

# Acid- and Alkali-Catalyzed Tannin-Based Rigid Foams

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## SYNOPSIS

Acid- and alkali-catalyzed polyflavonoid tannin-based rigid foams were prepared. These foams have comparable physical and mechanical properties to the synthetic phenolic rigid foam used as a comparative standard. The fluid polymer phase was based on a mimosa tannin-formaldehyde resin with a minor addition of a fortifier resin. Expansion of the fluid phase was brought about by a physical blowing agent, whereas dimensional stabilization was achieved through cross-linking at the desired density. In the case of the acid-catalyzed foam, a heat-generating agent in the form of furfuryl alcohol was employed. The polymer composition of tannin-formaldehyde/urea-formaldehyde systems as a function of pH was predicted from the respective gel times and rate constants, i.e., above pH 7, the copolymer proportion will tend to 100% and, that at pH 3.4, the polymer blend proportion will tend to a maximum. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Rigid foams based on synthetic phenol-formaldehyde (PF) resins have been known and used for a considerable time.<sup>1,2</sup> These rigid PF foams present valuable characteristics such as resistance to fire.<sup>2</sup> Polyflavonoid tannins are materials of vegetable origin that present reactive phenolic nuclei. They can undergo the same reaction as that of phenol with formaldehyde. In Mimosa bark tannin extract (from *Acacia mearnsii*, formerly *mollissima*, De Wildt), the flavan-3-ol repeating units (Fig. 1) are linked mostly as 4,6; such flavonoid units are repeated 2–11 times to produce a tannin with a number-average degree of polymerization of 4–5.<sup>3</sup> The nucleophilic centers on the A-rings of the flavonoid repeating unit are considerably more reactive toward formaldehyde than are those on the B-rings.<sup>3</sup> For mimosa bark tannin extract, the reactivity of the flavonoid A-ring is comparable, although slightly lower than that of resorcinol<sup>4</sup> (Fig. 1).

A rigid, chemically self-blowing, foam formulation based on tannin extract should comprise not only tannin and formaldehyde, but should also include an exothermic system capable of vaporizing in a

controlled manner a low boiling point solvent in order to foam the material. Due to the generally brittle nature of tannin-formaldehyde polycondensates,<sup>3</sup> a small amount of a fortifying synthetic resin should also be added. The difficulty then becomes to balance the system composed of tannin, formaldehyde, fortifying resin, solvent, and exothermic side reactions. This is essential, as an exotherm occurring much earlier or later than the setting caused by the polycondensation will cause the foam to partly or completely collapse once curing occurs. This article deals with the application of the tannin-formaldehyde reaction to the preparation of phenolic-like, tannin-based, rigid foams and the characterization of their properties.

## EXPERIMENTAL

### General Foaming Procedure

All the resins, blowing agents, and catalysts were thoroughly mixed with an overhead stirrer and then charged into a polyethylene-lined cardboard box of base dimensions 11 × 15 cm and height 11 cm. Most formulations foamed between 10 s and 2 min with subsequent stabilization. Within 1 h, the stabilized foam was removed from the box, separated from the polyethylene, and then cut into slices with a power saw.

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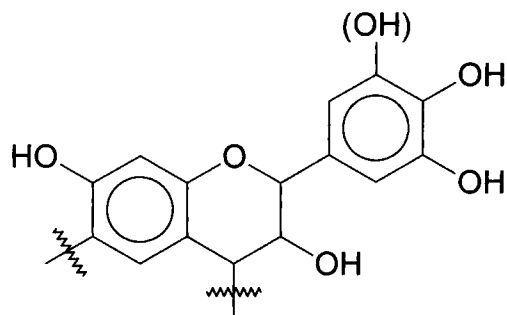


Figure 1 A Mimosa tannin flavonoid unit.

### Acid-catalyzed Foams Based on Mimosa Tannin Extract

Mimosa tannin extract (150 g) was thoroughly mixed with water (30 g) and a formaldehyde solution (30 g, 37%) using an overhead mechanical stirrer. Furfuryl alcohol (25 g) and diethyl ether (12 g) were then added stepwise with sufficient mixing between the two additions. With constant stirring, toluene-4-sulfonic acid (55 g, 65%) was charged into the mixture, which was then mixed thoroughly for about 10 s before being discharged into the box for foaming. The resin foamed within 2 min of mixing with a temperature rise of 40°C to yield a black foam of density 0.09 g cm<sup>-3</sup>.

The method was repeated exactly; however, varying amounts of urea-formaldehyde resin (UF, 12 and 24% on tannin solids) and diphenylmethane-4,4'-diisocyanate (MDI, 24 and 40% on tannin solids) were added. The density of the respective foams was varied by adding differing amounts of blowing agent. Finally, a common household surfactant, consisting mainly of sodium alkyl benzenesulfonates (2.5% on tannin solids), was added to a tannin foam with a UF addition (12%).

