

Morphologic Accessibility of Wood Adhesives

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Synopsis

Accessibility of wood adhesives was determined using a potassium bromide-embedding technique during resin cure. Cured resin was then extracted with water, followed by x-ray analysis of residual potassium bromide retention in the adhesive matrix. Cured urea-formaldehyde (UF), phenol-formaldehyde resol (PF), and phenol-resorcinol formaldehyde (PRF) accommodated large quantities of potassium bromide. However, only PRF adhesive showed crystallization of trapped potassium bromide, suggesting the presence of large pore sizes in the polymer lattices. Both UF and PRF adhesives, after room-temperature soaking, were equally resistant to water access. At higher temperature, water accessibility of UF increased greatly which may be attributed to thermal softening of the adhesive, while the accessibility of water to the PRF adhesive matrix was mainly a surface phenomenon and was not very temperature dependent. PF was highly accessible to water, even at room temperature, as a result of swelling from the presence of sodium hydroxide (catalyst). Accessibility of PRF adhesive was greatly increased by base (NaOH) solutions but not by acid (H₂SO₄) solutions. The UF resin showed slight increase of accessibility with increase in acidity and basicity of the water solution, but the accessibility increase of this adhesive in base solution was substantially less than that of PRF. The acid hydrolysis influence on accessibility increase of UF adhesive was far less severe than that of temperature.

INTRODUCTION

Three commonly used wood adhesives are urea-formaldehyde (UF), phenol-formaldehyde resol (PF), and phenol-resorcinol formaldehyde (PRF) resins. Both UF and PRF resins can be cured at room or higher temperatures, while PF resin is a high temperature-setting adhesive. A UF resin-bonded product is classified as nonweatherproof, while PF- and PRF-resin products are accepted for weatherproof commodities.

Morphologic structures of cured adhesives are as difficult to study as their chemical structures. This is apparently due to the three-dimensional complexity of polymer lattices, which limits the effective application of conventional instrumentation techniques. In general, a completely cross-linked structure for PF molecules is considered to be most unlikely.¹ The insoluble and infusible nature of hardened PF resin was attributed to entanglement of resin molecules which were immobilized.² Cured PF resins³ were reported to have softening temperatures in the range of 150° to 200°C. These resins, after conditioning at 99% relative humidity, absorbed 35% to 50% moisture, and their softening temperature decreased 30° to 50°C from the dry condition.

Erath and Robinson⁴ observed cured PF resin by electron microscopy and found that the predominant structure was an agglomerate of irregularly shaped particles with average diameter of about 810 Å. Megson¹ proposed that within the fine structure of PF resins a considerable proportion of voids could exist. Therefore, sponge-like structure was speculated to account for the comparatively high water absorption and the lower strength of phenolic resins when compared with their calculated theoretical strengths.⁵ It should be noted that the electron-microscopic observation of Erath and Robinson⁴ failed to show any voids in the PF resin examined. This may indicate that either the voids in PF resin are much smaller than the resolution power of the electron microscope used, or the existence of the sponge-like structure proposed by Megson for PF resin is in doubt.

Little is known about the morphologic structure of UF resin. The urea monomer molecules were reported to form inclusion compounds with foreign substances.⁶ In the inclusion compound, urea molecules are hydrogen bonded into three interpenetrating spirals which form the walls of a hexagonal cell. The center of the cell is a channel of 4 to 5 Å in diameter which can accommodate a wide variety of long-chain molecules, providing the guest substance does not radically distort channel dimensions. These urea inclusion complexes decompose on heating.

From practical experience, UF resins are well known to produce excessive shrinkage during the course of curing and to crack in the process of dehydration. The undesirable property of UF resin is its high sensitivity to heat as indicated by its low thermal softening temperature of 60° to 70°C.³ Another amino adhesive, which is not as widely used as UF resin but has a higher softening temperature (130–180°C), is melamine-formaldehyde resin (MF).³ Wohnsiedler⁷ found by electron microscopy that cured MF resin had a structure composed of primary sphere-shaped particles of 150 to 200 Å in diameter, aggregated in groups of 700 to 800 Å in diameter.

