

Effect of Reactant Ratio and Temperature on the Characteristics of Phenol-Formaldehyde Foams

DALJIT SINGH and SUNEETA OHRI, *Punjab Agricultural University, Ludhiana, India*

Synopsis

This study presents experimental results on the preparation and characteristics of high-density phenol-formaldehyde foams and compares their characteristics with the available patent literature. An extrapolation of the data has been used to identify the relevant process parameters used for the preparation of lower-density foams. The effect of catalyst combination and phenol formaldehyde molar ratio on the ease of foaming and its ultimate strength has been investigated. A total solids-refractive index correlation has been developed for following the reaction. The effect of foaming temperature on the density and strength of the foam was also studied.

INTRODUCTION

The preparation of plastic foams from phenol-formaldehyde resins has evolved essentially as an art commanding an impressively large number of patents.¹ Most of these patents specify a very wide range of process variables with little indication of preferred or desired process parameters.² Baer² has tried to compile the available data on these foams in the form of a graphic density-strength correlation. The process parameters (such as phenol-formaldehyde mole ratio, catalyst concentration, reaction time, foaming agents, and temperature, etc.) leading to these density strength correlations cannot be inferred from his compilation; nor has it been possible to identify these parameters from reference to the original patents.

This study was undertaken to investigate the effect of various process conditions on the density and strength of phenol-formaldehyde foams, primarily with a view to developing an optimum set of parameters for the preparation of high-density foams considered suitable for structural applications.³ An extrapolation of the data also helped in identifying the process parameters leading to Baer's correlations.²

EXPERIMENTAL

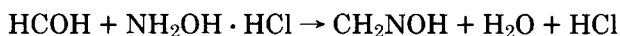
Resin Preparation

Phenol (A.R.) and formaldehyde solution (A.R.) were reacted for various lengths of time in a 1-L, four-neck (B-24) Corning resin reaction kettle, in the presence of sodium hydroxide-barium hydroxide octahydrate catalyst. Sodium hydroxide crystals were procured from Sarabhai M. Chemicals, while the other reagents were procured from Glaxo Laboratories. The reaction kettle was equipped with a flexible-shaft stirrer through a mercury seal gland, a 400-ml reflux Graham's condenser, a charging funnel, and a copper-Constantan ther-

mocouple lead connected to a Toshniwal potentiometer. The reaction kettle was charged with the reactants phenol and formaldehyde (37%) in mole ratios of 1:1.5 and 1:2. Sodium hydroxide (1% by weight of phenol) and barium hydroxide octahydrate (2.5% by weight of phenol) were then added to the reactants. The kettle was immersed in a KLB constant-temperature bath and the reaction temperature maintained at 70–72°C. The reaction was allowed to proceed up to 5½ h depending upon the experiment. The reaction mixture was stirred continuously to ensure a uniform product. After the preset reaction time, samples were drawn for determination of total solids of the mixture and the free formaldehyde.

Free Formaldehyde Determination

The hydroxylamine hydrochloride method outlined by Walker⁴ was employed to determine the unreacted formaldehyde. It is based upon the liberation of hydrochloric acid on addition of hydroxylamine hydrochloride to formaldehyde:



The liberated hydrochloric acid is titrated with potassium hydroxide solution using bromophenol blue as an indicator.

Percent Resin Solid Determination

This test is used to determine the percent nonvolatile solids content of the resin mixture; it was carried out by weighing the residue left after a preweighed quantity of the resin (1–3 g) was cured for 2 h at 130 ± 2°C on approximately 10 g sand.

Dehydration

The resinification reaction was quenched by neutralizing the hydroxide catalyst with oxalic acid. The reflux condenser was replaced by a Liebig condenser and the reaction mixture was dehydrated over an absolute pressure of 620–640 torr till the solids content of the resin was raised to approximately 70%. The refractive index of the sample was monitored at regular intervals during the dehydration by means of an Abbe's refractometer.

Foam Formation

For the preparation of foams, a measured quantity of the dehydrated resin was heated to a preset temperature. Then, 2.5% by weight sodium carbonate and 1% by weight hexamine (supplied by Allied Resins and Chemicals) were added to the resin and stirred thoroughly. Hydrochloric acid was then added to this mixture and the stirring continued till the approach of cream time. The resin was then left undisturbed to foam itself. The resin was cured partially due to the presence of hexamine and the heat generated by the reaction between sodium carbonate and hydrochloric acid. The overall foaming time was found to be less than 1 min. After complete rise of the resin, it was kept as such for about 30 min to allow further curing.

Foaming of the resin was also carried out at different temperatures to evaluate the effect of temperature on the compressive strength of the product.

