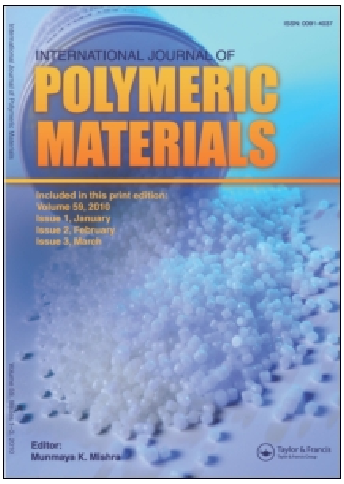

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Subtitution of Pentane by a Mineral Clay as a Blowing Agent for Phenolic Foam

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The main drawback of using pentane as a blowing agent for rigid phenolic foam is its flammability. It presents a real risk of explosion and therefore requires specific conditions for handling and storage. In this article its replacement by a mineral clay composed mainly of calcium carbonate as the major component in addition to some other metal oxides, was investigated in terms of performance requirements. The proposed formulations contained instead of pentane different proportions of the clay and a mixture of toluene sulphonic acid and sulfuric acid. It was found that, except for a slight increase in the thermal conductivity, all other properties such as foam density, water absorption, permeability to water vapor, compression resistance, and flexural resistance were within the plant specifications. To complete the study, it is recommended to investigate possible adverse long-term effects in terms of chemical resistance and foam morphology.

Keywords: blowing agent, calcium carbonate, pentane, phenolic foam

INTRODUCTION

Among the different types of rigid foams that can be prepared from thermoset resins, the phenolic resins may be considered to be the first

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polymeric products produced commercially from simple compounds of low molecular weight [1]. Although their growth rate has been less spectacular than those of some other materials such as expanded polystyrene or rigid polyurethane foams, rigid phenolic foams have gained acceptance in recent years in most fields of application and particularly for building board insulation.

Blowing agents, which are substances that give up a great amount of gas or vapor resulting in a cellular structure, are a major ingredient composing a foam formulation. Depending on their decomposition mode, blowing agents can be classified as either chemical or physical blowing agents. With physical blowing agents the release of gas is caused by the change of state of the substance such as the vaporization of a liquid. However, the release of gas by chemical blowing agents is caused by the decomposition of a substance or could result from the chemical reaction between two products. In the manufacture of phenolic foams various types of blowing agents have been used, each of which is used under specific conditions or is suitably treated. Examples of these are ammonium or magnesium carbonates [2–3], powdered aluminum, zinc, and magnesium [4], and benzene sulfate [5].

Pentane, a low boiling point hydrocarbon, has been used as a blowing agent for rigid foams including rigid phenolic foam and polyurethane foam. However, a major drawback of the use of pentanes is their flammability and their risk of explosion. In fact, they form explosive mixtures with air. Therefore they require specific handling and storage conditions. Moreover, rapid and efficient ventillation must be ensured and all possible ignition sources such as sparks, static electricity, or smoking should be eliminated [6]. Due to all these risks, it was aimed to replace pentane by a mineral clay. In this case the liberation of carbon dioxide would be caused by the reaction of calcium carbonate ($CaCO_3$), present in the clay as the major component, with the acidic catalyst, which is a mixture of toluene sulfonic acid and sulfuric acid used for curing the resin.

This article presents a study of the effect of replacing pentane by $CaCO_3$ clay in the formulation of rigid phenolic foam. The general performance of the foam will be assessed through the measurement of the thermal and mechanical properties.

EXPERIMENTAL

Preparation of the Foam

The phenolic resin used in this study, which is of the Resol type, is manufactured by ENPC (Entreprise Nationale des Plastiques et Caoutchoucs, Algeria). The $CaCO_3$, containing clay (trade name PH

TABLE 1 Composition of PH West Clay

Component	%
$CaCO_3$	90.20
SiO_2	5.90
Fe_2O_3	2.10
Al_2O_3	0.90
MgO	0.30
others: Na_2O, K_2O, TiO_2, H_2O	0.60

West), which has an average particle size of 27–35 μm was supplied from FERPHOS-Algeria. Its composition is given in Table 1.

