

# Dynamic Foaming Behaviour of Polyurethane vs Tannin/Furanic Foams

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**ABSTRACT:** Simultaneously monitoring the variation of temperature, foam rising rate, internal foam pressure and dielectric polarisation, the latter being a direct measure of setting and curing of a thermosetting foam, has allowed the comparison of the dynamic variation of determinant parameters of polyurethane foams and of tannin/furanic foams of different formulation and characteristics. This monitoring provides a good description of the process and possible characteristics of the prepared foam and constitutes an invaluable tool for foam formulation. Such a comparison indicates that fundamental differences, but also similarities, exist between the foaming processes of the two classes of foam. The dynamics of the foams were compared for (i) a tannin/furanic foam formulation using formaldehyde and a low-boiling blowing agent (STD); (ii) a tannin/furanic foam containing neither formaldehyde nor blowing agent (MN65), (iii) the same as (i) but with the addition of a small proportion of surfactant (MN8'), and (4) a commercial PUR foam formulation.

**KEYWORDS:** Tannin foams, furanic foams, polyurethane foams, foaming temperature, dielectric polarisation, foaming pressure, foam rising rate, foam curing, simultaneous measure

## 1 INTRODUCTION

Polyflavonoid tannin-furanic rigid foams have been developed and tested for a number of different applications [1–3]. They are composed of renewable materials and have excellent performance under a number of different conditions [4–11]. Conversely, polyurethane (PUR) foams are the most used commercial foam materials today. Tannin-furanic foams have several similarities to synthetic phenolic foams; however, they are very different from PUR foams. Tannin-furanic rigid foams have some major advantages over PUR foams; they are made from up to 98% natural renewable resources, are relatively inexpensive and totally fire resistant, while PUR foams are oil-derived and very flammable. Apart from these obvious differences, there are major differences in

the dynamics of the foaming process between the two types of foams. These differences need to be addressed to possibly adapt tannin-furanic foams to the plants used today to manufacture PUR foams. To this purpose, it is interesting to investigate if their foaming dynamics can approach those of PUR foams so that some principles for their use on existing plants can be established.

Recently, a method and relative equipment capable of dynamically monitoring the main parameters from which the preparation of any foam depends have been used to study the process of foaming leading to tannin-based rigid foams [12]. These parameters are: (i) the rise and fall of the temperature of the exotherm of reaction on which foaming depends; (ii) the setting and curing rate of the polymers or copolymers that are the main constituents of the foam that are measured by dielectric polarisation (dielectric polarisation is a well-known technique used in other fields to monitor setting and curing of a thermoset resin [13] by measuring the decrease in molecular mobility during crosslinking), (iii) the velocity of rising of the mixture during foaming, and

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(iv) the internal pressure developing inside the mixture during foaming. It is the combination and the monitoring of these parameters *in situ* that allows the rapid determination of what type of foam one is preparing.

This paper deals with the study of the dynamic foaming phase of a commercial PUR and its comparison with four different formulations of tannin-furanic foams.

## 2 EXPERIMENTAL

### 2.1 Tannin

Commercial tannin powder, sold under the name Mimosa OP and supplied by the company SilvaChimica (St. Michele Mondovi, Italy) has been used. Tannin was extracted industrially in Tanzania from the whole, dried, bark of 10-year-old Mimosa trees (*Acacia mearnsii*, formerly *mollissima*, de Wild). Tannin contains more than 80% phenolic (flavonoid) materials, the remainder being water, amino- and iminoacid fractions, hydrocolloid gums and carbohydrates, in general, broken pieces of hemicelluloses [14]. In Mimosa tannin, prorobinetidin represents about 70% of the phenolic component. More details about degree of polymerization and average molecular weight of the oligomers have been given elsewhere [14, 15].

