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Alkali Catalysed Curing of Starch-Melamine Resin Systems

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SUMMARY

The curing process in starch adhesives modified with melamine resin can take place by co-condensation or self-condensation. A high degree of co-condensation is required to provide a good water resistance of a cured glue joint. This can be attained by using melamine resins with a high concentration of hydroxymethylamino groups. The reduced effect of the adhesive on storage is due to a degradation of the melamine resin through the elimination of formaldehyde.

INTRODUCTION

Pure starch is still a customary binder in the paper and textile industries. In many cases, starch is employed as the sole binder; a combination of cooked starch and starch slurry often gives the best result.

Binders based on starch are often used at a high pH. For example, in the manufacture of corrugated board a pH of between 11 and 13 gives the best result. In addition,small amounts of disodiumtetraborate or boric acid are often added to control the viscosity and flowability of the binder.

Unmodified starch, however, yields a relatively hydrophilic film after curing. An amino or ketone resin is often added to the starch solution before use to provide a better water resistance. Melamine resins have been found to function well as hydrophobizing agents and low-molecular, non-etherified types, produced by condensation of melamine and formaldehyde, are frequently employed. Fig. 1 shows the structures of the conceivable substituents on the triazine rings of these resins.

It has not been established whether the melamine resin functions as a crosslinking agent in these systems, i.e. reacts with the starch component, or whether it cures by self-condensation. Several investigations have shown that co-condensation predominates for the system alkyd (polyester) - melamine resin with acid catalyst (SEIDLER and STOLZENBACH 1975, HOLMBERG 1978). However, the curing of melamine resins and hydroxyl-containing polymers in alkaline medium seems to

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have been studied to a very small extent. The present work aims at providing a contribution to the understanding of this process.

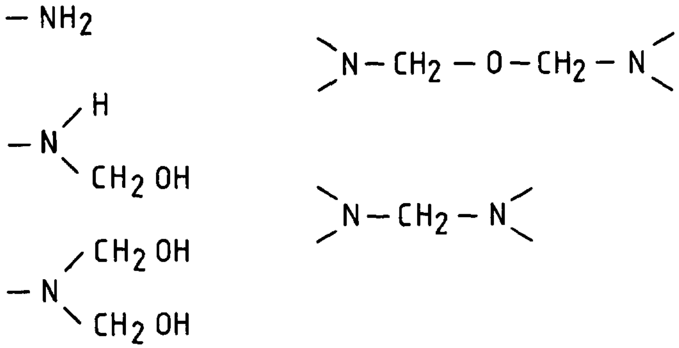

Figure 1. Structures in melamine resin

EXPERIMENTAL AND RESULTS

Two different melamine resins were synthesized with a melamine/formaldehyde ratio of 1:3 and 1:5, respectively. The resins were analysed with regard to the concentrations of $-NH_2$, $=NH$ and $=N-CH_2OH$ groups using H-NMR-spectroscopy according to the method recommended by I.U.P.A.C. (CHRISTENSEN 1980.) The ratio $[=N-CH_2OH]/[=NH]$ appears from Table 1. No detectable amounts of $-NH_2$ were obtained.

Adhesives for corrugated board manufacture based upon the above-mentioned melamine resins were produced according to the Stein-Hall method. Starch in an amount of 5.0 kg were added to 20 l of water. The mixture was heated to 65 °C, and then 1.0 kg NaOH dissolved in 1.3 l of water was added. After agitation for 20 min, 80 l of water, 20 kg of starch and 0.9 kg of borax were added. After agitation for 20 min at 40 °C, a melamine resin was added in an amount that appears from Table 1.

From the newly prepared adhesives, 50 μm thick films were applied and cured for 2 min at 120 °C. After curing, the films were stored for 24 h at 23 °C and the water resistance was then determined by immersion of the films in water at 23 °C. Corresponding experiments were also made with an adhesive stored for 48 h at 23 °C before application. The results appear in Table 1.

TABLE 1

Water resistance of films based on different types of melamine resins

Ratio melamine/ formaldehyde	[=N-CH_2OH] / [=N-H] in melamine resin	Melamine resin %	Water resistance (min)
1:3	0.8	1	5
1:3	0.8	2	9
1:3	0.8	4	11
1:5	2.2	1	8
1:5	2.2	2	18
1:5	2.2	4	20
1:5	2.2	2	9 *)

*) After storage for 48 h before application

The above Stein-Hall type adhesives with an addition of 2 % melamine resin were studied in gelling experiments illustrated in Fig. 2. Films having a thickness of about 100 µm were cured at 100 °C. Samples were taken every minute and leached in water for 30 seconds. The nitrogen content of the solutions was determined according to Kjeldahl and converted to melamine resin content on the basis of the nitrogen content of the original resin. Corresponding gelling experiments were also made with the same adhesives after storage for 48 h at 23 °C. The amount of water soluble melamine resin in percent of the total amount of melamine resin was used as a measure of the proportion of non-crosslinked resin.

Attempts were made to use IR to study the formation of an ether bond between the hydroxyl groups of the starch and the hydroxymethyl groups of the melamine resin. The cured films were analysed with regard to absorption in the frequency range of 1200-1050 cm^{-1} (C-O-C-stretching). All films showed a characteristic peak at 1153-1155 cm^{-1}, the band increasing in strength with increasing proportion of crossed-linked melamine resin (i.e. reduced proportion of water-soluble melamine resin according to Fig. 2). Pure starch, however, absorbes strongly at this frequency and the relative differences between the samples are small. Therefore, the method is hardly suited for quantitative estimations of the degree of etherification.

DISCUSSION

A high formaldehyde-melamine ratio in the melamine resin seems to be a prerequisite for attaining a good water resistance of starch adhesives modified with melamine resin and employed at a high pH. This yields a binder having a high content of =N-CH_2OH groups and a low content of =N-H groups.

