Long-term thermal conductivity of cyclopentane-water blown rigid polyurethane foams reinforced with different types of fillers

Mercedes Santiago-Calvo[1,*], Josías Tirado-Mediavilla[1], J. L. Ruiz-Herrero[1], Fernando Villafañe[2], Miguel Ángel Rodríguez-Pérez[1]

1 Cellular Materials Laboratory (CellMat), Condensed Matter Physics Department, Faculty of Science, University of Valladolid, Campus Miguel Delibes 7, 47011 Valladolid, Spain

2 GIR MIOMeT-IU Cinquima-Química Inorgánica, Faculty of Science, University of Valladolid, Campus Miguel Delibes 7, 47011 Valladolid, Spain

Abstract

The understanding of the long-term thermal conductivity of rigid polyurethane (RPU) foams presents a great interest in the building field considering the conservation of energy efficiency. In this study, the effect of different types of particles (talc (T), diatomaceous earth (DE), and non-porous silica (NPS)) on the thermal conductivity of RPU foams blown with cyclopentane (CP) and water as blowing agents has been investigated along three years of aging. The characterization of the cellular structure shows how the addition of particles causes a cell size reduction of the foams, and consequently an enhancement of the thermal properties just after production. However, this initial reduction was not maintained, because each foam shows a different thermal conductivity evolution with time. We have found for the first time, a relationship between the slope of the thermal conductivity *versus* time at the first measurements and the internal temperature reached during the foaming process. The evolution of the RPU foams in which higher internal temperatures were reached is more pronounced than in those RPU foams where lower foaming temperatures were observed. This effect is related to the kinetics of the diffusion of the gas occluded inside the cells and imposes a new criterion for the selection of particles to reduce the thermal conductivity of RPU foams, these additives should ideally decrease the temperature reached during the foaming process.

[*] Corresponding author.

E-mail address: *mercesc@fmc.uva.es* (Mercedes Santiago-Calvo).

Moreover, the effect of aging on the thermal conductivity is explained by using theoretical models.

Keywords

Polyurethane; foams; thermal conductivity; foaming temperature; composites

INTRODUCTION

Rigid polyurethane (RPU) foams with a closed-cell structure are mainly used for thermal insulation and for structural applications especially in buildings, due to their low thermal conductivity, low density, high compression strength, and low moisture permeability [1, 2]. RPU foams are usually prepared by the polymerization reaction of a polyol with an isocyanate, which produces urethane linkages. At the same time, foam expansion occurs due to the presence of a chemical blowing agent, a physical blowing agent, or a mixture of both. Until recently, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were commonly used as physical blowing agents, but they have been recently prohibited because they play a decisive role on the destruction of the ozone layer. For this reason, more environmentally friendly blowing agents such as cyclopentane (CP) or water are currently used in many industrial applications. Water acts as a chemical blowing agent reacting with isocyanate to form CO_2 and urea linkages, giving rise to water-blown RPU foams. On the other hand, CP evaporates during as a result of the heat produced during the polymerization reaction.

Thermal conductivity is the most important property for RPU foams used as insulating materials. The thermal conductivity is determined by the following heat transfer mechanisms [3-6]: conduction along the solid phase (λ^s), conduction through the gas phase (λ^g), thermal radiation (λ^r), and convection within the cells (λ^c). The latter is negligible for the foams with small cell sizes (less than 2 mm) [7, 8]. The thermal conductivity of RPU foams depends mainly on the types and amount of blowing agents contained in the closed cells, due to the high contribution of λg to the total thermal conductivity (higher than 60%) [8, 9]. Thus, the use of

blowing agents with low thermal conductivities is one of the key strategies to improve the thermal properties of RPU foams. Moreover, the addition of fillers to the RPU matrix may also decrease the cell size and/or block the infrared radiation, reducing the radiation contribution to the thermal conductivity [5, 10, 11].