Accessibility of cured adhesives is one of the important polymer properties that is not well understood. Since air, water, and chemical access to the polymer lattice is a prerequisite to in-depth chemical degradation or the development of heterogeneous stresses in a resin, the accessibility of cured adhesives will be critical to their long-term durability. The purpose of this paper is to, firstly, develop an x-ray method for examining the accessibility of a cured adhesive, using the concept of incorporating KBr salt into the resin system during cure. The amount and size of voids in the cured polymer lattices will be determined from the amount of total trapped KBr and the size of crystals of KBr found in the resins. Secondly, the experiment is intended to determine morphologic accessibility of cured resins to water at different temperatures and, thirdly, to examine the effect of caustic swelling and acid hydrolysis of the accessibility of cured resins. It is assumed that the accessibility or mobility of potassium bromide in low-concentration water solution is equal to accessibility of water to the adhesive lattices.

EXPERIMENTAL

Materials

Adhesives. Three commercial wood adhesives of known formulation were used in the experiment: urea-formaldehyde, phenol-formaldehyde, and phenol-resorcinol formaldehyde resins.

The PF resin (42% solid content) was prepared by reacting 2:1 molar ratio of formaldehyde to phenol in the presence of 8% sodium hydroxide.

The PRF resin was prepared by first reacting formaldehyde and phenol in a molar ratio of 0.5 with sodium hydroxide (1.5% w/w) as a catalyst. The phenol-formaldehyde polymer was then mixed with 24% (w/w) resorcinol. The solids content of the resulting mixture was 61.5% at a pH of 7.7. Similar to commercial practice, this type of adhesive was polymerized by the addition of 15% to 20% paraformaldehyde.

The UF resin was prepared by reacting formaldehyde to urea in the molar ratio of 2:1, with final resin solution having pH 7.5 and a solids content of 60%. In this experiment, 5% (resin solids basis) of ammonium chloride the usual catalyst for this adhesive, was used for curing.

Potassium Bromide. Reagent-grade KBr crystals were used in all experiments except that infrared pellet-grade KBr was used for the crystalline KBr content control curve.

Methods

Adhesive Curing and Sample Preparation

Experiment A. To determine if the KBr-embedding technique can be useful for the study of water accessibility and its relationship with resin cure, 30 g each of all three resins with catalyst which were premixed thoroughly with 10% w/w KBr (based on resin solids) were spread on glass plates and heated in a forced-draft oven (air speed 450 ft/min) at 120°C. Two to 4 g of each resin were removed from the oven at 10-, 20-, 40-, 60-, and 80-min intervals and stored in a deep-freeze unit at -15°C to stop further curing.

One hour later, the resins were ground to pass a 60-mesh screen and about 2 g of the samples were placed in a 500-ml beaker containing 300 ml distilled water under stirring. The solution was decanted 2 hr later and fresh water (300 ml) was added. The mixture was then filtered and washed with 500 ml water. The solid resin was dried in the oven at 60°C for 24 hr.

A supplemental experiment of curing PF resin with KBr added at 160°C for the same period of time was also performed.

One gram of the samples was then mixed thoroughly with 1 g Whatman CF 11 cellulose powder and pressed under a 10-ton (9072 kg) load to make a 1.5-in. (3.81 cm)-diameter pellet for x-ray analysis.

A supplemental experiment for examining the possible influence of sodium hydroxide (catalyst) on PF resin holding capacity for KBr under aqueous conditions was carried out as follows: 20 g PF resin was cured in

the forced-draft oven at 120°C for 20 min until a degree of cure of about 40% was reached as determined by the ultraviolet spectrophotometer method.⁸ The gelled resin was then placed in a 1-l beaker with 800 ml distilled water under continuous stirring to remove sodium hydroxide. The water was changed every half hour in the first 6 hr, five to ten times a day for the next four days and finally washed until the water solution had pH 7 to 7.5 to indicate total removal of free sodium hydroxide catalyst. The resin was recovered and placed in a beaker (200 ml) containing 100 ml KBr-saturated water solution.