### 2.2 Preparation of Foams

The method for preparing rigid tannin-based foams has already been described elsewhere [4, 16, 17]. In short, mimosa bark tannin extracts (ex SilvaChimica, St. Michele Mondovi, Italy), is mixed with furfuryl alcohol as a co-reagent, then water is added with or without formaldehyde as a further crosslinker and with or without diethyl ether as blowing agent. The other additives, as indicated in Table 1, are premixed with the furfuryl alcohol and the mixture is mechanically stirred to a homogeneous viscous liquid. Finally a solution of 65% p-toluensulphonic acid (pTSA) is added as catalyst. The exotherm caused by the self-polymerization of furfuryl alcohol and its reaction with the tannin leads to the boiling of the blowing agent and consequent almost simultaneous foaming and setting of the mixture. In the case in which no blowing agent is added, foam expansion is driven by the CO<sub>2</sub> generated by the reaction of the isocyanate with both the water and the -CH<sub>2</sub>OH groups of the furfuryl alcohol. After foaming, the samples were left to age for a few days and then cut into specimens in order to measure their properties (Table 1) as reported previously [12]. The foams shown in Table 1 correspond to (i) a tannin foam formulation using formaldehyde and a low-boiling blowing agent (STD); (ii) a foam containing neither formaldehyde nor blowing agent (MN65); (iii) the same as (i) but with the addition of a small

**Table 1** Foam formulations (in grams) used for dynamic testing during foaming.

Formulation	STD	MN65	MN8'	PUR
Mimosa Tannin Extract	30	30	30	
pTSA 65%	11	11	11	
Formaldehyde 37%	7.4		7.4	
Furfuryl alcohol	10.5	21	10.5	
Water	6	6	6	0.3
Diethyl ether	3		3	
PEG-35 castor oil			0.6	
PEG400			8	
pMDI		0.4		29
Polyol				15
Polyether-polysiloxane copolymer				0.4
N,N- dimethylcyclohexylamine				0.4
Tris(2-chlorisopropyl)-phosphate				1.7
Cyclo-isopentane blend 70:30				2.5
Density (g/cm <sup>3</sup> )	0.06	0.07	0.055	
Thermal Conductivity (W/(K.m))	0.05	0.044	0.044	
Stress at 20% deformation (MPa)	0.16	No plateau	0.09	

proportion of surfactant (MN8'), namely PEG400 (a low molecular weight polyethylene glycol) and PEG-35 castor oil (an ethoxylated castor oil), and (iv) a commercial PUR foam.

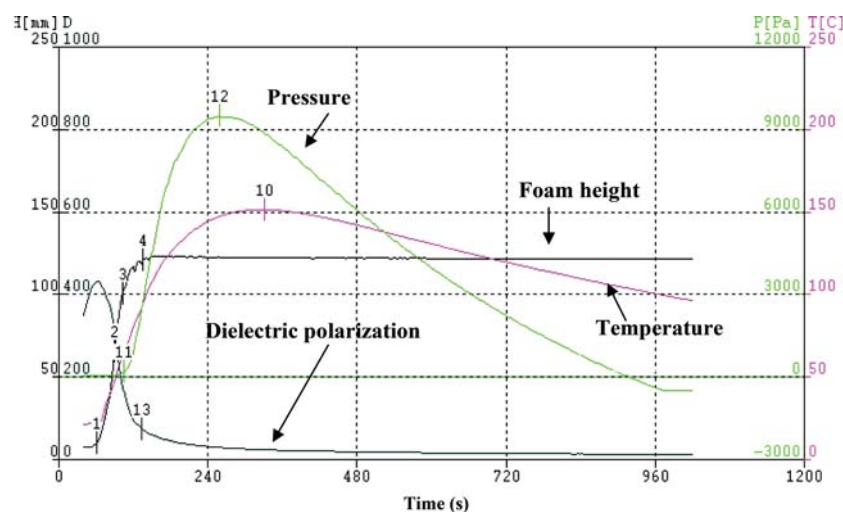
### 2.3 Foaming Process Characterization