Foam Characterization

For evaluation of density and compressive strength, the foam samples were prepared after removing the hard skin surfaces. The density was determined in accordance with the method specified in ASTM Standard 1622-63. For determination of compressive strength, the loading surfaces of the specimen were made parallel and the load was applied perpendicular to the face in accordance with the method specified in ASTM 1621-73. The test was carried out on a Universal Testing Machine supplied by Tinius Olsen Testing Machine Company, USA. The results of the compressive strength of various specimens are presented in Figure 1.

RESULTS AND DISCUSSION

Resinification Reaction

Condensation of phenol and formaldehyde with a formaldehyde/phenol (F/P) mole ratio varying from less than 1 to 3 in the presence of single alkali catalysts has already been investigated in general, the most recently reported data being that of Meier and Frank.⁵ However, for production of good-quality foams, Ferigno⁶ has recommended the use of mixed catalysts. Preliminary experiments confirmed this recommendation. Further, it was observed that the resin prepared under milder temperature conditions (70-72°C) was easier to foam and

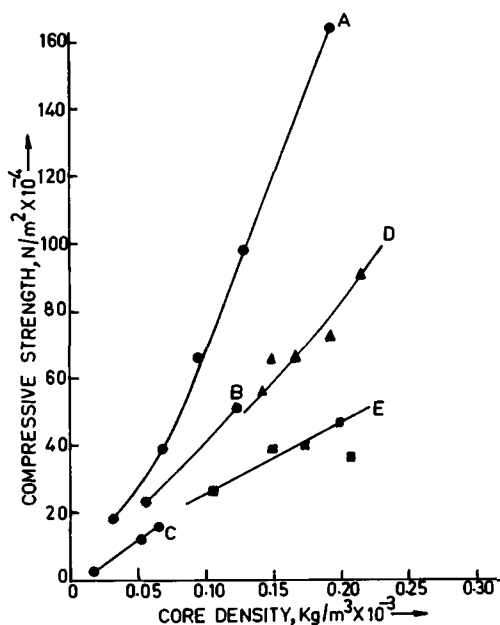


Fig. 1. Density vs. strength for phenolic foams: A, B, and C, Ref. 2, p. 1011; D, this work (P/F mole ratio 1:1.5); E, this work (P/F mole ratio 1:2).

yielded a more uniform product. Condensation of phenol and formaldehyde in the presence of sodium hydroxide–barium hydroxide octahydrate catalyst was therefore studied under mild temperature conditions, i.e., 70–72°C. The reactions were carried out for F/P mole ratios of 1.5 and 2.0.

The percent free formaldehyde at various time intervals is shown in Figure 2. As is obvious from the figure, most of the formaldehyde is consumed during the early part of the reaction. In case of a F/P mole ratio of 1.5, over 90% of the formaldehyde was consumed within the first half-hour. The resin at this stage was found to yield good- and uniform-quality foams. The foam samples for this study, however, were prepared after a reaction time of 4 h.

Comparison with Single Catalysts

The data of Meier and Frank⁵ for single catalysts (sodium hydroxide and sodium carbonate) have also been plotted in Figure 2. It is obvious that use of barium hydroxide octahydrate does not have a significant effect on the rate of the reaction and leads to about the same percentage of free formaldehyde after a 1 h of reaction time.

