Physical Properties of Tannin/Furanic Resin Foamed With Different Blowing Agents

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Tannin/furanic rigid foam made from raw materials of natural origin could be used to replace polyurethane and phenolic foams in many future applications. In this study, diethyl ether, pentane, and a mixture of the two were used to prepare tannin/furanic foams having different microstructures. It was found that the bulk density of the foam could be significantly extended, up to 180 kg/m^3. The cell size of the pentane foam was larger than that of diethyl ether foam with comparable density; however, both presented a sudden increase in cell size when the density decreased. The thermal conductivity and mechanical properties were determined for the two foam types at the same density but different cell size. The minimum thermal conductivity for diethyl ether and pentane foams were presented, along with a suggested method for lowering the thermal conductivity of such foam. Additionally, the results of mechanical tests indicate that cell size does not play a role in compressive strength.

Keywords: Tannin/furanic rigid foam; Different blowing agents; Cell size; Thermal conductivity; Mechanical property

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INTRODUCTION

Foams based on metals, ceramics, polyurethane, phenolic resin, polyolefin, *etc.*, are commercial materials of increasing interest (Kim *et al.* 2005; Chen *et al.* 2006; Abdalla *et al.* 2003; Ligoure *et al.* 2005; Checchin *et al.* 1999; Greco and Lionetto 2009; Greco *et al.* 2005; Indennidate *et al.* 2009). However, new tannin/furanic rigid foams present the following advantages: low cost, about 95% of the constituent raw materials are from renewable sources, high thermal insulation, good mechanical properties, and excellent fire resistance (Meikleham and Pizzi 1994; Tondi *et al.* 2009a; Tondi and Pizzi 2009; Celzard *et al.* 2010). Moreover, their high carbon yield makes them an excellent precursor for cellular vitreous carbon (Tondi *et al.* 2009b).

For the foam material, the microstructure is of utmost importance because of its properties and applications. Recent work has shown that polymeric 4,4'-diphenyl-methane diisocyanate (pMDI) can be used to modify the cell structure of tannin/furanic foams (Li *et al.* 2012). However, pMDI is expensive and difficult to disperse. Until now, all of the studies concerning tannin/furanic foam have been conducted with diethyl ether (DE) as the blowing agent. When the density of the foam is higher than 80 kg/m^3, it becomes difficult to control with the proportion of diethyl ether. Especially when the density is higher than 160 kg/m^3, foams are always flawed (Zhao *et al.* 2010). Pentane has been widely used in PF foams because it is available at a low cost and presents low toxicity. Considering that pentane is not soluble before foaming (unlike DE), it will affect foam performance by causing differences in the foam microstructure. Thus, diethyl ether,

pentane, and mixtures of the two were all used as blowing agents. The density, cell size, thermal conductivity, and mechanical properties were also measured. Thermal conductivity is a very important parameter for foams used in thermal insulation; hence the relationship of thermal conductivity and microstructure was also investigated.

EXPERIMENTAL

Chemicals

The company Silvachimica supplied the commercial mimosa tannin (*Acacia mearnsii*, de Wild), which was predominantly composed of prorobinetinidins and contained more than 80% oligomers of A, B, and C flavonoid units (Pasch *et al.* 2001), as represented in Fig. 1.
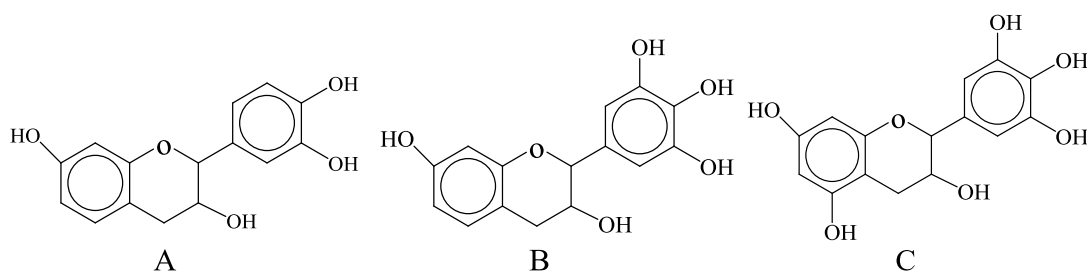