The mixture was then placed inside a vacuum desiccator and 25 in. of vacuum was applied for 1 hr to facilitate the penetration of KBr solution into the resin lattices. After vacuum release, the mixture was allowed to stand for 2 hr at room temperature and the excess water decanted. The solid resin remaining was heated at 160°C for 30 min to complete cure, followed by soaking in water for 1 hr, washing with fresh water, and drying at 60°C overnight. One gram of the sample was embedded with 1 g cellulose powder as before for the x-ray diffraction study.

Experiment B. To study the water accessibility at different temperatures of the three cured resins, a measured weight of KBr, in an amount equivalent to 10% resin solids, was dissolved into 30 ml water. This KBr solution was then poured into 500-ml beakers each containing 200 g resin with catalyst. The resin-KBr combination was thoroughly mixed and poured into Syracuse watch glasses.

The PRF and PF resins were cured in a forced-draft oven (450 ft/min air speed) at 160°C for 1 hr, while the UF resin was cured in the same oven at 100°C for 16 hr. The cured resins were ground to pass a 60-mesh screen and stored in plastic bags.

Four 20-g samples of each cured-ground resin were placed in separate beakers (1 l) containing 500 ml distilled water. One beaker of each resin was placed in a constant-temperature bath at either 20°, 40°, 60°, or 80°C. Approximately 2 g resin was withdrawn from each beaker at the following times: 10, 30, 60, 90, and 120 min. The sample was thoroughly washed with cold water (1 l) and then dried in the oven at 60°C for 24 hr. One gram of the resin was then mixed with 1 g cellulose powder for x-ray determination.

Experiment C. To determine the acid and base accessibility of the resins, 2 g each of the resins were soaked in 2%, 5%, and 10% by weight of H₂SO₄ and NaOH water solution, respectively, at 25°C for 2 hr. A control sample was soaked in water for the same period of time. The samples were then filtered and washed with water (1 l), dried at 60°C for 24 hr, and readied for x-ray analysis as before.

X-Ray Instrumentation

A Siemens x-ray spectrophotometer and diffractometer were used for the determination of total KBr content and the crystalline KBr content in the resins.

The total KBr content was determined by exposing a resin-cellulose pellet to x-ray beams generated at 45 kV, 35 mA with gold target from the spectrophotometer. A proportional counter and LiF crystal analyzer were used with a counting time of 12 sec. The differentiator was set for 20 V window width and 10 V for baseline. The KBr content was measured from counts taken at the bromine K_{α} peak at 29.8° Bragg angle.

The same sample was then analyzed by the diffractometer. The x-ray beams were generated with a copper target at 35 kV and 20 mA. A gas-flow counter with methane-argon (10:90) gas at a flow rate of 5 ml/hr was used with a counting time of 1 min. The crystalline KBr content was determined by the count at [200] plane KBr diffraction peak at 27.1° Bragg angle.

The standard samples for calibration of total KBr content were prepared by mixing different quantities of KBr (0.1% to 20% of resin solid) with the respective resin solution for curing. One gram each of the prepared resin was then pelletized with 1 g cellulose powder.

For determination of the crystalline KBr content, the standard samples were made by mixing various weights of dry, fine KBr crystals with finely ground cured resin and then pelletized with 1 g cellulose powder to give a KBr content range between 0.1% to 20%.

RESULTS AND DISCUSSION

Experiment A. The potassium bromide content of the cured or partially cured UF, PRF, and PF resins, which were heated at 120°C as thin film on glass plates, ground, and then washed with cold water for 1 hr, is shown in Figure 1. The KBr retention of UF and PRF resins increased with curing time and leveled out after 40 min. At each curing time studied, the UF resin had a higher KBr retention than PRF. The PF resin retained a negligible amount of KBr at all curing times, both at 120°C and 160°C .

The above results indicate that the KBr embedding technique can be a convenient method to determine the degree of cure of UF and PRF resins. The reason for lack of applicability of the present method to PF resin can probably be attributed to the presence of sodium hydroxide (catalyst) which swells the polymer lattice. This will be discussed further later.

