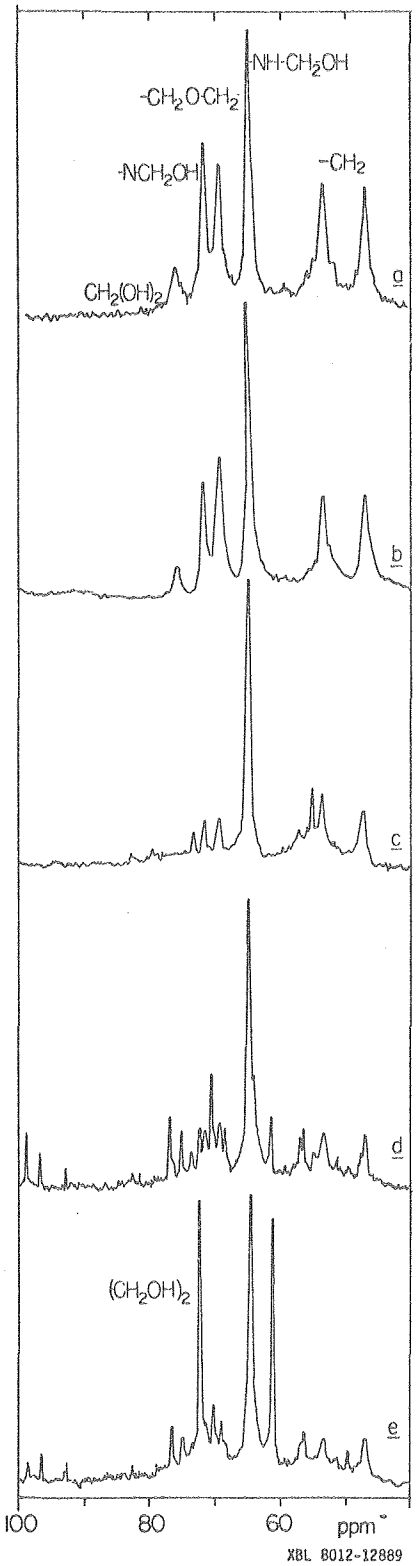
Figure 1: C-13 NMR of 5 commercial urea-formaldehyde resins. a) Particleboard adhesive with a U-F ratio of 1.4; b) Particleboard adhesive with a U-F ratio of 1.3; c) Reconsituted liquid foam resin; d) Liquid foam resin, and e) Manufacturer modified resin # d).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-CH2
CH2(OH)2
a
b
c
d
(CH2OH)2
e
100
80
60
ppm
XBL 8012-12889

Fig. 1