Fig. 1. Mimosa tannin flavonoid units

Formulation and Preparation

The formulation of the foams is given in Table 1. First, water, furfuryl alcohol, formaldehyde, blowing agent, and tannin were mixed together using strong agitation. Then para-toluene-4-sulphonic acid (catalyst) was added with violent stirring for 20 s, and the foaming began after a short induction time. Black foam was thus obtained within a few minutes.

Table 1. Formulation of Tannin/Furanic Foams with Different Blowing Agents

Component	Amount (g)
Water	6
Furfuryl alcohol	10.5
Formaldehyde (37% water solution)	7.4
Blowing agent	1 - 10
Tannin	30
Para-toluene-4-sulphonic acid (65% solution)	11

The foams were left in a constant temperature and humidity room for 3 days. Diethyl ether, pentane, and the mixture of diethyl ether and pentane (1:1 w/w) were all used as blowing agents. The corresponding foams were called DE foam, pentane foam, and DEP foam.

Measurement

Bulk density and mechanical test

The samples were cut in to $30 \times 30 \times 15$ mm^3 specimens. The bulk density is defined as the weight of the bulk divided by its volume.

The compression was tested with an Instron 4467 universal testing machine equipped with a 30 kN head at a constant load rate of 2.0 mm·min^{-1}.

Scanning Electron Microscope (SEM)

The samples were put into freezer at a temperature of -40 °C and then cut into $5 \times 5 \times 4$ mm^3 samples for observation with a Hitachi S 4800 scanning electron microscope (SEM) with a magnification of ×20.

Thermal conductivity

The samples were cut to dimensions of $100 \times 50 \times 30$ mm^3 and put in a vacuum oven for 1 day to drive away any possible blowing agents in the foam. The thermal conductivity was measured by the thermal conductivimeter FP2C (NeoTim) at room temperature with a sensor of 13.6 Ω, power of 0.04 W, and testing time of 180 s.

RESULTS AND DISCUSSION

Density and SEM

The single most important structural characteristic of any foam is its relative density ρ_r, which is defined as,

$$\rho_r = \rho^* / \rho_s \qquad (1)$$

where ρ^* is the bulk density and ρ_s is the skeleton density (sometimes also called true density). The skeleton density ρ_s has been found to be 1,580 kg/m^3 (Celzard *et al.* 2010). As expected, an increase in blowing agent content always lowers the density of the foam, as shown is Fig. 2. The error bars in Fig. 2 indicate that it is more reliable and repeatable to produce foams with a density of 30 to 80 kg/m^3 with diethyl ether and to produce the foams with density of 120 to 180 kg/m^3 with pentane. Foams with a density in the 80 to 120 kg/m^3 range can then be produced by mixtures of DE and pentane.
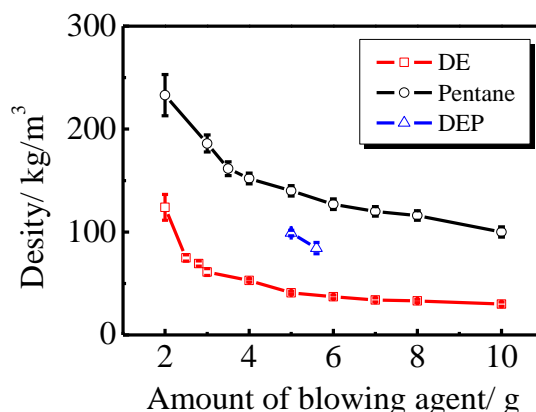
Fig. 2. Relationship of density and amount of blowing agent for tannin/furanic rigid foams