Another important aspect to consider is the aging of the RPU foams, since the thermal conductivity values always increase with time. This aging phenomenon occurs because the blowing agents slowly diffuse out of the cells, being replaced by atmospheric air which diffuses into them. Each blowing agent presents a different diffusion rate, for example, the diffusion rate of CO_2 out the foam is high, and in fact it is replaced by air after a few weeks [11]. CP shows a very low diffusion rate out the foam, and several years are needed to be completely replaced it by atmospheric air [12]. Given its significance, different authors have thoroughly studied the aging of RPU foams. Ostrogorsky et al. [9] developed an analytical model to predict the effective diffusion coefficient of RPU foams. This model allows to determine the rate of gas diffusion and of foam aging. The theoretical predictions of CO_2, O_2 and N_2 differed *ca.* 29% from the measured values. Wilkes et al. [13] studied the effect of storage temperature on the thermal conductivity of RPU foams containing HCFC-141b, hydrofluorocarbon (HFC)-134a, HFC-245fa, or CP. This study described the behaviour of these foams used for refrigerators and freezers after one year of aging. Two types of samples were used: full-thickness simulated refrigerator panels in which the foam is enclosed between solid plastic sheets (acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS)), and slices of core foam cut from similar panels. The authors concluded that the aging rate increases with the storage temperature, and it is higher for unenclosed full-thickness core-foams compared to those enclosed between plastic sheets foams. In following works [12, 14], this group continued the study of the previous samples, measuring their thermal conductivities during four years, and comparing them with theoretical predictions of aging models. Modesti et al. [15] determined experimentally the effective diffusion coefficient of HFC-245fa, CO_2 and air in RPU foams, by means of flame ionization detector gas chromatography (FID-GC) and fourier-transform infrared spectroscopy (FT-IR). They found that the slope of the aging curves depended only on the effective diffusion coefficients, and that the comparison of the experimental and predicted thermal aging curves confirmed the accuracy and reliability of the method proposed for the determination of the

effective diffusion coefficients. In a later study, the same group [16] studied the aging of foams with different blowing agents, such as HFCs, hydrocarbons (HCs), dimethoxymethane, CO_2, or air, following the method previously described for the determination of the effective diffusion coefficients. Marrucho et al. [17] measured the thermal conductivity of mixtures of N_2 and CP at different temperatures and pressures, what allowed to evaluate the thermal conductivity evolution of RPU foams. The obtained results were correlated with the modified Wassiljewa mixing rule and predicted using the extended corresponding states theory (ECST). Murphy et al. [18] studied the effects of moisture infusion and blowing agent diffusion by means of previous literature studies, own experiments, and long-term aging studies. Their main conclusions were that water vapour worsens the thermal conductivity of foams, that there is no correlation between molecular weight of blowing agents and the thermal conductivity of the foam, and finally that the blowing agent (CFCs, HCFCs and ecomate®) diffusion out of the foam is much slower than atmospheric gas infusion. Kuranska et al. [19] investigated the effect of different type of blowing agents (methylal, isopentane, CP, mixture of isopentane and CP, CO_2) on the foaming process, cellular structure, mechanical properties and changes of thermal conductivity during one year aging. RPU systems with isopentane and mixture of isopentane and CP showed the lowest thermal conductivity after 360 days.

In previous reports [9, 12-19], thermal aging has been studied for RPU foams containing different blowing agents, but so far thermal aging of RPU foams reinforced with fillers have not been studied. The use of fillers is of great interest in the field of RPU foams because their addition can improve the thermal insulation of these materials [10, 11, 20-22]. In this work we report the effect of different types of particles (talc, diatomaceous earth and non-porous silica) on the long-term thermal conductivity of RPU foams containing CP and water as blowing agents. In addition, another aim of this paper is to establish, for the first time, a correlation between the effect of the fillers during foaming and the aging performance.

MATERIAL AND METHODS

Materials

A formulation of RPU foam with water and CP as blowing agents was used in this investigation. The polyol component, Elastopor H 1501/1 (OH index 651 mg KOH/g, density 1.07 g cm^{-3}, viscosity 650 mPa•s) from "BASF Poliuretanos Iberia S.A.", is a mixture of components containing polyether polyol, catalysts, stabilizers and water. The isocyanate component, IsoPMDI 92140 (31.5% NCO, density 1.23 g cm^{-3}, viscosity 170-250 mPa•s) from "BASF Poliuretanos Iberia S.A.", is a polymeric diphenylmethane diisocyanate (pMDI). The free foaming density of this formulation is 30 kg/m^3. Cyclopentane (99.9% purity) from Sigma Aldrich was used as blowing agent. The proportions of the three components were set at 100/160/13 by weight for the polyol, isocyanate and cyclopentane in order to have a free foaming density of 30 kg/m^3.