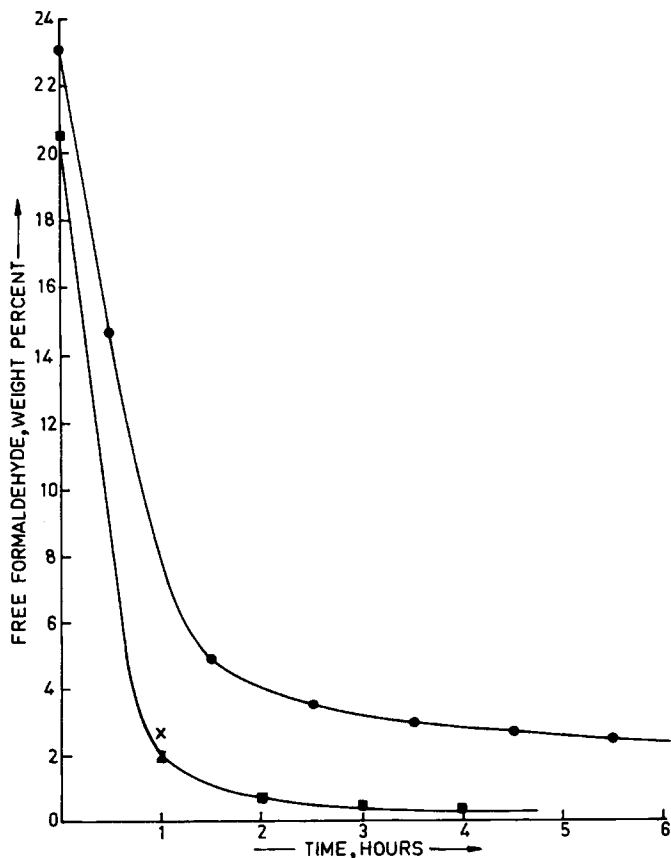


Fig. 2. Kinetics of phenol–formaldehyde resinification: (●) this work (P/F mole ratio 1:2; catalyst sodium hydroxide–barium hydroxide octahydrate); (■) this work (P/F mole ratio 1:1.5; catalyst sodium hydroxide–barium hydroxide octahydrate); (X) Meier and Frank (1977) (P/F mole ratio 1:1.5; catalyst sodium carbonate).

Total Solids-Refractive Index Correlation

The resinification reaction was followed by dehydration to raise the total solids (TS) value to around 70% so as to obtain good-quality foams. The refractive index of the resin was closely monitored during this step. These values have been correlated with the total solids by a straight-line correlation depicted in Figure 3. The correlation can be highly time-saving as it can eliminate the necessity of cumbersome TS determinations.

Foam Characteristics

The foaming of the resin was done using anhydrous sodium carbonate as a blowing agent in combination with hydrochloric acid. Hexamine was used as curing agent. After preliminary laboratory trials, it was found that 2.5% by weight of anhydrous sodium carbonate and 1% by weight of hexamine in combination with a little excess of 10% hydrochloric acid was sufficient for a foaming phenol-formaldehyde resin having a solid contents of the order of 70%. The density and compressive strength of the various phenol formaldehyde foams so obtained are presented in Figure 1. These values are plotted in Figure 1 along with the data available in the literature.² As pointed out earlier, Baer's data² do not give any details about the characteristics of the resin used for foaming. However, an extrapolation of the two curves obtained in this work clearly indicates that the two sets of foams conform to F/P mole ratios of 1.5 and 2.0, respectively, with percent solids of the order of 70%. This may be considered to be a fairly good set of parameters for obtaining the range of foams indicated in Figure 1.

Effect of Foaming Temperatures

Foaming of the resin was also carried out at different temperatures. The effects of foaming temperatures on foam density and compressive strength are shown in Table I. Both the compressive strength and the density increase with increasing temperature. It may be noted, however, that the density-strength correlation given in Figure 2 is independent of the temperature used for foaming.

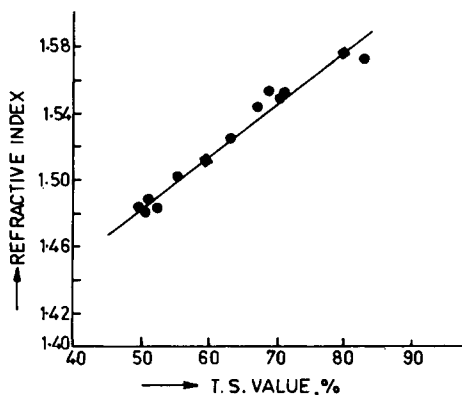


Fig. 3. Refractive index vs. total solids content.

TABLE I
Effect of Temperature on Foam Characteristics^a

Series no.	Temperature, °C	Core density, g/cm ³	Compressive strength, kg/cm ²
1	60	0.1420	5.68
2	70	0.1490	6.65
3	80	0.1664	6.88
4	90	0.1925	7.50
5	100	0.2150	9.20

^a Reaction conditions: phenol/formaldehyde mole ratio 1:1.5; reaction temperature 70–72°C; reaction time 4 h; percent solid after dehydration 69.1%.

This work was supported by a grant from the Department of Science and Technology, Government of India, on "Conversion of Agricultural Wastes and Other Available Materials to Plastic Foams for Use as Roofing Panels."

References

1. Y. L. Metzger, *Foamed Plastics—Recent Developments*, Noyes Data Corp., 1976.
2. E. Baer, Ed., *Engineering Design for Plastics*, Reinhold, New York, 1964, pp. 995–1071.
3. S. Chandra and D. Singh, in *Proceedings of 2nd Iranian Congress of Civil Engineering, Shiraz (Iran)*, May 1976, Vol. 1, pp. 544–559.
4. J. F. Walker, *Formaldehyde*. Reinhold, New York, 1964, pp 493–494.
5. J. F. Meier and P. P. Frank, *J. Appl. Polym. Sci.*, **21**, 1383 (1977).
6. T. H. Ferigno, *Plastic Foams*, Reinhold, New York, 1963.

Received January 15, 1981

Accepted August 25, 1981