More details about the microcellular structure of the foams are shown in Fig. 3. The SEM photos clearly show that each cell is made up of edges, cell walls (also called faces or membranes), and windows in the cell walls. In general, there are always one or two faces that present a small window, though most faces are intact. Furthermore, the cell walls are thinner than the cell edges so that it would be difficult to tell a membrane from a window if the samples were not metalized before SEM scanning (photos not shown). It is interesting to point out that the mixture of the two blowing agents did not result in different cell size distribution.
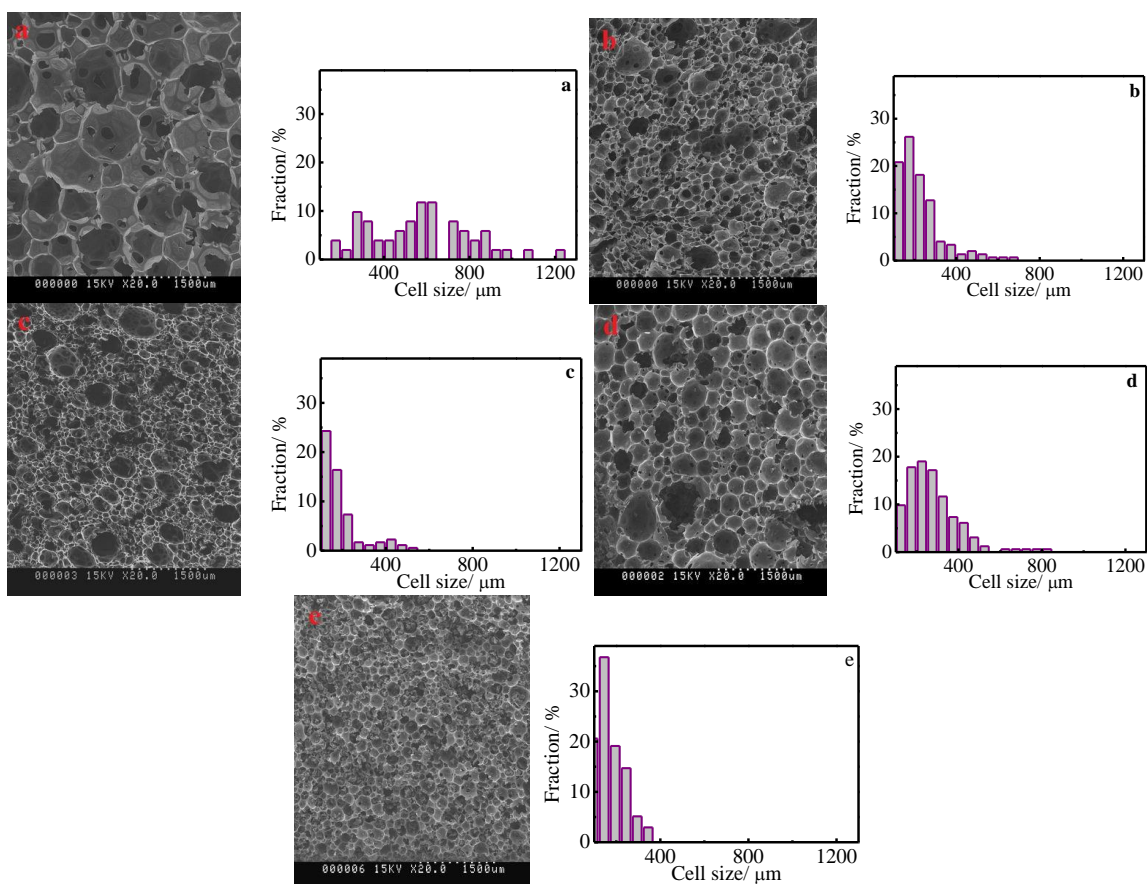
Fig. 3. SEM and cell size distribution of (a) DE foam with density 32 kg/m^3; (b) DE foam with density 62 kg/m^3; (c) DE foam with density 87 kg/m^3; (e) pentane foam with density 120 kg/m^3; (f) DEP foam with density 100 kg/m^3