### Alkali-catalyzed Foams Based on Mimosa Tannin Extract

Mimosa tannin extract (100 g) was thoroughly mixed with water (30 g) and a formaldehyde solution (20 g, 37%) using an overhead mechanical stirrer. To this mixture, diethyl ether (10 g) was added with sufficient mixing. With constant stirring, NaOH (30 g, 33%) was charged into the mixture, which foamed vigorously within seconds of mixing with a temperature increase of 33°C to yield a black foam with a density of 0.09 g cm<sup>-3</sup>.

### Compressive Strength Determination

All compressive strengths were measured on a converted increasing load testing machine using foam

specimens of dimensions 2 × 2 × 2 cm, at a crosshead speed of 6 mm/s.

### Water Adsorption Determination

Blocks of foam of dimensions 4 × 2 × 1 cm were immersed in water (22°C, 1 atm) for a period of 1 h. The weight increase was represented as a percentage.

### Fire Properties

A block of foam with face dimensions 4 × 2 cm and height 1 cm was placed over a Bunsen burner. The flame was allowed to wash over the face of the foam. The time to any ignition followed by the time for the burning foam to extinguish was measured. Furthermore, foams of equivalent volume were weighed pre- and postexposure to a flame for 1 min to determine the weight percentage remaining.

## RESULTS AND DISCUSSION

### Acid-catalyzed Foams Based on Mimosa Tannin Extract

The most important process in the preparation of low-density plastic cellular materials (foams) consists of expanding (foaming) a fluid polymer phase.<sup>5</sup> The fluid polymer phase was based on mimosa tannin extract. The most important cross-linking reaction is, therefore, the acid-catalyzed reaction of formaldehyde at the activated sites of the flavonoid A-rings leading to polycondensation through methylene bridges.<sup>3</sup> The rate of reaction of the A-rings with formaldehyde is particularly fast. For example, at pH 4.9 and temperature of 25°C, the rate constant is of 6.94 × 10<sup>-3</sup> L/(mol s).<sup>4</sup> It is the rate of this acid-catalyzed reaction that determines whether there is dimensional stabilization of the foam. If the resin gels too quickly, i.e., before the resin foams, then a high-density, unfoamed, hard-cured resin will be produced. Conversely, if the resin does not gel in time, then the foaming resin will collapse as the blowing agent is completely used up and a high-density, hard-cured resin is also produced.

For environmental reasons, a low boiling point solvent different from chlorofluorocarbons (CFC) was used. As the exotherm generated in the acid-catalyzed polycondensation of the mimosa tannin-formaldehyde reaction was inadequate to boil any of the blowing agents investigated, a "heat-generating agent" was added to increase the exotherm of

the system. The heat-generating system used is based on the self-condensation reaction of furfuryl alcohol in acid medium.<sup>6</sup> There are a number of advantages in using this particular heat-generating system: (i) It is an acid system corresponding to the correct acid conditions for the mimosa tannin-formaldehyde reaction. (ii) A large exotherm is generated in a very short period of time. (iii) Before the exotherm occurs, there is an induction period; this is advantageous as it gives time for the resin to be transferred from the mixer to a more appropriate container before foaming occurs. (iv) The methylol group on furfuryl alcohol is able to react with the tannin A-ring and can therefore be incorporated into the main body of the resin as a copolymer.<sup>6</sup> This reaction, furthermore, should also contribute to the total exotherm generated.

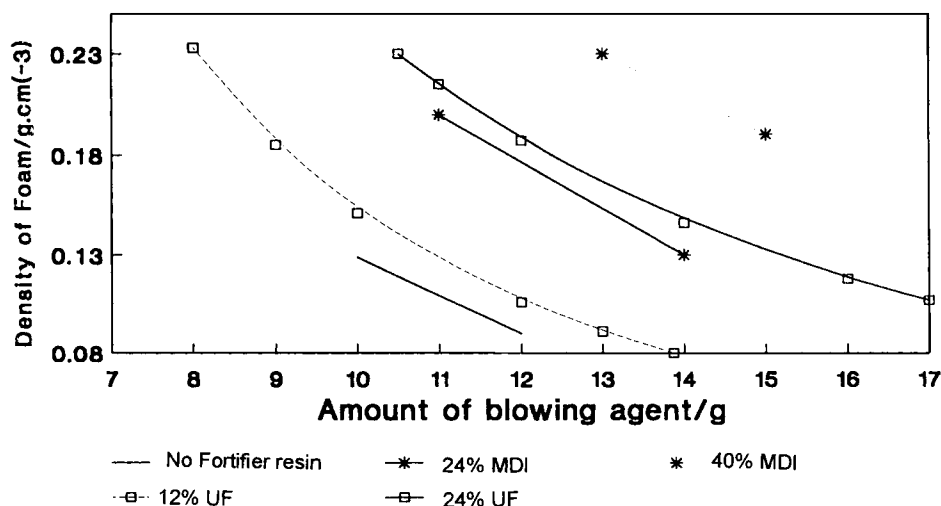
Diethyl ether, which has a boiling point of 34.5°C, was found to be the most suitable blowing agent. The proportion of the blowing agent used is found to determine, in a different way for different formulations, the density of the foam produced (Fig. 2).