The particles chosen to carry out this study are: talc (T), diatomaceous earth (DE), and non-porous silica (NPS). T used is from Imerys, which has a mean particle size of 2 microns. DE used is from Cekesa, with a particle size from 0.58 to 28 microns. NPS used is manufactured by Glantreo, with a particle size of 0.15 microns. The surface of the particles has been treated with C18 groups. Both T and DE were selected mainly due to their low cost, and also because as micrometric particles they are easier to disperse. In the case of DE, these particles have a porous silica structure at the nanoscale [23] which increases their superficial area and therefore it could improve their efficiency as nucleating agents. On the other hand, NPS were selected because being nanometric particles their nucleation potential is very high with low contents. Due to the low contents used and their nanometric size it is expected a smaller impact on the properties of cell walls and therefore on the diffusion of the gases.

Preparation of rigid polyurethane nanocomposite foams

Different RPU foams were studied: the pure material (without particles, obtained as reference material), and those containing either 1.5 wt% T, 1 wt% DE, 3 wt% DE, 5 wt% DE, 0.05 wt% NPS, 0.1 wt% NPS or 0.2 wt% NPS with respect to the final mass of the RPU foams.

An overhead stirrer (EUROSTAR Power control-visc P1, IKA) with a 50 mm diameter Lenart disc stirrer was used to premix the polyol with the particles at 250 rpm for 5 minutes. Then, CP was mixed with the polyol blend at 250 rpm for 3 minutes. Finally, polyol blend with CP and the isocyanate were mixed in a plastic cup at 1200 rpm for 10 seconds. The mixture was then

poured into an open wooden mould of dimensions 35 x 35 x 5 cm^3. After 2 days the foam was demoulded and cut into samples with appropriate dimensions in order to measure the thermal conductivity and to characterize the foams.

The foaming temperature reached during foaming process by each system was measured in a plastic cup. Three thermocouples type K were introduced at different positions of a plastic cup of 11.5 cm of diameter and 14 cm of height in order to obtain the temperature measurements. The thermocouples were placed vertically in the centre of plastic cup at the following heights: 2.0 cm, 6.5 cm and 12.5 cm from the bottom. The data collected by the thermocouples during foaming process were registered in a computer. Then, for each experiment the curves given by each thermocouple were averaged to obtain the curve average foaming temperature vs time. From these curves, the maximum values were also analysed. Three experiments were carried out for each sample The standard deviation of the average foaming temperature vs time curves (for each time) was always lower than ± 1.

Foams characterization

Foam density was measured as described by ASTM D1622/D1622M-14 [24]. Density was determined in three different samples for each material, with a diameter of 30 mm and a height of 25 mm.

After measuring the densities in the samples, open cell content (OC%) was measured by using a gas pycnometer Accupyc II 1340 from Micromeritics, according to ASTM D6226-10 [25].

The cellular morphology of the foams was observed by Scanning Electron Microscopy (SEM) with a JEOL JSM-820 microscope. The growth plane (z plane) of cured foams was examined by SEM after vacuum coating with a gold monolayer. An image analysis technique [26] of SEM micrographs was used to determine the main characteristics of the cellular structure of the foams: mean cell size (Φ_{3D}), anisotropy ratio (AR), and cell size distribution by using histograms and gaussian fitting. More than 150 cells of different areas of each material were used for this analysis. The methodology used to measure the cellular structure parameters are explained in the work by Pinto et al. [26].

The thermal conductivity measurements of the foams were performed using a Rapid K heat flowmeter from Holometrix. Measurements were performed under steady heat flow conditions through the test samples, in accordance with the UNE12667 method [27], by using samples of 30 x 30 x 2.5 cm^3. The measurements were performed at 20°C, where the temperature gradient (ΔT) goes from 5°C in the bottom surface plate to 35°C in the top surface plate. Several measurements (at least four during the first two months, see Supplementary material) were performed from the fourth day of foams production, in order to know the thermal conductivity evolution with time. These experiments were conducted along three years. The samples were stored in opened plastic bag at room temperature and atmospheric pressure. The measurements of thermal conductivity versus time were fitted to a sum of exponential functions as observed in Figures S1-S8 (Supplementary material) in order to obtain the thermal conductivity values at any time. Therefore, the thermal conductivity at time 0 of foams production (collected in Table S1 in the Supplementary material) was obtained by extrapolation using the curve fitting functions.