If the growing direction of the foam is defined as its z-axis, the plane perpendicular to such a z-axis is defined as the xy-plane. The SEM images in Fig. 3 are obtained from xy-plane; however we must point out that previous work has shown that the cells are elongated in the direction of the z-axis. The mean cell diameter is defined by De Hoff and Rhines (1968) as,

$$\overline{L} = \frac{1.5}{N_c} \tag{2}$$

where N_c is the number of the cells per unit length of a straight line lying parallel to each of the three principal directions. In this paper, only the mean cell diameter of the xy-plane

is discussed, which is shown in Fig. 4. The cell size increases as the relative density decreases, especially when the relative density is lower than 0.03 for DE foams and 0.08 for pentane foams.

Furthermore, in Fig. 4, the mean cell size of pentane foams is larger than DE foams at the same relative density, especially at lower densities. This is of consequence when the foam is used for metal absorption and/or as a catalyst carrier, where a large cell size is sometimes preferred. DE is soluble in the mixture of raw materials but pentane can not, so pentane is more like to congregate during the foaming process, which results in a larger cell size than DE foam.
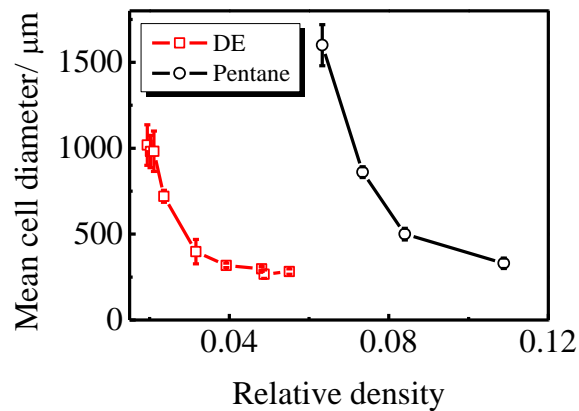
Fig. 4. Changes in mean cell diameter of tannin/furanic rigid foam as a function of relative density

Thermal Conductivity

Thermal conductivity is very important to foam materials (Venkatesan *et al.* 2001; Klett *et al.* 2004; Modesti *et al.* 2004; De Micco and Aldao 2006). The effective thermal conductivity of the foam materials, λ^*, is considered to be made by four factors (Gibson and Ashby 1997),

$$\lambda^* = \lambda_s^* + \lambda_g^* + \lambda_c^* + \lambda_r^* \tag{3}$$

where λ_s^* is the heat conduction through the solid, λ_g^* is the conduction through the gas, λ_c^* is the convection within the wall, and λ_r^* is the radiation through cell walls and across the cell voids. The contribution of radiation and the convection in the foam are very complex. According to Schuetz and Glicksman (1984),

$$l_s^* = \frac{2}{3}\left(\frac{r*}{r_s}\right) l_s \tag{4}$$

and

$$\lambda_g^* = \left(1 - \frac{\rho*}{\rho_s}\right)\lambda_g \tag{5}$$

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where λ_s and λ_g are the effective thermal conductivity of the solid- and the gas-filled foams, respectively. Thermal conductivity was tested when the foams were left for more than 3 months, so that the filling gas in the foams was air, which has a thermal conductivity of 0.025 W/m k at room temperature.