Depending on the amount of furfuryl alcohol and of acid used, different exotherms were obtained for the system.<sup>6</sup> The exotherm generated, as well as the rate of dimensional stabilization, was optimized by varying the amount of furfuryl alcohol and *p*-toluene sulfonic acid (pTSA). The optimized value was found to be 17% furfuryl alcohol and 24% pTSA on mimosa tannin extract solids.

Cured tannin-formaldehyde resins present some inherent brittleness and weakness.<sup>3</sup> A number of mimosa tannin-formaldehyde-based foams were

produced, all of which showed these characteristics to some extent. A bridging agent was therefore added to the foam formulation to overcome this problem. Thus, a number of foams with different amounts of added urea-formaldehyde (UF, 1 : 1.8 U : F molar ratio) resin (12 and 24% addition on mimosa tannin extract solids) and of added 4,4'-diphenylmethane diisocyanate (MDI, 24 and 40% on mimosa tannin extract solids) were produced at different densities.

The exotherm generated when all the reagents were mixed was monitored as a function of time (Fig. 3). The exotherm curves for all foams follow a similar pattern in the first minute of reaction, but as the reactions progress, the curves tend to differ. The reason for the early similarity in the exotherms can be attributed to the fact that in all cases an equivalent amount of the heat-generating agent and the acid catalyst is used with the result that similar exotherms are produced. However, as the heat increases and the acid begins to catalyze the other reagents, further exothermic reactions begin to contribute to the total exotherm. Thus, in the case of the mimosa tannin/UF foam system, increasing the proportion of UF in the system tends to decrease the apparent exotherm. The reactions of this system, however, continue for a longer period of time than those of the systems without UF. It is the UF self-polycondensation reactions occurring later than the main tannin-formaldehyde reaction, as well as the tanning-UF copolymerization, that explains the lower initial exotherm and yet why this is sustained for a longer period than either the tannin alone or the tannin/MDI system.



**Figure 2** Density of mimosa tannin-based foam as a function of blowing agent with varying additions of fortifier resins.

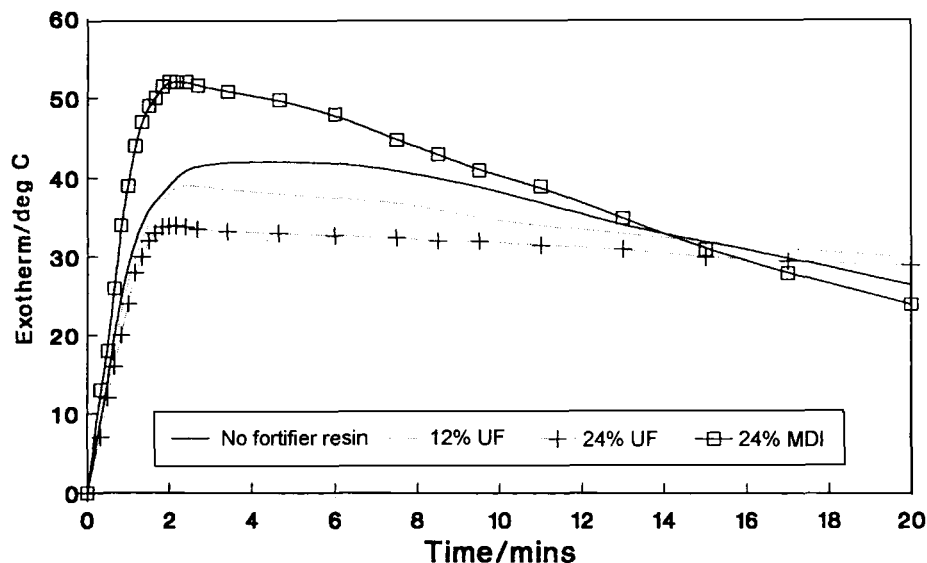


Figure 3 Exotherms of acid-catalyzed mimosa tannin-based foams with varying additions of fortifier resin.