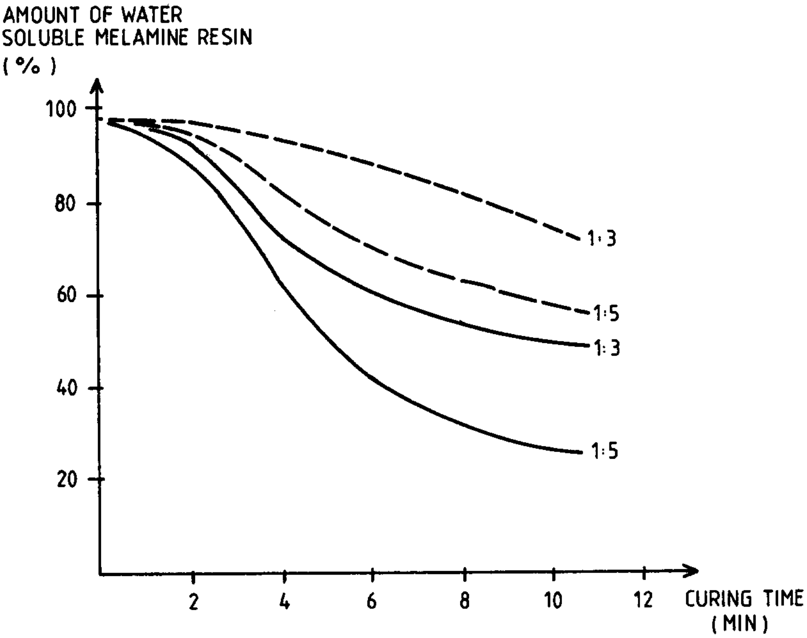

Figure 2. Proportion of water-soluble melamine resin in films as a function of curing time

Symbols 1:3 and 1:5 indicate the original ratio of melamine/formaldehyde in the melamine resins.

— signifies that the films have been applied directly after the preparation of the adhesive

-- signifies that after preparation, the adhesive was stored for 48 h at 23 °C before application

When this system is cured, the hydroxymethylamino groups can undergo both co-condensation and self-condensation. The former process can take place by two different routes, represented by reactions a and b in Fig. 3. Reaction a is slow (BLANK and HENSLEY 1974), and in the presence of secondary amino groups reaction b therefore predominates.

Co-condensation between hydroxymethylamino groups in the melamine resin and hydroxyl groups in the starch component takes place according to reaction c.

The $=N-CH_2OH$ group is not stable under alkaline conditions but emits formaldehyde with formation of secondary amino groups (reaction d) (PETERSEN et al. 1981). The formaldehyde reacts further in a Cannizzaro reaction under formation of formic acid and methanol.

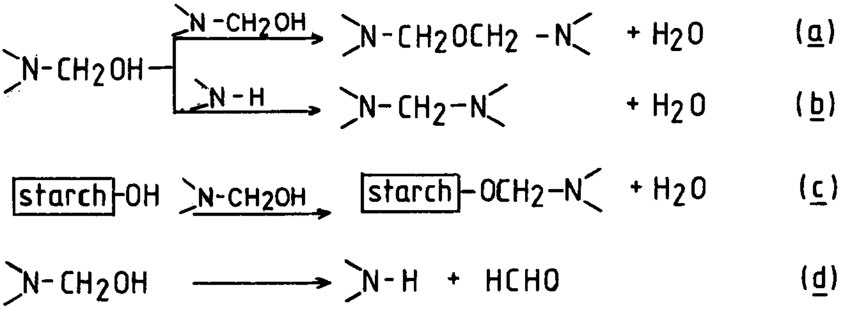

Figure 3. Curing reactions for starch-melamine resin adhesives

The results obtained with regard to both water resistance of the films (Table 1) and solubility of melamine resin upon leaching the films with water (Fig. 2) can be explained against this background. If $[=N-CH_2OH] >> [=N-H]$, co-condensation according to reaction c predominates. The melamine resin functions as a crosslinking agent between the starch molecules and the water resistance of the cured film is considerably improved.

If $[=N-CH_2OH] \leqslant [=N-H]$ self-condensation according to reaction b predominates. Several earlier works have shown that this reaction is kinetically favoured when both hydroxymethylamino and secondary amino groups are present i sufficient amounts (BLANK and HENSLEY 1974, van ZUYLEN 1969). In this case, two parallel curing processes occur: a self-condensation of the melamine resin and a curing of the starch, which mainly is a physical drying process. The cured film will have a poorer water resistance than when the co-condensation between the polymers predominates.

The water resistance of the glue joint of an adhesive based on starch-melamine resin deteriorates relatively rapidly when stored (Table 1). This is probably due to the hydroxymethylamino groups being degraded according to reaction d. This reaction can be followed by pH measurement of the adhesive solution. The Cannizzaro reaction which takes place subsequent to reaction d lowers the pH of a typical adhesive by 0.5 to 1.0 units after storage for 48 h at room temperature.

If reaction d is allowed to proceed for a sufficiently long period of time, the reactivity of the melamine resin disappears with respect to both co-condensation and self-condensation. In this case the glue joint will not be more water-resistant than with the use of an adhesive based on starch only.

Relatively small amounts of melamin resin are required to provide a water-resistant glue joint. As will appear from Table 1, it is hardly worthwhile increasing the amount of melamine resin above a given threshold value. (The addition of 2 %, which seems to be suitable in this case, corresponds to a starch/melamine resin ratio of 10:1.) It is probable that the large starch molecules, which in aqueous solution lie balled together with a relatively small accessible surface area, cannot utilize more than small amounts of the highly functional, low-molecular crosslinking agent.

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