When the same samples were examined by the x-ray diffractometer, a striking difference between the three resins was observed. Both UF and PF resins showed a very small diffraction peak of KBr at its [200] plane (27.1° Bragg angle) in the nonsoaked condition, indicating little in the way of crystal structure, regardless of the high bromine content determined by x-ray spectrophotometer. This [200]-plane diffraction peak for the two resins disappeared completely once the samples were soaked in water.

In contrast to UF and PF resins, PRF resin showed a strong [200]-plane KBr crystal diffraction which remained strong even after water soaking (Fig. 2). The half-band widths of the peaks were similar for PRF resin cured at different periods of time, suggesting a similar crystal size of about

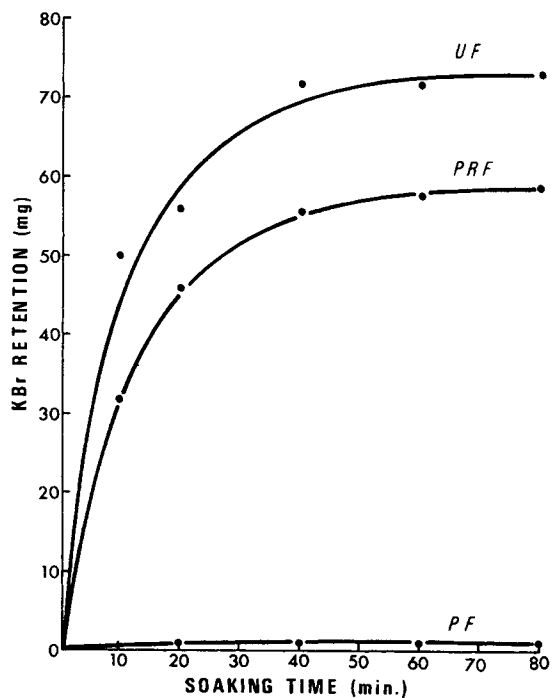


Fig. 1. KBr retention of adhesives cured at 120°C for different time periods and then submerged into water (25°C) for 1 hr. UF, Urea-formaldehyde; PRF, phenol-resorcinol formaldehyde; PF, phenol formaldehyde.

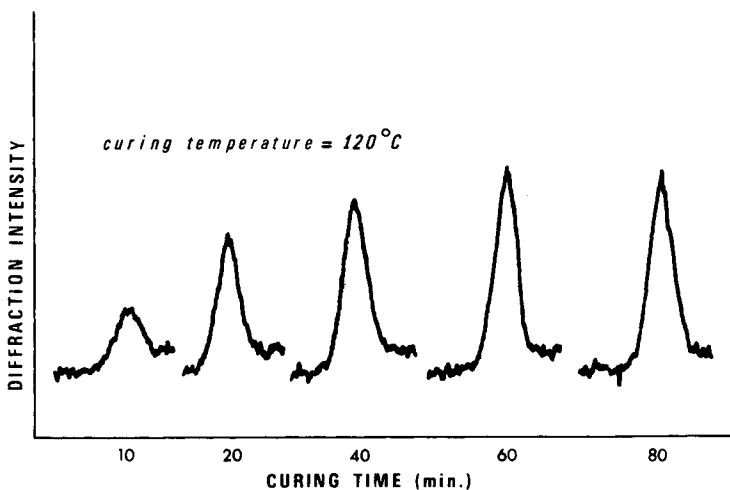


Fig. 2. Crystalline KBr diffraction (at $27.1^\circ \pm .1^\circ$ Bragg angle) in phenol-resorcinol adhesive after soaking in water for 1 hr.