### Compressive Strength of the Tannin-based Foams Produced

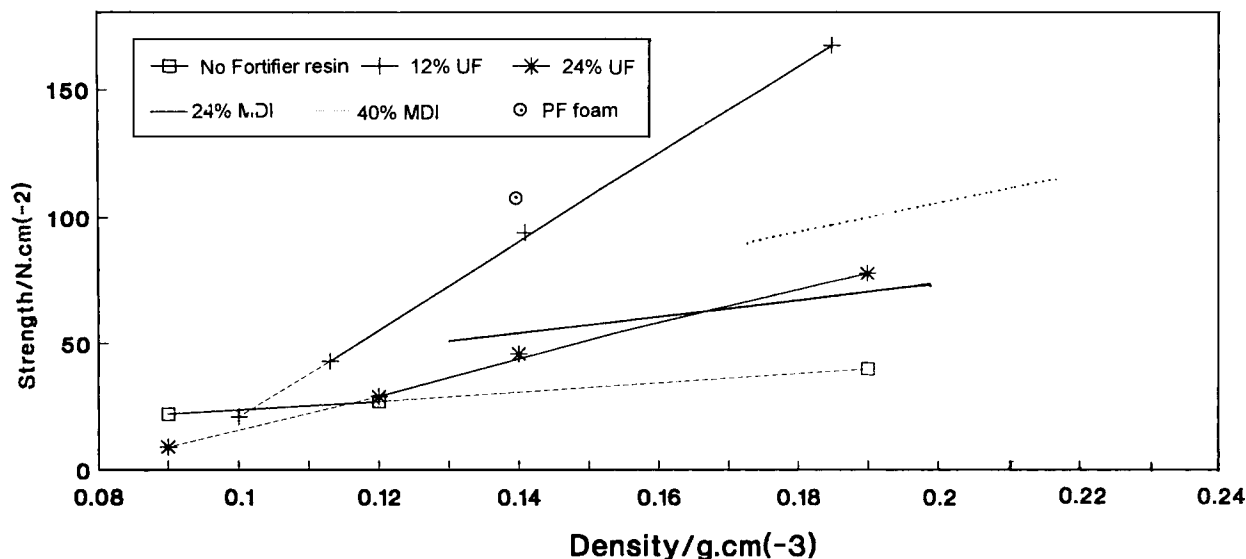
An industrially produced synthetic phenol-formaldehyde (PF) foam of density  $0.14 \text{ g cm}^{-3}$ , and, thus, an average commercial foam, was used as a standard control. Rigid cellular polymers do not generally exhibit a definite yield point when compressed but, instead, show an increased deviation from Hooke's law as the compressive load is increased. The compressive strength is usually reported at some definite deflection. The tannin foams investigated were no different from other rigid foams in this respect.

Within 1 h after foaming, the foam was fairly soft and elastic and it was at this stage that the bulk foam was cut into appropriate slices for structural determination. Within 24 h, most of the elasticity had disappeared, leaving a weak rigid foam. The curing of the foam from a soft elastic material to a rigid material was found to take time, with approximately 90% of the final strength being achieved after 60 days. By increasing the density of the foam, the compressive strength per unit area also increases, as expected (Fig. 4).

The effect of a bridging agent on the compressive strength per unit area of the foam shows that for tannin foams fortified with UF and with MDI (Fig. 4) that the effects depend on the density. At the lower densities, the effect of the bridging agent on the foam compressive strength is less than at higher densities. The relationship between the amount of added UF resin and compressive strength does not

appear to be a linear one, as maximum strength is reached in the region of 12% addition. The reason why a maximum of compressive strength is observed in this region is due to the fact that two chemical effects are competing against each other: First, the addition of a bridging agent induces a decrease in brittleness with a corresponding increase in compressive strength as the foam composition moves from no UF addition to increasing amounts of UF resin. The second chemical effect involved is that by adding more UF resin a point is reached where optimum cross-linking between the two resins does not occur anymore and any further UF resin that is added will react only with itself. Thus, the proportion of copolymers will decrease with a respective increase in the proportion of the polymer blend. This results in a change in the compressive strength of the foam. It is an indication that an increase in the proportion of the polymer blend has a detrimental effect on the compressive strength of the final foam. This infers that in a rigid tannin-based foam it is necessary to maximize copolymerization. Conversely, if a floral foam application is required, which must have lower mechanical strength to allow the flower stems to break into the foam body, then the polymer blend proportion should be maximized.

The strength of tannin-UF and tannin-MDI foams at 24% addition of the synthetic resin are similar. Although it could have been expected that the MDI foam would be stronger, its more violent foaming interferes considerably with the formation of the foam cell structure that plays an important



**Figure 4** Compressive strength as a function of density of tannin-formaldehyde foams fortified with varying amounts of UF and MDI after 60 days ambient temperature curing time.

role in the mechanical strength of the foam.<sup>6</sup> If the foam cells are not formed properly, this results in lower mechanical strength of the material.

A standard industrial PF foam of density  $0.14 \text{ g cm}^{-3}$ , which is within the standard commercial range for a rigid foam, was found to have a relative compressive strength of  $110 \text{ N cm}^{-2}$  (Fig. 4). A tannin-based foam, with 12% UF resin addition, of the same density, yields a strength of  $94 \text{ N cm}^{-2}$  at 60 days curing time. As this is approximately 90% of the final strength, this can then be expected to be of  $104 \text{ N cm}^{-2}$ ; a value comparable to that of the commercial PF foam. This is a favorable indication of the potential for the commercial application of tannin-based foams.