The effective thermal conductivities of tannin/furanic foams are shown in Fig. 5. As the relative density decreases, both DE foams and pentane foams showed two thermal conductivity regions: a region of gradual linear decrease (region I) and a region of sharp increase (region II). The minimum thermal conductivity for DE foam and pentane foam is 0.037 W/m k (when $\rho_r = 0.0237$) and 0.053 W/m k (when $\rho_r = 0.0842$), respectively. As we can see from Eq. 4 and Fig. 5, the decrease of the thermal conductivity in region I is caused by the decrease of relative density. For DE foam, the conduction through the air contributes as high as 0.024 W/m k. When the cell size is small and the relative density of the foam is high, the contribution of radiation and natural convection can be ignored, and the foam's thermal conductivity presents a linear trend. The following equation fits the linear region of the thermal conductivity of the DE foam:

$$\lambda^* = 0.031 + 0.299 \left(\rho^* / \rho_s \right) \tag{6}$$

According to Eqs. 2 to 4, the intercept of Eq. 5 should be 0.025, which is the thermal conductivity of air. This is supposed to be caused by the fact that radiation contributes more at low relative density and less at higher relative density.
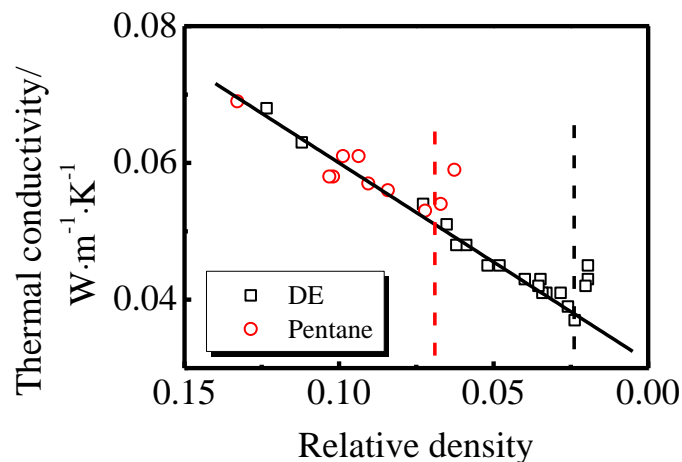
Fig. 5. Effect of relative density of tannin/furanic rigid foam on thermal conductivity. The straight line fits the linear region of DE foam.

In region II the thermal conductivity increased dramatically as the relative density decreased. This may be caused by two factors: 1) a sudden increase of the radiation, and 2) a sudden increase of natural convection. Theoretically, the natural convection is important when the Grashof number, G_r, is higher than 1000, which means that the mean cell size should be larger than 10 mm (Gibson and Ashby 1997). Experimental results showed that heat transfer by convection does not exist for cell diameters smaller than 4 mm (Skochdopole 1961). From Figs. 4 and 5 it can be seen that the transition occurs when the cell size is greater than 700 μm. Thus, at this cell size, heat transfer due to natural convection can still be negligible. According to Eqs. 2 to 4, the sudden, rapid

increase of thermal conductivity is caused by the sharp increase of radiation. Glicksman (1994) used Rossland's equation and found that radiative heat transfer could be expressed as,

$$l_r = 16 S T^3 / 3K^*$$ (7)

and

$$K^* = 4.10 \sqrt{\frac{\phi(\rho*/\rho)}{l}} + \frac{3.46}{l} \times \frac{1 - \exp - (2k_s t_f)}{1 + \exp - (2k_s t_f)}$$ (8)

where σ is Stefan's constant, T is temperature, ϕ is the volume fraction of solid in the cell edges, K_s is the extinction coefficient of the solid, λ is the cell size, and t_f is the face thickness. Equations 6 and 7 and Fig. 4 show that the decrease of ρ^*/ρ and the sharp increase of cell size will result in a dramatic increase of radiative contribution. Therefore, the way to lower the thermal conductivity should be to always keep the mean cell size of the foam under 700 μm.