RESULTS AND DISCUSSION

Density and cellular structure characterization

Different physical properties of the foams were determined, and the values obtained are collected in Table 1. The data indicate that the sample containing 1.5 wt% T has the highest density, which is ca. 4 kg/m^3 higher than that of the reference material. However, the rest of the samples with particles present similar densities respect to that of the reference material.

In general, the open cell content (Table 1) for the foams with particles slightly increases, being the foam containing 0.2 wt% NPS that showing the highest value (*ca.* 13%).

The main characteristics of the cellular structure have been obtained with image analysis from SEM micrographs in the growth plane (Figure 1), and are summarized in Table 1 and Figure 2. Most notably, the addition of different types of particles into the polyol component promotes a mean cell size reduction of up to 50% for T particles, 46% for DE particles and 33% for NPS particles, respect to the value of the pure foam. Thus, the smallest mean cell size of all the

samples studied is that containing 1.5 wt% T. In regard to DE systems, cell sizes are even more reduced as the amount of DE particles increases. In contrast, the cell size of foams containing NPS is minimum for the material containing 0.05 wt% NPS. The reduction of cell size with particles addition is not related to the anisotropy ratio, which does not increase for most of the samples in comparison to the reference foam. Nevertheless, the sample containing 1.5 wt% T and that containing 0.05 wt% NPS show a slight increase in their anisotropy ratio, whereas the increase of the sample with 3 wt% DE is even higher.

The analysis of the SEM micrographs (Figure 2) provides also extra information about the cell size distribution. The study of the histograms and gaussian fitting corroborates the qualitative observations in SEM micrographs, and supports the cell size reductions, discussed above. In general, the foams with particles show a symmetric distribution and a good homogeneity.

Foaming temperature measurements

The foaming temperature of RPU foams can be followed because the reactions involved in PU formation are exothermic. Figure 3 shows the average foaming temperature versus time for some representative systems. It is observed that with the addition of particles into the PU foam the temperatures reached during the foaming are higher than that of reference foam. Moreover, maximum of the average foaming temperature curves reached for each system are collected in Table 2.

Study of the thermal conductivity aging

The foams under study were produced using water as a chemical blowing agent and CP as physical blowing agent. Their thermal conductivity was measured along *ca.* three years in order to study their thermal conductivity aging (Figure 4 A, C and E). The low thermal conductivity of all these foams (ca. 21 mW/m•K at the initial time of the foams production) is due to their low density (ca. 30 kg/m^3), and also to the use of CP (which has a low thermal conductivity and a low diffusion coefficient) as physical blowing agent. This initial value of thermal conductivity increases with time and reaches *ca.* 30 mW/m•K after three years of the foams production. The main reason for the increase of the thermal conductivity is the diffusion of the gases initially occluded inside the cells. Their thermal conductivity (14.5 mW/m•K for

CO$_2$ and 12 mW/m•K for CP at 20 °C) is very low, but these gases slowly diffuse out of the cells, being substituted by atmospheric air, whose thermal conductivity (25.6 mW/m•K at 20 °C) is higher. The CP is retained in the cells for longer periods of time compared to those of CO$_2$, this last gas leaves the foam in a time period smaller than 30 days [11].