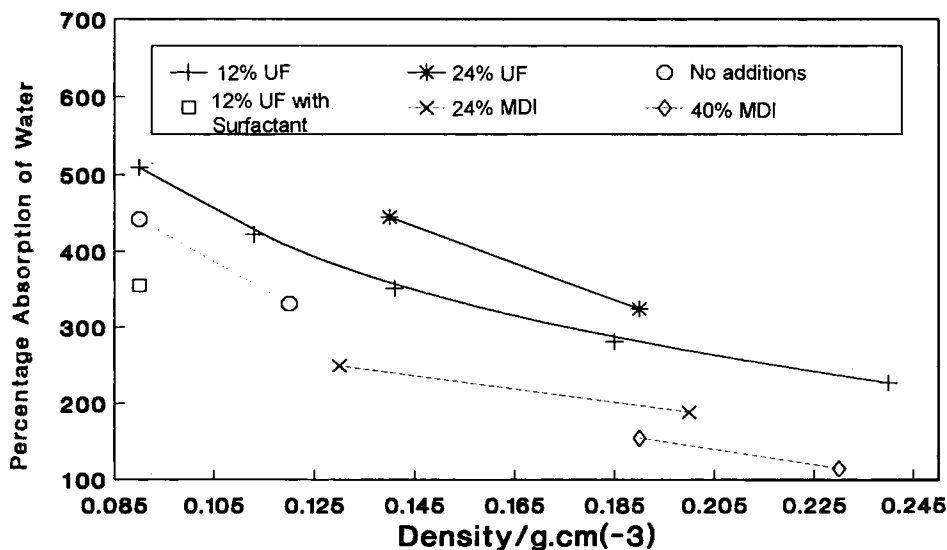
A property related to the mechanical strength of the foams is that of friability. Friability is the capability of a material of being easily crumbled into a powder. The foams produced from tannin alone are more friable than are the synthetic PF foam. However, both the tannin-UF and especially the tannin-MDI foams are less friable than are the synthetic PF foams.

The effect of adding a surfactant, which consists of sodium alkyl benzenesulfonates, appears to increase the compressive strength of the tannin-UF foams. A tannin-UF foam with no surfactant and a density of  $0.09 \text{ g cm}^{-3}$  has an extrapolated compressive strength of about  $17 \text{ N cm}^{-2}$  when completely cured. Under identical conditions but with a 2.5% addition of the surfactant, the compressive

strength increases to  $33 \text{ N cm}^{-2}$  on complete curing, an increase of 194%, meaning that tannin-UF foams of considerably higher strength than that of PF foams could be produced. The increase in strength on the addition of a surfactant has been explained by the surfactant increasing the proportion of the close-cell content of the foam.<sup>6</sup> The result of this is an increase in strength due to the improved stress distribution throughout the whole structure.

#### Water Adsorption and Open- to Closed-Cell Content

To give an indication of the open- to closed-cell character of the tannin-based foams, it was decided to determine the water adsorption of the foams prepared. The water adsorption of foams is related to the density of the respective foam (Fig. 5): As the density of the foam decreases, more water is adsorbed. Furthermore, the foam's water adsorption tends to increase with increasing UF contents (Fig. 5). This is due to the susceptibility of UF resins to undergo bond deterioration in the presence of water due to hydrolysis of the aminomethylene bond.<sup>7</sup> This indicates that the greater the proportion of polymer blend and therefore the amount of aminomethylene bonds in a tannin-UF foam system the greater the amount of water that will be adsorbed.<sup>8</sup> The effect of adding an MDI resin on the water adsorption of the foams is opposite to that of adding a UF resin because the urethane bonds formed are hydrophobic.<sup>9</sup>



**Figure 5** Percentage adsorption of water as a function of density for mimosa tannin-based foams with varying additions of fortifier resin (a synthetic PF foam of density  $0.14 \text{ g cm}^{-3}$  has a water adsorption of 49%).

Surfactants are used in synthetic PF foams to increase the proportion of closed cells.<sup>8</sup> A surfactant consisting mainly of sodium alkyl benzene sulfonates was used in the best type of tannin-UF foam. The foam with such an added surfactant absorbs much less water than does the foam without it (Fig. 5, 70%), indicating that the proportion of closed cells is markedly increased and has been estimated at about 30% greater than the foam without a surfactant.<sup>6</sup> This is given exclusively as an example to indicate that by the use of surfactants the proportion of closed cells in tannin-based foams can be considerably increased and that optimization of both surfactant type and amount is likely to yield for tannin foams positive effects as obtained in synthetic PF foams.<sup>6</sup>

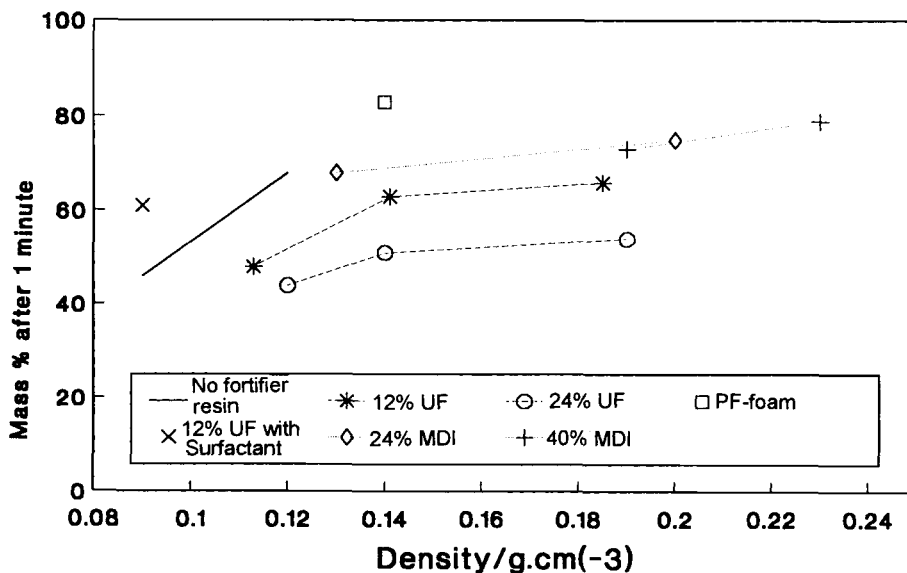
#### Fire Properties of Mimosa Tannin-based Foams