A laboratory batch reactor equiped with a high speed agitator run at 1,500 Rpm was used for mixing the resin with the different ingredients of the formulations at temperatures ranging from 70 to 80°C. The cream time was 10 seconds whereas the foaming time varied between 4 minutes and 7 minutes depending on the clay content.

To assess the effect of each component of the recipe on the performance of the foam, different formulations, presented in Table 2, were prepared varying the amount of the catalyst and the clay. The reference formulation (RF) is the one where pentane was initially used as the blowing agent in addition to boric acid as a flame retardant. Preliminary tests revealed that a surfactant was needed to impart a homogeneous cellular structure.

Testing

As required by the plant specifications, all the performance properties were tested according to the French norm NFT, except for the thermal conductivity coefficient, which was evaluated using the Fourier's law of heat conduction [7].

TABLE 2 Different Formulations Prepared

	Formulation			
Component	A1	A2	A3	RF
Resin (Phr)	100	100	100	100
Clay (Phr)	4	5	6	0
Catalyst (cm^3)	22	26	28	20
Pentane (Phr)	0	0	0	7.5
Boric acid (Phr)	0	0	0	13
Surfactant (Phr)	2	2	2	7

Apparent Density

The foam apparent density was measured according to NFT 56107 standard. Prior to being tested all samples were conditioned during 24 hours at 23°C. The square specimens (50 mm × 50 mm × 40 mm) were then immersed in distilled water and their density determined using a picnometer.

Water Absorption

This test was performed according to NFT 56123 standard. The dimensions and weight of the square specimen (50 mm × 50 mm × 40 mm) were accurately measured before and after immersion in distilled water for 7 days at room temperature. The percentage volume of water absorbed (W) was calculated as follows:

$$\mathrm{W}(\%) = \left(\frac{\mathrm{m}_2 - \mathrm{m}_1}{\rho \cdot \mathrm{V}}\right) \times 100 \tag{1}$$

where m_2 and m_1 are the sample's weight (gr) after and before immersion, respectively, ρ is water density (gr/cm^3), and V is the sample volume (cm^3).

Permeability to Water Vapor

This test was performed according to NFT 56105 standard. It consisted of measuring the change in weight of a sample exposed to water vapor at 38°C and 88% relative humidity. A desiccant was placed in a dish containing calcium chloride and a circular test piece having a diameter of 65 mm and a thickness of 25 mm was sealed with paraffin wax at its side across the mouth of the dish. The dish assembly was then placed in a vessel at the specified conditions of temperature and relative humidity.

The Index of Permeability to Water Vapor (I.P.W.V.) was calculated as the ratio of the gain in weight to the sample's area.

Compression Resistance

The compression test was carried out according to NFT 56101 standard using an Instron 4465 Tester. A compressive force was applied on square samples (50 mm × 50 mm × 40 mm) at a rate of 5 mm/min. The compression strength was calculated as the ratio of the force corresponding to 10% deformation to the area of contact with the compressive load.

Flexural Resistance

The flexural resistance was measured using an Instron 4465 Tester and a three point loading rig at a speed of 1.7 mm/min according to

NFT 56102. The dimensions of samples were 120 mm × 25 mm × 20 mm. The flexural strength was calculated as:

$$б_r = \left(\frac{3\,l}{2b \cdot h^2}\right) \times F_r \qquad (2)$$

where $б_r$ is the flexural strength, h is the thickness of the sample, l is the span length, b is the sample's width, and F the force at break.

RESULTS AND DISCUSSION

One of the most important characteristics of rigid foams as insulation materials is their cellular structure. In fact, these types of materials have very small pockets or cells that contain trapped air. These cells resist the transfer of heat through the material. As a result of this cellular structure the material's density is low. Figure 1 presents the effect of increasing the amount of the acidic catalyst on the foam density. It was found that increasing the concentration of the catalyst resulted in an increase of the foam density. On the other hand, as shown in Figure 2, it was found that increasing the amount of the blowing agent by 2 parts caused a sharp decrease in the density. These two results suggest that the foam density is much dependent