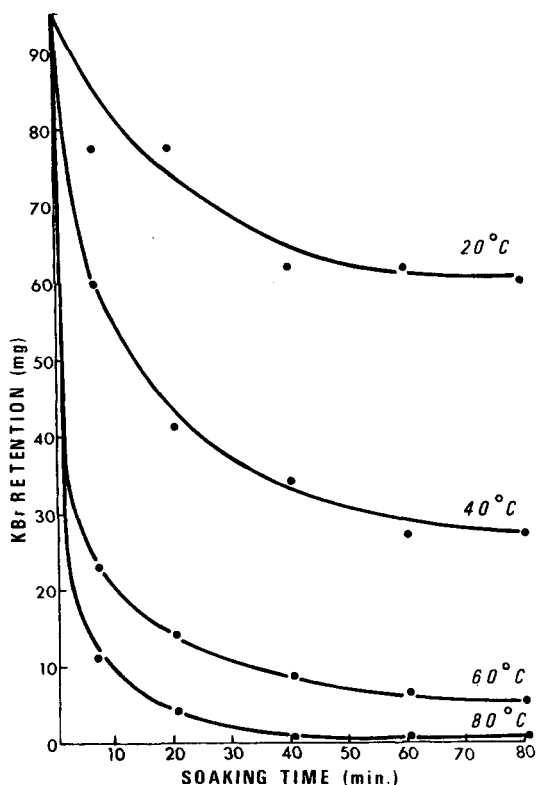


Fig. 3. KBr retention of urea-formaldehyde adhesive after soaking in water for different times and temperatures.

200 Å as calculated from Scherrer's equation⁹ without taking instrumental broadening of the [200] peak into consideration.

Samples which were prepared by mixing KBr separately with ammonium chloride (catalyst for UF) and NaOH (catalyst for PF) in water solution and heated on glass plates in oven at 120°C for 1 hr to remove water showed very strong KBr diffraction peaks with crystal size of about 230 Å. This indicates that the lack of KBr diffraction peaks in UF and PF resins is due to the nature of the polymer lattices, which do not allow the crystallization of KBr to occur, rather than to interference by ionic contamination from the catalysts.

These results indicate that the voids existing in polymer lattices for both UF and PF resins must be much smaller than 200 Å, and they do not allow the KBr to crystallize. The majority of the pore spacings in PRF resin could be in the 200-Å range. The present observation using KBr embedding and x-ray methods support the postulation of Megson¹ that sponge-like structures exist in phenolic resins.

Experiment B. The loss of embedded KBr from the cured resins in water at different temperatures is shown in Figures 3, 4, 5, and 6. The

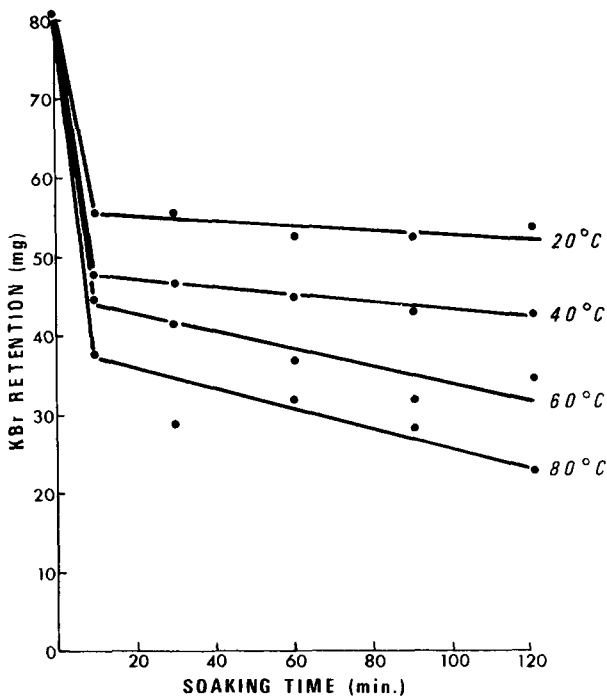


Fig. 4. Total KBr retention of phenol-resorcinol formaldehyde adhesive after soaking in water for different times and temperatures.

rate of loss of KBr from UF resin by water soaking (Fig. 3) increased with increasing temperature. The KBr retention for samples soaked for 60 min is 62, 34, 8.5 and 1 mg per gram of resin for soaking temperatures of 20°, 40°, 60°, and 80°C, respectively. This loss of KBr-holding capacity of the UF resin with temperature may be attributed to the thermal softening of the resin³ resulting in increase of free volume in the polymer and allowing a greater accessibility of water, analogous to swelling of the polymer lattice. In addition, surface desorption and chemical hydrolysis of the resin may have to be taken into consideration.