All the tannin-based foams presented have no ignition, with, therefore, zero afterburning. The control synthetic PF foam, instead, ignites within 2 s of flame contact; it burns for 1 s after removal from the flame, then it self-extinguishes. Returning it to the flame, it soon extinguishes itself and then the foam no longer burns. The initial burning observed is possibly due to the presence of free phenol. The smell given off by the PF foam is considerably stronger and more pungent than that given off by the tannin-based foams. In the tannin-based foams, the greater the proportion of UF the greater the

amount of smoke given off on burning; however, in all cases, this is still noticeably less than in the PF foam. Determination of the weight left after 1 min of direct contact with the flame indicates that the more UF is in the foam the less is the weight left after burning (Fig. 6). Only the tannin foam with no UF has comparable burning properties to the PF, which has 83% of its original weight left after burning (Fig. 6). However, the closed-cell content of the foam affects the weight left after burning. Based on this the performance of tannin foams with surfactant can be expected to approach that of the synthetic PF foams. The weight percentages left after burning of the tannin-MDI foams are less than for tannin foams with no fortifier resin (Fig. 6). This is because urethanes burn considerably more readily. Furthermore, the weight percentages left after burning of the tannin-MDI foams are greater than those of the tannin-UF resin foams (Fig. 6). This is because there is a greater proportion of copolymers in the tannin-MDI system than in the tannin-UF system,<sup>6</sup> and, therefore, the tannin has a greater inhibitory effect with respect to burning.

#### Prediction of Polymer Composition

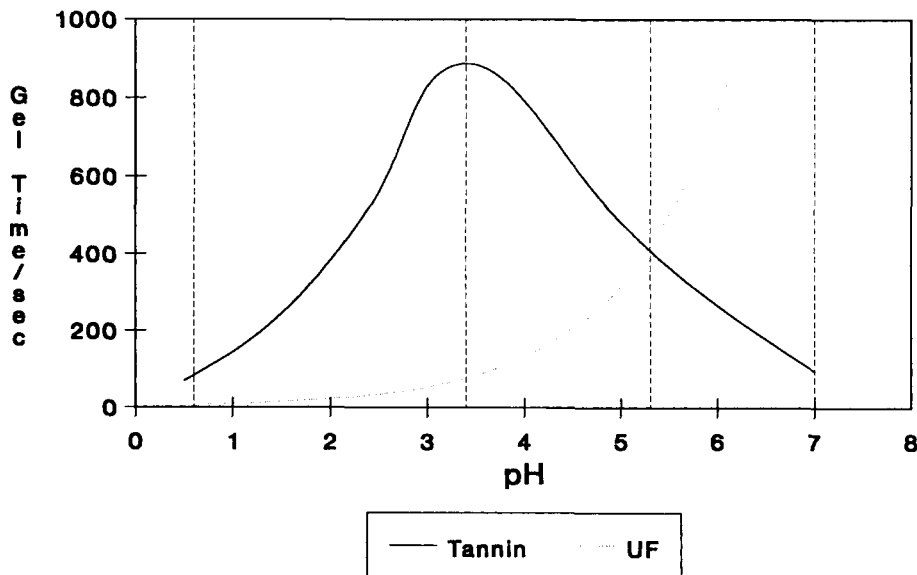
The exact ratio between the copolymer-to-polymer blend produced with these systems of tannin-based foams depends on such factors as the proportion of the individual reactant monomers used and their relative reactivities. In polycondensates, the relative



**Figure 6** Mass percentage left after burning mimosa tannin-based foams for 1 min as a function of density and of foam composition.

reactivities of the constituent species can be directly related to their gel times and, therefore, an approximation of the ratio of copolymer-to-polymer blend can be predicted from gel times vs. pH curves for two-component polycondensate, thermosetting resin systems. In the case of tannin-based foams, as well as for other applications,<sup>6</sup> consider a system consisting of both a mimosa tannin-formaldehyde resin and a urea-formaldehyde (UF) resin. The gel times of each resin by itself as a function of pH are shown

in Figure 7. Equally, the rate constants of the self-condensation of each resin as a function of pH are shown in Figure 9. Considering first the UF resin curve (Fig. 7), it can be seen that the gel time increases exponentially, and, therefore, the rate of self-condensation decreases exponentially (Fig. 8) as the pH moves from 1 to 7. The tannin-formaldehyde curve (Figs. 7 and 8) indicates that a minimum rate of condensation is experienced at pH 3.4, with an increase in condensation rate as the pH becomes