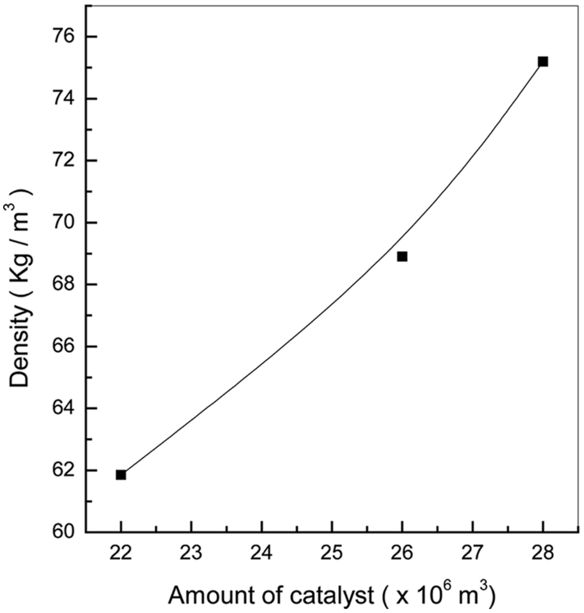

FIGURE 1 Variation of the foam density with the amount of catalyst.

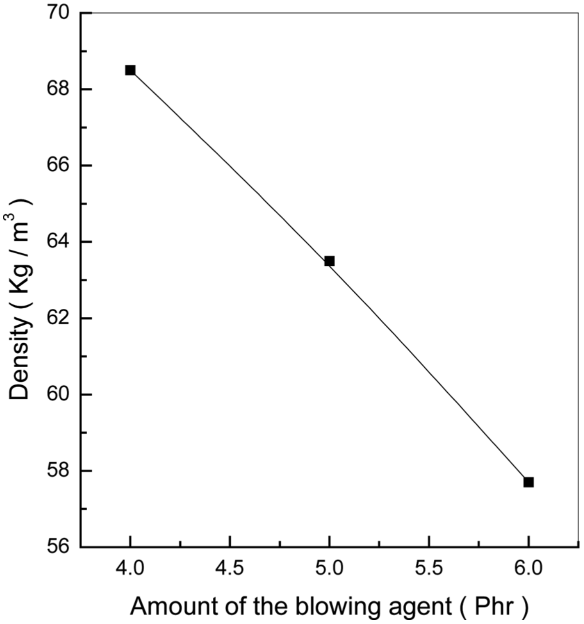

FIGURE 2 Variation of the foam density with the amount of the clay.

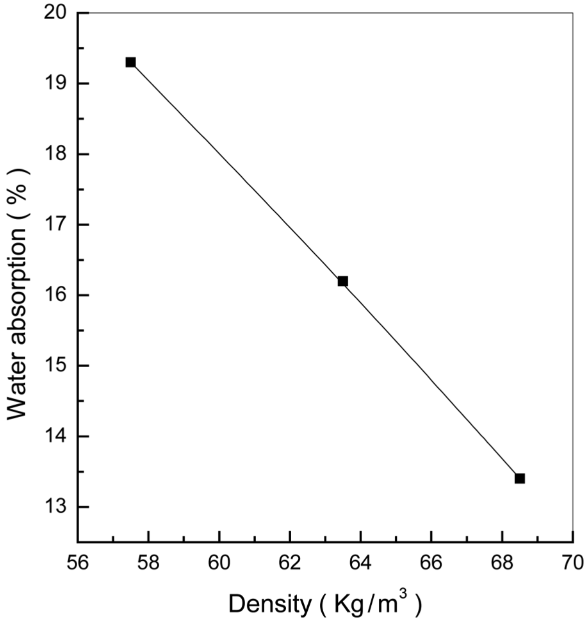

FIGURE 3 Variation of water absorption with the foam density.