Therefore, the analysis of the thermal conductivity evolution for the first 30 days is discussed first. The thermal conductivity values at initial times are clearly reduced for all foams with fillers in comparison with the reference material, as shown in Figures 4 (B, D and F). This lower value of the thermal conductivity is mainly due to the smaller cell sizes of the foams containing the filler. This reduces the radiative contribution to the thermal conductivity, as discussed below. Nevertheless, Figure 5 indicates that there is not a clear relationship between the cell sizes, the open cell contents or the density and thermal conductivities measured at initial times (less than 5 days after foam production). Therefore, other factors are playing a major role on to the thermal conductivity values. One possible explanation would be that different content of gasses inside the cells are present in each foam after the same time, i.e. the gasses diffusion rates just after foam production are different for the different materials under study. Moreover, the initial improvement of the thermal properties is not maintained in many systems. For some of systems with the exception of 5%DE, 0.1%NPS and 0.05%NPS the conductivity of the filled material increases very quickly with time and becomes higher than the thermal conductivity of the reference material. Different reasons might explain why the concentration of gasses varies at diverse rates for each system: the properties of the foam (density, cell size, open cell content, cell window thickness, blowing agents used, initial cell gas composition, etc), the solubilities and diffusion coefficients of the gasses, and also the differences in temperature and pressure between the gasses contained in the cells and the external atmosphere, among others.

In order to analyse this change in thermal conductivity with time in the first 30 days after production, the slope of the thermal conductivity *vs.* time curve has been calculated between time 0 and 30 days. This analysis allows evaluating the variation of the rate of the concentration of gasses. We have found a clear relationship between the thermal conductivity slope vs time and the foaming temperature reached inside the foams during their production (Table 2), as shown in Figure 6. Those samples reaching lower foaming temperatures (such as

the systems with 5%DE, 0.05%NPS, or 0.1%NPS) display lower thermal conductivity slopes. By contrast, those samples reaching higher foaming temperatures (such as the systems with 1.5%T, 1%DE, 3%DE, or 0.2%NPS) gave higher thermal conductivity slopes. This means that the latter systems provide a very quick diffusion of the gasses out the cells. This effect can be explained taking into account the different pressure gradient of the gas inside the cells vs. the external atmospheric pressure. The developing foam is expanding against the ambient pressure until the polymerization reaction finishes, and after that the foam cools down to room temperature. Therefore, the pressure inside the cells growths depending on the amount of gas produced (which is constant in the systems herein studied) and on the temperature reached during the foaming process. When the foam finally cools down (at a cell volume approximately constant), the pressure inside the cells drops below ambient pressure, and thus the pressure in the cells would be different depending on the temperature reached during foaming. A higher temperature during foaming would cause a lower value of the pressure inside the cells and as a consequence a higher pressure gradient with the atmosphere, causing higher gas diffusion rates.

Clearly, the foaming temperature in all the systems with fillers increases compared to that of the pure foam (105.9°C). A first group of foams (5%DE, 0.05%NPS and 0.1%NPS) are obtained with lower foaming temperatures displays a thermal conductivity evolution at initial time similar to that of the pure foam, as shown in Figure 4 (D and F). In these systems there is lower pressure gradient between the cells and the atmosphere. On the other hand, the group of foams (1.5%T, 1%DE, 3%DE and 0.2%NPS) which reaches higher foaming temperatures (giving higher differences of pressure difference between the cells and the atmosphere), show a rapid growth of their thermal conductivity compared to that of the reference material. In these foams the low thermal conductivities achieved in the first days is quickly lost, due to the high diffusion of gases in them, as shown in Figure 4 (B, D and F).

Figure 4 (A, C and E) show the thermal conductivity evolution for pure foam and for foams with fillers along 900 days. Samples with lower foaming temperatures (5%DE, 0.05%NPS and 0.1%NPS) maintain during longer times lower thermal conductivity values, because the gas diffusion is slow. Even the thermal conductivity of the system with 5%DE, which has the lowest thermal conductivity slope, is lower than that of the pure material during all the measured

time (Figure 4 D). On the other hand, for the group of systems (1.5%T, 1%DE, 3%DE and 0.2%NPS) with higher foaming temperatures, there are some that recover the enhancement of the thermal conductivity over time. For example, the thermal conductivity value of the foam containing 1.5 wt% T is again lower than that of value of the pure material after *ca.* 400 days (Figure 4. A), whereas the thermal conductivity of the foam with 3 wt% DE is improved after *ca.* 300 days (Figure 4. C). In these cases, the recovery (1.5%T and 3%DE) or maintenance (5%DE) of the thermal conductivity reduction shown in the first measurements is remarkable (Figure 4). Moreover, it should be expected that the improvement of the thermal conductivity observed in the first measurements would be recovered for all the foams with fillers once they reach a stationary state where the gas concentration is the same for all of them. This is because all the foams containing fillers have lower cell sizes than the reference material.