The curves describing the expansion, hardening, and temperature and pressure variation as a function of time for the three foam formulations have been determined simultaneously with a FOAMAT apparatus Model 281 (Foamat Messtechnik GmbH, Karlsruhe, Germany). The different measuring sensors were controlled by the MOUSSE programme version 3. For each foaming after mixture preparation, the mixture was quickly poured in a suitable foaming chamber, namely a carton cylinder for each case, which was previously placed upon the manometer of the FOAMAT equipment. The pressure generated by the expansion of the material on foaming was then measured by the force applied to this metal plate sensor. The temperature was measured simultaneously by a thermocouple immersed into the mixture. The setting/curing/hardening rate profile of the foams was measured simultaneously by a dielectric polarisation sensor composed of two comb-shaped electrodes disposed on a printed circuit in such a manner as to form a type of flat condenser. This sensor was integrated into the pressure-measuring device located at the bottom of the foaming chamber, i.e. the carton cylinder. The blowing pressure ensured the contact between the foaming sample and the polarisation sensor, and consequently ensured the direct penetration of the electrical field.

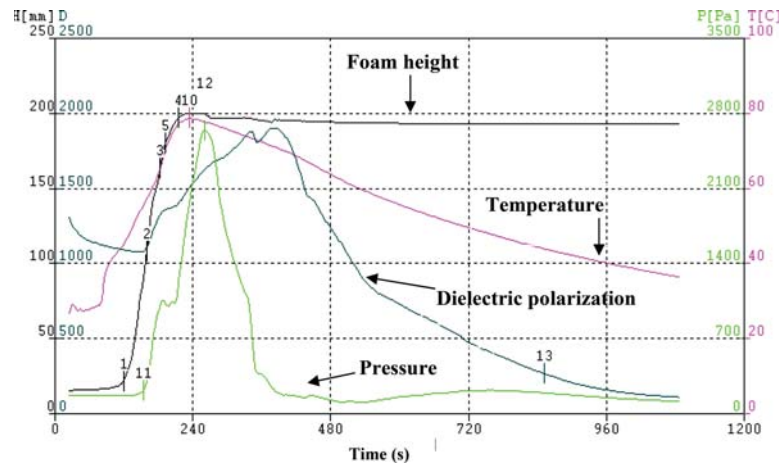
The foam height during its expansion was constantly monitored by an ultrasound sensor placed over the foaming chamber. This device functions according to the "pulse-echo" method. This means that foam height, hence its rising rate, is determined at every instant by the time needed for the acoustic pulse to strike the surface of the expanding foam and to return to the sensor. The ultrasonic sensor is a membrane-type converter used as both acoustic transmitter and receptor.

### 3 RESULTS AND DISCUSSION

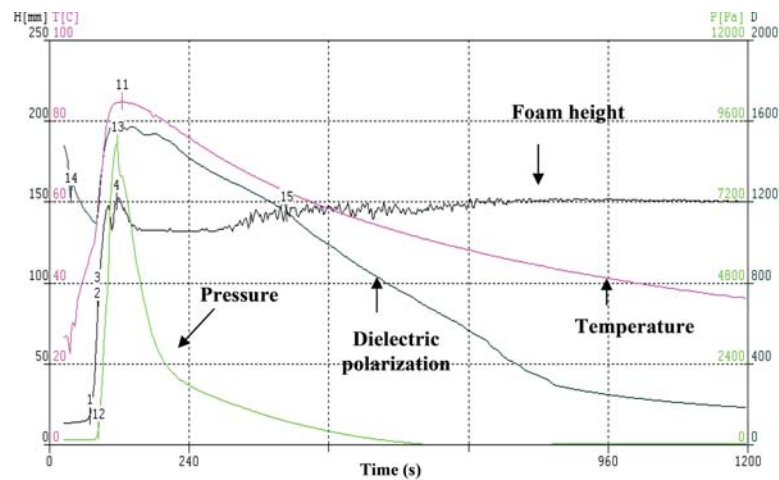
Figures 1–4 show the curves of variation of pressure, temperature, foam height and dielectric polarisation for a polyurethane resin (PUR) and for experimental tannin/furanic foams. In the case of the PUR (Fig. 1) the curves obtained are rather regular. The decrease in dielectric polarisation in this figure shows that for this resin crosslinking is already practically completed at 130°C (Fig. 1). The results obtained show that the variation of temperature implies that while the temperature increase rate is similar for the three tannin/furanic foams MN8', STD and MN65, it is lower for the PUR formulation. The PUR foam maximum temperature (150°C) is markedly higher than that of the MN8' (78°C) and STD (85°C) foams, and is also higher than that of the MN65 foam (102°C). Thus, there is a marked difference in the time at which the maximum temperature is reached (230s for the MN8', 120s for the STD, 200s for the MN65 and 250s for the PUR). The decrease of temperature shows a similar slow trend for the four formulations, with cooling rate appearing