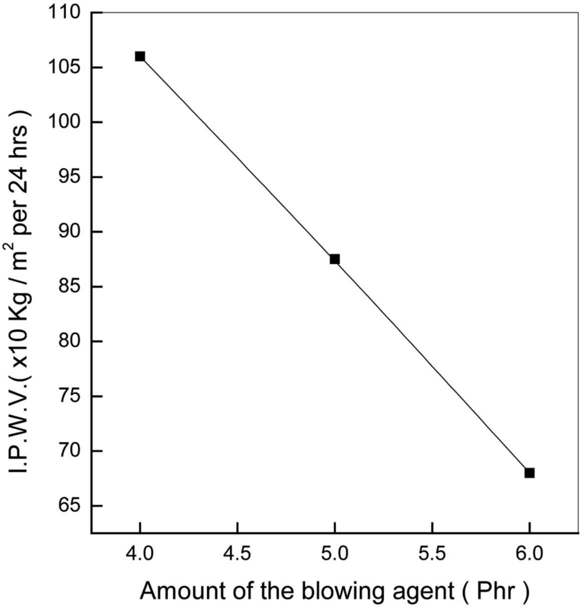

FIGURE 4 Variation of the index of permeability to water vapor with the amount of the clay.

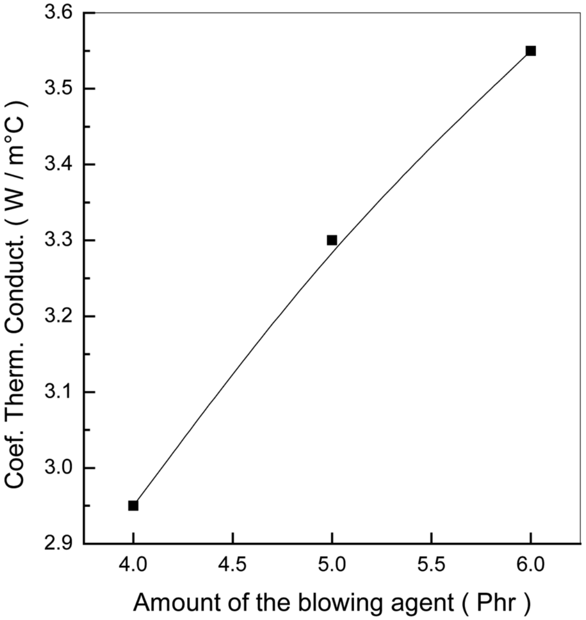

FIGURE 5 Variation of the thermal conductivity coefficient with the amount of the clay.

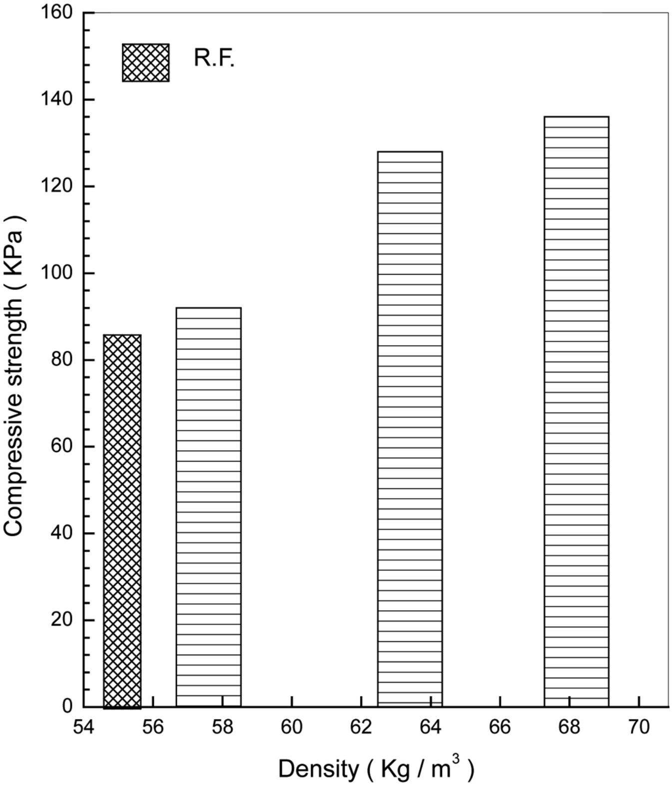

FIGURE 6 Variation of the compressive strength with the apparent density for the proposed formulations and that of the reference formulation (R.F.).

on the ratio of the catalyst to the clay. Because the liberation of carbon dioxide gas will be accompanied by the formation of calcium oxide (CaO), a mineral residue, therefore the density will be a function of these two conflicting factors, which both depend on the amount of $CaCO_3$. The higher the amount of CO_2, the higher will be the number of cells formed, the lower the density. At the same time, as the amount of $CaCO_3$ increases the amount of the resulting CaO residue increases also leading to an increase in the density.