**Figure 7** Gel times of mimosa tannin-formaldehyde and UF resin as a function of pH.

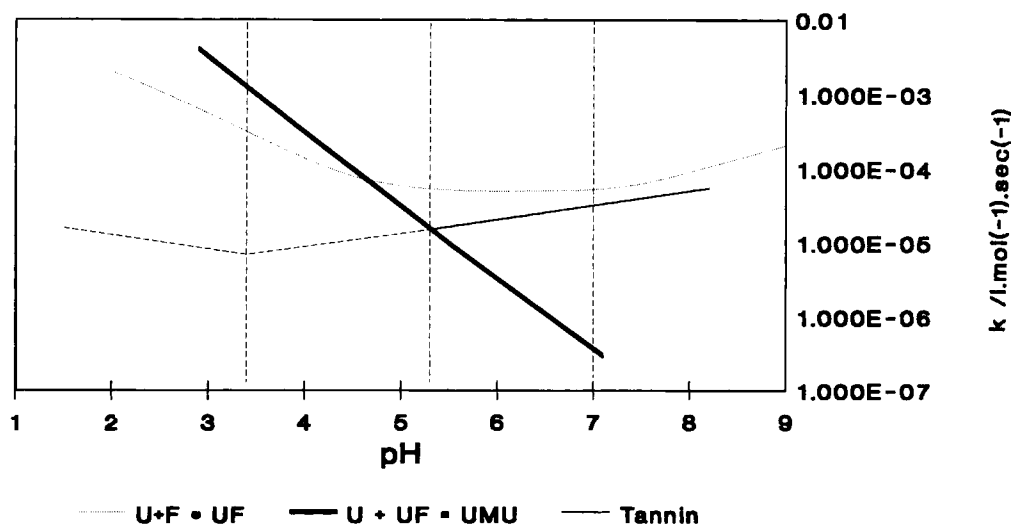


Figure 8 Reaction kinetics of mimosa tannin-formaldehyde and UF resin as a function of pH.

more acidic or alkaline. Finally, in Figure 8, it can be seen that the formation of methylol urea from any free urea and formaldehyde ( $U + F \rightarrow UF$ ) has a minimum rate of reaction in the pH range 5–8.

By comparing the two curves in Figure 7, it can be seen that in the basic region (above pH 7) the rate of self-polymerization of the UF resin is negligible compared to the rate of the mimosa tannin reacting with formaldehyde to form a methylol group, which then reacts with another tannin nuclei. The methylol condensation is due to the alkali activation of the tannin nuclei and, therefore, any urea methylol groups will react preferentially with the phenolic rings of the tannin to produce  $-\text{NH}-\text{CH}_2\text{-tannin}$  bridges. The implications of this are that a tannin-formaldehyde-UF resin system in an alkaline environment, which is above pH 7, will produce a final product that will consist mainly of copolymers (tending to 100%) with a negligible proportion of polymer blend.

As the pH decreases, the reaction rate of the self-polymerization of the UF resin increases until pH 5.3, where it intersects the reaction rate curve of the tannin-formaldehyde resin, which, instead, decreases throughout this pH range (Figs. 7 and 8). The result of this decrease in pH is an increase in the percentage of the polymer blend with a corresponding decrease in the percentage of copolymers. This can be seen as the proportion of  $-\text{NH}-\text{CH}_2\text{-tannin}$  bridges decreases with a corresponding relative increase in the proportion of  $-\text{NH}-\text{CH}_2\text{-NH}-$  and, therefore, tannin- $\text{CH}_2\text{-tannin}$  bridges. Thus, on the microscopic scale, a change from a copolymer to a polymer blend in-

volves a decline in the proportion of mixed methylene bridges.

At the point of intersection (pH 5.3), the rate of self-polycondensation of both the tannin-formaldehyde and the UF resin systems are equivalent. As there are two self-polymerization reactions and one copolymer reaction with twice the proportion of reaction products, it can be expected that at this pH (5.3) the percentage of copolymers to polymer blends will be 50:50.

Decreasing the pH to below 5.3 takes the combined resin system for the first time to a greater polymer blend percentage over copolymers. This is because the rate of methylation at the tannin nuclei is lower than that of the self-condensation of the UF resin. Thus, as the pH drops below 5.3, formation of  $-\text{NH}-\text{CH}_2\text{-NH}-$  bridges becomes more favored than that of  $-\text{NH}-\text{CH}_2\text{-tannin}$  bridges. This percentage increase in the polymer blend cannot be said to tend to about 100%, however, as was the case for the copolymer percentage in the basic region. This is because the rate of the tannin-formaldehyde condensation reaction reaches a minimum at pH 3.4 (Fig. 8), whereas the pure UF system reaction rate decreases exponentially through a pH of 1–7. This minimum in the tannin-formaldehyde curve implies that the self-condensation reaction cannot be taken as negligible, as was the case for the UF self-condensation reaction in the alkaline region. If the methylation reaction is not taken as negligible, then a certain amount of copolymers will form and therefore the percentage of polymer blend will not tend to 100%. The actual percentage of the polymer blend, however, cannot be determined from



these curves, and all that can be said is that at pH 3.4 the proportion of  $\text{—NH—CH}_2\text{—NH—}$  bridges reaches a maximum.