The loss of KBr content of PRF resin in water soaking is shown in Figure 4. There is a rapid decrease in the first 10 min, which can be attributed to the surface exposure of the coarse spacings (in comparison with UF resin). The much slower rate loss after 10 min indicated that the polymer structure of the resin hindered water access to the inner portion. Thus, the removal of KBr from PRF resin occurs in two stages: fast removal from the surface, followed by much slower removal from the inner structure. The removal of KBr from PRF is much less temperature dependent than the UF resin. For example, the PRF resin after soaking at 80°C for 120 min retained about 30% of the original KBr, while the KBr in UF resin was completely removed.

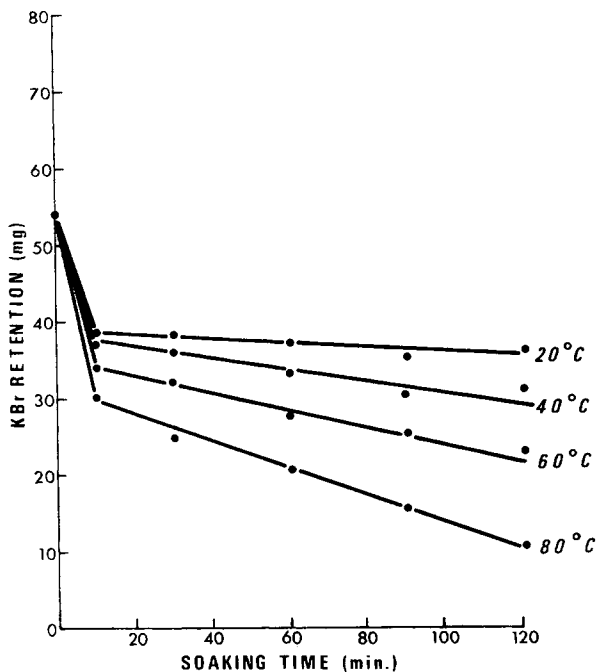


Fig. 5. Crystalline KBr retention in phenol-resorcinol formaldehyde adhesive after soaking in water for different times and temperatures.

Figure 5 shows the amount of unaccessible large pores in PRF resin, as indicated from the retention of the crystallized KBr content in the resin determined by x-ray diffractometry. This trend is similar to that shown in Figure 4 which was derived spectrophotometrically for the total KBr content.

The retention of KBr in PF resin after being heated at different temperatures in water is shown in Figure 6. Although KBr retention at different temperatures showed some difference at 10 to 30 min of heating, the difference is small and can be considered as insignificant. The final retention of KBr in PF resin at 90 min of soaking, regardless of heating temperature, is about 1.5 mg per gram of sample. When this value is compared with the retention of the other resins at 20°C soaking for 90 min, PF resin possessed only about 2.5% of the UF and 2.8% of the PRF resin retention capacity. The lack of temperature dependence of PF resin indicated that the removal of KBr from the resin lattice is not only a surface phenomenon, but also may be attributed to the sodium hydroxide swelling effect.

Experiment C. The effect of different concentrations of acid (H_2SO_4) and base (NaOH) in water solution on the KBr removal from UF and PRF resins at 20°C soaking for 1 hr are shown in Figure 7. This figure indicates that the KBr retention of UF resin showed little change with increasing acid or base concentration. The retention was greater in