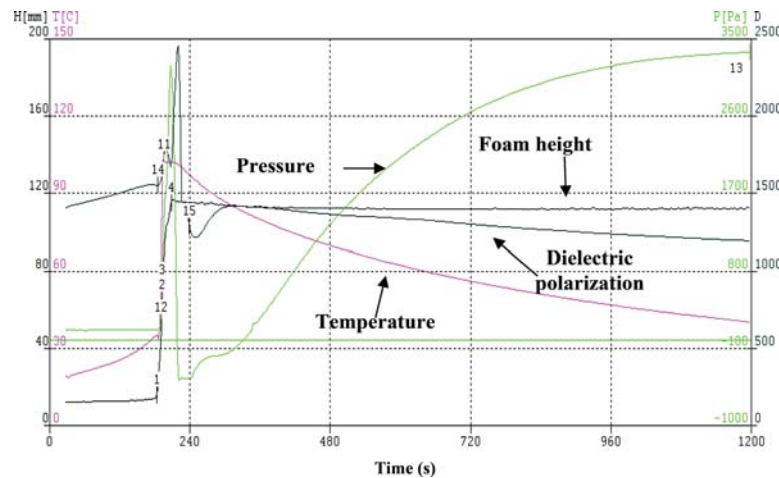
**Figure 1** Curves describing the variation of temperature, dielectric polarisation, foam height and foam pressure for a polyurethane foam (PUR).



**Figure 2** Curves describing the variation of temperature, dielectric polarisation, foam height and foam pressure for a tannin/furanic foam using formaldehyde, a low-boiling blowing agent and a small proportion of surfactant (MN8').



**Figure 3** Curves describing the variation of temperature, dielectric polarisation, foam height and foam pressure for a tannin/furanic foam using formaldehyde and a low-boiling blowing agent (STD).



**Figure 4** Curves describing the variation of temperature, dielectric polarisation, foam height and foam pressure for a tannin/furanic foam containing neither formaldehyde nor blowing agent (MN65).

slightly slower for the PUR foam in relation to the other three. Although the slopes of the cooling part of the curves appear similar, the cooling is also slower for the PUR foam in relation to the other three due to the higher peak of temperature reached by this foam.

The situation is rather different when observing Figures 1–4, since the variation during foaming of the dielectric polarisation values in this respect is a measure of crosslinking. The rate of increase of the dielectric polarisation value is different, being faster for the PUR with the maximum molecular mobility identifiable with the highest value of the curve. The increase in dielectric polarisation of the PUR foam appears to occur earlier than for the other foams, occurring practically simultaneously to the foam expansion. This is not the case for the three tannin/furanic foams, where the peak of dielectric polarisation is shifted to after expansion. The STD and MN65 foams increase of dielectric polarisation is almost as rapid as the PUR foam, but presents a much higher peak. This can be explained by the lower molecular weight of the initial components of the STD and MN65 formulations; hence the higher molecular mobility of these systems is close to the maximum temperature reached. This correlation is even more marked for the MN8'. The MN8' is the one with the slowest rate of increase of dielectric polarisation, hence slower potential crosslinking. Comparing the STD and MN8', the latter attains a dielectric polarisation peak higher than the former due to the addition of the PG400 plasticizer. For the MN65 the peak is higher due to the substitution of the formaldehyde with a much higher proportion of furfuryl alcohol. Furthermore, in the PUR foam, dielectric polarisation decreases very rapidly, much more rapidly than in the other three foams, thus complete reticulation is reached much more rapidly than for the tannin furanic foams. This may be the cause of the much higher temperature reached by the PUR foam, hence the faster curing and consequent faster molecular immobilisation in a hardened network. For the three tannin foams cooling is similar with, in order of cooling rate, MN65 (very slow), MN8' and STD. Thus, for all the foams, the higher the temperature reached, the faster the decrease in dielectric polarisation, hence the faster the crosslinking and hardening. Conversely, the lower the temperature reached, the slower the decrease in dielectric polarisation (MN8'). There appears then to be a certain correlation between the curves of the exotherm's temperature and the curves of dielectric polarisation; thus indicating that the temperature reached, and possibly also the initial molecular weight of the reactants, is one of the main driving parameters in the gelling and hardening of the resin constituting the foam.