Compressive Strength

A typical full stress-strain curve of tannin/furanic foam under compression is shown in Fig. 6a. The compression curve always shows an elastic failure with three regions: elastic deformation, plateau, and densification. However, the tensile stress-strain curve showed a fragile break (Tondi *et al.* 2009a). The stress-concentration effect always leads to a crack, which will cause damage to the material, no matter if in compression or tension. However, the crack increases far more quickly in tension than in compression, so tannin/furanic foams are elastic in compression and brittle in tension.
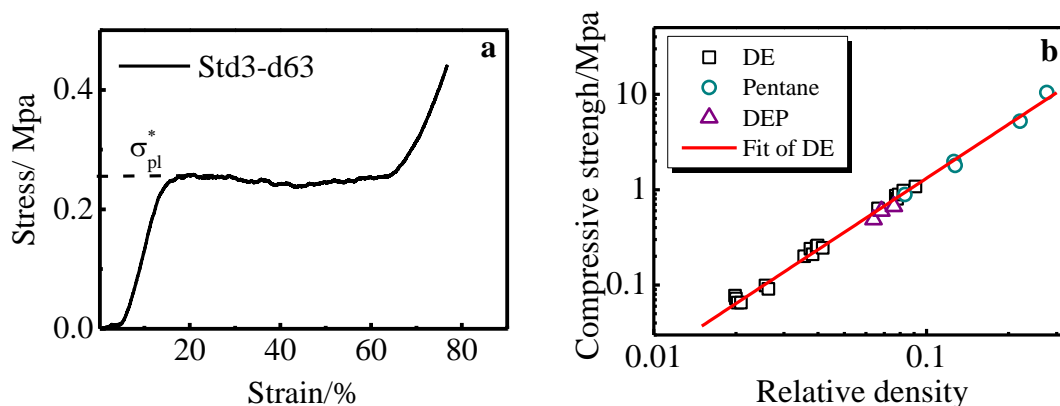
The relative density and compressive strength obey a power law (Gibson and Ashby 1997).

$$\sigma_{pl}^* \propto \sigma_{ys} \left(\frac{\rho^*}{\rho_s} \right)^a$$ (9)

where σ_{pl}^* is the compressive strength of the foam, σ_{ys} is the compressive strength of solid, and a is constant. By fitting Eq. 8 to the results of DE foams, the following equation is obtained,

$$\sigma_{pl}^* = 100 \times \left(\frac{\rho^*}{\rho_s} \right)^{1.88}$$ (10)

The fitting results are shown in Fig. 6b. The compressive strength of the DE foam, pentane foam, and DEP foam are just on this line, so there was no mechanical difference in the foams blown by different blowing agents. This means that the cell size does not determine the compressive strength. Thus, pentane can improve the mechanical properties of the foam by extending the density of tannin/furanic foams to 180 kg/m^3. Pentane foams have greater density and higher compressive strength than DE foams of the same cell size. This is of great interest when the cell size is the only concern, as in applications like metal absorption and catalyst carriers.

Fig. 6. (a) Typical strain-stress characteristics of a tannin/furanic rigid foam; (b) compressive strength of different tannin/furanic foam as function of relative density

CONCLUSIONS

1. Blowing agents such as DE, pentane, and a mixture of the two, are suitable blowing agents to produce foams with density in the ranges of 30 to 80 kg/m^3, 120 to 180 kg/m^3, and 80 to 120 kg/m^3. Moreover, each blowing agent showed a very quick increase in cell size when the density was lower than a certain value.

2. For the thermal conductivity of tannin/furanic foams, lowering the relative density (or bulk density) is an efficient way to decrease thermal conductivity. However, there is a minimum thermal conductivity for DE and pentane foams, which is 0.037 W/m k and 0.050 W/m k, respectively. This occurs when the mean cell size is higher than 700 μm. Both the decrease of relative density and the increase of cell size lead to a sharp increase of radiation, which results in a sudden, rapid increase in thermal conductivity. The way to lower the thermal conductivity should be then to always keep the mean cell size of the foam under 700 μm.

3. Though different blowing agents result in different cell sizes, the mechanical performance of the foams is the same. Thus, pentane can improve the foam's mechanical properties by extending the density of tannin/furanic foams to 180 kg/m^3.

4. Pentane foams have greater density and higher compressive strength than DE foams of the same cell size. This is of great interest when the cell size is the only concern, as in applications like metal absorption and catalyst carriers

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