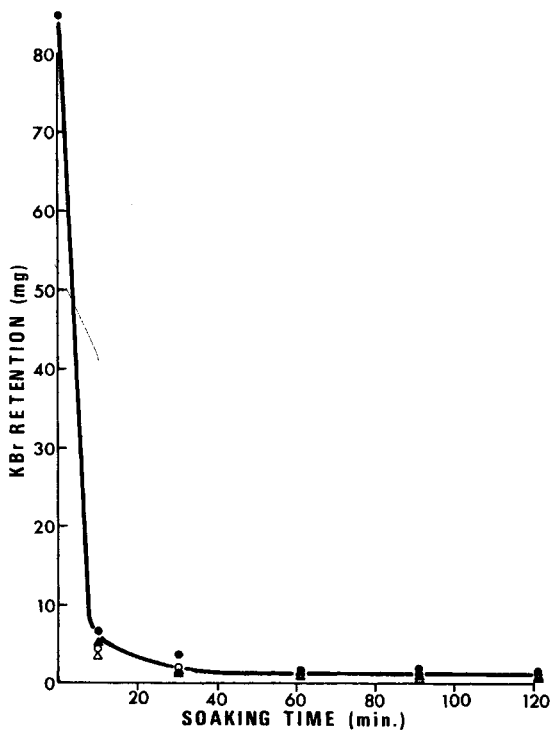


Fig. 6. KBr retention of phenol-formaldehyde adhesive after soaking in water for different times and temperatures.

the acid solution than in the base solution. For example, at 10% concentration, the UF lost about 13% KBr in acid solution and about 28% KBr in sodium hydroxide solution.

On the other hand, the KBr in PRF resin is not removed by treatment with sulfuric acid in the concentration range as shown in Figure 7, but the removal of KBr from PRF resin is greatly enhanced with the sodium hydroxide soaking. With 10% sodium hydroxide solution, the KBr retention of the PRF resin is only 7% of the amount retained after distilled water soaking. The effect of the sodium hydroxide on the KBr retention of PRF resin supports the previous reasoning that the poor KBr retention of PF resin is the result of sodium hydroxide swelling of the resin. This is further demonstrated in the experiment designed to eliminate the sodium hydroxide catalyst from the PF resin, which was first cured to a 40% degree of cure, thoroughly washed with water to remove sodium hydroxide catalyst, and then impregnated with KBr solution. This was followed by heating the resin at 160°C for 30 min to complete the cure. The resin, after 1 hr of soaking in water and drying showed a [200] diffraction peak of KBr similar to PRF resin, with a crystalline content of about 15%.

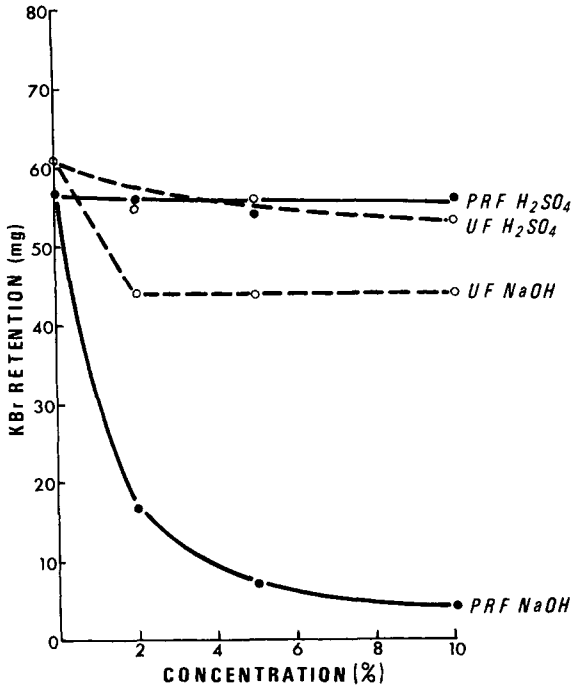


Fig. 7. KBr retentions of cured urea-formaldehyde and phenol-resorcinol formaldehyde adhesives after soaking in different concentrations of H_2SO_4 and $NaOH$ solutions at room temperature.

Industrial Significance. The results of the present study indicate that the UF resin used in the wood industry has a water accessibility similar to PRF resin at $20^\circ C$. Since accessibility is prerequisite to an internal chemical degradation, it is reasonable to state that the UF resin is fairly stable to chemical attack during room-temperature soaking. The detrimental factor that influences the UF resin is temperature. The phenolic resins, on the other hand, are stable to temperature but easily swelled by alkaline solution. While the alkaline attack on the cured phenolic resins may not cause chemical changes in the resin, the impact of the swelling action on creep or other rheological behavior of the resin products in practical application deserves attention.

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