Also of interest is the trend in pressure of the four foams in Figures 1–4. The pressure rapidly increases and then rapidly decreases for the STD and MN8' foams. It shows a slower rate of increase but higher maximum pressure reached for the PUR foam followed by a much slower decrease. This behaviour of the PUR foam is again in line with the type of exothermal reaction of the PUR that is different from that driving the tannin/furanic STD and MN8' foams, and particularly relates to the much higher temperature reached by the PUR foam. It means that the PUR has a higher percentage of closed cells in relation to the two tannin/furanic foams, and that the blowing agent remains trapped in it giving a much higher pressure and a much longer decrease in pressure over time during cooling. Moreover, it is much more likely that for the PUR foam the blowing agent remains trapped within the foam cells, as foam expansion and hardening occurs almost simultaneously, while for the STD and MN8' the two occur sequentially. Even more unusual and interesting is the behaviour of the MN65 tannin/furanic foam. Here the pressure increase rate, after an initial period of apparent inactivity, is almost explosive, and reaches values almost as high as that of the PUR foam, but its rate of pressure decrease is equally rapid as its rate of increase. This is then followed by a continuous, regular and rather slow increase in pressure that stabilises at a very high level, thus a behavior that is totally different from the other types (Fig. 4). And effectively the MN65 formulation is very different from the others. The very high proportion of furfuryl alcohol reacting exothermally strongly accounts for the very fast first peak of pressure contemporary to the equally fast, almost explosive increase in temperature. The higher elasticity of this foam is observable by the absence of the stress/strain compression curves plateau (Table 1) in which no formaldehyde has been added as a further hardener of the system; the lack of a solvent other than small amounts of water may account for the slow and regular second increase of pressure that occurs. The further generation of CO<sub>2</sub> appears unlikely. It also indicates that the number of close cells in this foam is higher than for the other foams, and its difference in behaviour is already known for other properties [12].

## 4 CONCLUSIONS

Dynamic monitoring of the foaming of very different tannin/furanic formulations and of an industrial polyurethane foam formulation indicates that some characteristic differences, but also many similarities, exist between the two different classes of foam. Thus, for all the foams, the higher the temperature reached, the faster the decrease in dielectric polarisation, hence

the faster the crosslinking and hardening. Conversely, the lower the temperature reached, the slower the decrease in dielectric polarisation. This indicates that the temperature reached, and possibly also the initial molecular weight of the reactants, is one of the main driving parameters in the gelling and hardening of the resin constituting the foam. The type of exothermal reaction of the PUR appears to be different from that of the other foams, and its pressure variation infers that a higher percentage of closed cells are formed in relation to some of the tannin/furanic foams, as the blowing agent remains trapped in the PUR foam. This would also explain the well-known worsening of the thermal insulation capacity of the PUR foam as a function of ageing due to the slow loss of this trapped solvent. It also explains the stability with ageing of the equally excellent thermal insulation capacity of tannin/furanic foams. One of the tannin/furanic foams characteristics also infer the formation of a majority of closed cells.

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