In summary, therefore, above pH 7, the system will tend to 100% copolymer. Between pH 7 and 5.3, the proportion of copolymers drops from 100 to 50% as the pH drops from 7 to 5.3, to yield a final product with a mix of copolymers and polymer blends. The region between pH 5.3 and 3.4 corresponds to a further drop in the copolymer percentage with the percentage of the polymer blend reaching a maximum at pH 3.4. The region between pH 3.4 and 0.6 corresponds to an increase in the copolymer percentage as the system becomes more acidic. The region below pH 0.6 corresponds to an increase in the copolymer percentage to its maximum. This maximum is, however, unlikely to exceed 50% as the rate of methylation of the tannin nuclei will be similar, if not less than that of the rate of UF self-condensation. In the case of a tannin other than mimosa being used (much faster- or slower-reacting with formaldehyde), the relative position of the different regions outlined above changes according to the relevant gel time curve of the particular tannin used with formaldehyde.

#### Alkali-catalyzed Foams Based on Mimosa Tannin Extract

The residual acidity of acid-catalyzed tannin extract-based foams with the respective increase in the potential for corrosivity might be considered a drawback in certain applications. Furthermore, the copolymer-to-polymer blend ratio of a tannin-UF resin system could not be expected to rise over 50% in an acid environment as discussed. If it is necessary to increase the copolymer percentage, to maximize cross-linking of an added synthetic resin as well as to remove the residual acidity of the foam, then the foam must be produced in an alkali environment. Any residual alkalinity will not create corrosion problems and, furthermore, the tannin-UF copolymer ratio would approach 100%.

The fluid polymer phase was based on mimosa tannin extract, and the most important cross-linking reaction would be the alkali-catalyzed reaction of formaldehyde with the flavonoid tannin A-ring. Above pH 10, formaldehyde attack on the flavonoid B-ring also becomes possible<sup>3</sup> such that the reactivity of the tannin to methylation increases substantially. Because of this, it was found that an adequate exotherm is obtained without having to use an added heat-generating agent.

Below pH 10.4 and using diethyl ether as a blow-

ing agent, cross-linking did not occur in time and, thus, the subsequent stabilization of the foam was not achieved. However, at and above this pH, the reactions began immediately and proceeded at such a fast rate that blowing started before the mix could be discharged from the mixer into a suitable container for foaming. The foaming was quite vigorous and, consequently, there was improper cell formation. Thus, optimization of the exotherm was not possible through pH manipulations, as a more appropriate exotherm could not be obtained at a lower pH, i.e., pH 9.5, as this would not produce a foam: Dimensional stabilization would not occur before the foaming mass collapsed. It was then only possible to prepare alkali-catalyzed foams at pH 10.4, with relatively poor cell formation and with larger cavities in the body of the foam also being present. This was consistent with the observation that the alkali-catalyzed foams were foamed in under 10 s, whereas the acid-catalyzed ones took over 1 min to foam.

Another important difference between alkali and acid-catalyzed foams with no added fortifier was the lack of cracks within the body of alkali-catalyzed ones. It is well known from tannin-formaldehyde adhesives<sup>3</sup> that the structure and relative strength of a tannin-formaldehyde gel is very different when attained in an acid rather than in a neutral or alkaline medium, with the alkali-cured resin giving much stronger products. Furthermore, as the reaction was done at a pH greater than 10, it can be expected that the B-ring could also participate in cross-linking.<sup>3</sup> As a consequence, the alkali-catalyzed reaction produces a foam that is more resistant to the stresses involved by the blowing agent attempting to escape within the period of 24 h after foaming is completed.

Within 6 h from preparation, the alkali-catalyzed foam was considerably softer and more elastic than were the acid-catalyzed foams at equivalent curing times. The compression strength of the alkali foams was about  $18 \text{ N cm}^{-2}$  at a density of  $0.09 \text{ g cm}^{-3}$  against a value of  $22 \text{ N cm}^{-2}$  of acid foams of equivalent density (Fig. 4). The strength of the alkali foam can then be considered reasonably good if it is considered that proper cell formation did not occur. Water adsorption of the alkali-catalyzed foam was 741%. In the acid-catalyzed case, at equivalent density, water adsorption was of 442% (Fig. 5). This implies that the alkali foam has a considerably higher proportion of open cells. The alkali foam also did not burn on exposure to a flame. The smell and smoke given off was, however, considerably less than that of the acid foams. This is a considerable advantage.

## CONCLUSIONS

Flavonoid tannins can be used to prepare acid- or alkali-catalyzed rigid foams similar to those produced with synthetic PF resins. The open- to closed-cell content was not as good as that for the PF foam. However, it appears that by optimizing the type and proportion of surfactant and possibly with the use of an additional nucleating agent the tannin-based foams are likely to have a closed-cell content quite similar to that of PF foams. The crushing strengths achieved were comparable to those obtained with PF foams. It was also shown that an increase in the closed-cell content brought an increase in compressive strength. It can therefore be expected that further optimization of tannin-based foams is likely to lead to a higher proportion of closed cells with an increase in strength to a value greater than that of corresponding PF foams. The fire-resistance properties of the tannin-based foams appear to be better than those of PF foams, i.e., there is less smoke and smell given off. These results indicate that tannin-based foams could be used in most applications in which phenol-based foams are currently used.

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