The variation of the foam density with catalyst to blowing agent ratio was further correlated with water absorption as illustrated in Figure 3. It is shown that an increase in the density resulted in a decrease of water absorption owing to a reduction in the void volume rendering, hence, the foam less porous.

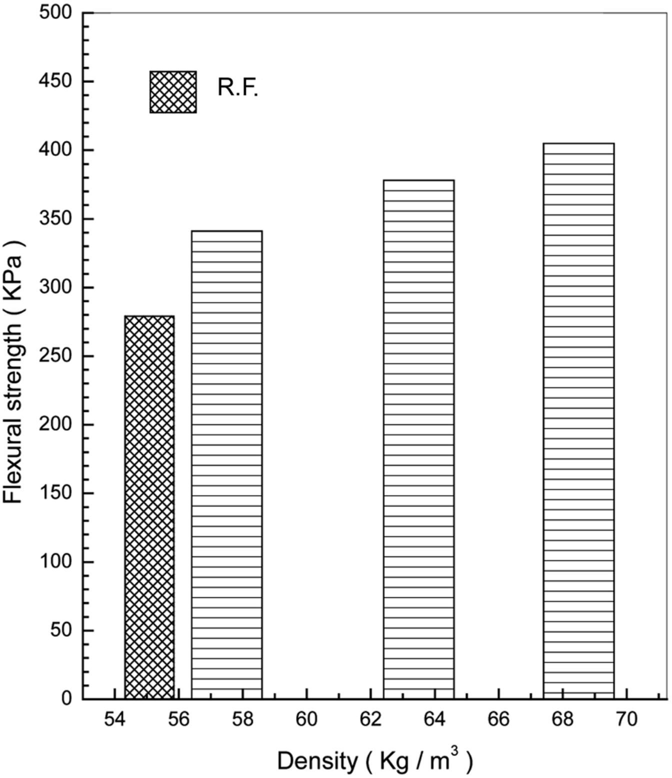

FIGURE 7 Variation of the flexural strength with apparent density for the proposed formulations and that of the reference formulation (R.F.).

This remarkable increase in the density could also be attributed to the formation of $CaSO_4$ residue resulting from the reaction of H_2SO_4 present in the catalyst with the $CaCO_3$ composing the clay. Overall, the aforementioned results affecting the foam density indicate that the carbon dioxide resulting from the reaction between the catalyst and the clay acted not only as a blowing agent but also as a nucleating agent giving rise to a closed cell structure.

Figure 4 presents the effect of increasing the concentration of the clay on the Index of Permeability to Water Vapor (I.P.W.V.). It is shown that as the amount of the clay was increased, the I.P.W.V. decreased. This could be attributed to the fact that in addition to $CaSO_4$ and CaO residues, the metal oxides Al_2O_3, SiO_2, MgO, and Fe_2O_3 present in the clay, even at a minor content, acted as a physical barrier against the diffusion of water vapor inside the foam.

The presence of $CaSO_4$ and those metal oxides caused also the slight increase in the thermal conductivity as shown in Figure 5. This increase in the thermal conductivity might be considered as a drawback as far as the insulation capacity of the material is concerned, but it is to be noted that even the highest value of the thermal conductivity coefficient was still within the plant specifications.

The most striking performance characteristic of using the clay in place of pentane was the improvement in the mechanical properties. As shown in Figure 6 and 7, the incorporation of the mineral clay resulted in an increase of both the compressive strength and the flexural strength; two basic properties desired for the handling of the foam. This effect was expected due to the increase of the foam density and to the reinforcing effect of the filler that improved the material's stiffness. This reinforcing effect could be due to a possible interaction between the $CaCO_3$ and the polymeric matrix via the functional groups of the catalyst.

CONCLUSION

The major conclusion to be drawn from this study is that the use of a type of clay composed of calcium carbonate can replace pentane as the blowing agent for rigid phenolic foam without a great loss of the main performance requirement properties. Consequently its use would generate great economical benefits and would offer a safer additive. To complete the study, it is recommended to investigate the long-term effects of the solid residues in terms of chemical and solvent resistance, and to study the effect of the filler particle size on the foam morphology.

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