Therefore, we have found an interesting behaviour in these systems. For those fillers increasing significantly the temperature reached during foaming there are two cross-over points of its thermal conductivity curve vs time in comparison with that of the reference foam. The first cross-over point at times lower than 30 days is due to a higher diffusion rate of the gasses inside the foam due to a low pressure inside the cells when the material cools down after foaming. The second one, occurring between 300 and 400 days after production, is due to the lower cell size of the foams containing fillers. Therefore, when the gas composition is similar to that of the reference foam the thermal conductivity is once again below that of the reference system. These considerations will be taken into account to model the thermal conductivity of the foams.

Thermal conductivity modelling

In this section, a thermal conductivity modelling is proposed in order to understand the thermal conductivity aging of the samples under study. The thermal conductivity of a RPU foam (λ^t, containing solid and gas phases) is well represented by the sum of four mechanisms: conduction along the cell walls and the struts of the solid polymer (λ^s), conduction through the gas phase (λ^g), thermal radiation (λ^r), and convection within the cells (λ^c). The addition of these contributions gives the total heat flow (λ^t) (equations 1)[7, 28]:

$$\lambda^t = \lambda^s + \lambda^g + \lambda^r + \lambda^c \tag{1}$$

The very small cell size of the foams under study (600-300 µm) makes the convective mechanism (λ^c) to be considered negligible [7, 8]. The conductive terms of the gas and of the solid phases can be estimated by equations 2 and 3 [29]:

$$\lambda^g = \lambda_g V_g \tag{2}$$

$$\lambda^s = \lambda_s \frac{V_s}{3}\left(\left(f_s \sqrt{A}\right) + 2(1 - f_s)(A)^{1/4}\right) \tag{3}$$

where V_g is the volume fraction of the gas phase (1-ρ_r), V_s is the volume fraction of the solid phase (ρ_r), A is the anisotropy ratio, λ_g is the thermal conductivity of gas mixture, and λ_s is the thermal conductivity of solid PU (0.26 W/mK) [29]. ρ_r is the relative density (ρ_f/ρ_s), where ρ_f is the foam density and ρ_s is the solid PU density (1160 Kg/m^3).

The radiative mechanism refers to the transport of energy by electromagnetic waves, and the attenuation of radiation takes place in the forms of reflection, absorption, and scattering. The radiative conductivity can be calculated by the Rosseland equation [7]:

$$\lambda^r = \frac{16n^2\sigma T^3}{3K}$$

$$\tag{4}$$

Where n is the effective refraction index, σ is the Stefan–Boltzmann constant, T is the mean temperature, and K is the extinction coefficient. In this case, n is ca. 1 because the volume of gas (porosity) of the PUR foams herein studied is around 97%. The radiative conductivity can be estimated by the Rosseland equation (equation 4) using the Glicksman extinction coefficients (K_G) that is described in the following section (equations 5 and 6).

Extinction coefficient modelling: Glicksman extinction coefficient (K_G)

The Glicksman extinction coefficient (K_G) is herein calculated for all systems studied in order to evaluate the radiative contribution of the thermal conductivity. The equation to predict the extinction coefficient of closed cell PU foams was proposed by Glicksman and coworkers [7]. They considered pentagonal dodecahedral cells as a set of randomly oriented blackbody struts

that scatter radiation, and cell walls that absorb radiation. The Glicksman extinction coefficient (K_G) includes the contribution of struts (K_{edges}), and that of cell walls ($K_H K_W$)[7]:

$$K_G = K_{edges} + K_H K_W \qquad (5)$$

$$K_G = 4.10 \frac{\sqrt{f_S \dfrac{\rho_f}{\rho_s}}}{\phi} + (1 - f_S) \frac{\rho_f}{\rho_s} K_W \qquad (6)$$

The extinction contribution depends on the cell size (ϕ), foam density (ρ_f), solid polyurethane density (ρ_s), mass fraction in the struts (f_S), and a constant related to the cell geometry (4.10). A value of 0.7 for the mean mass fraction in the struts is considered for this type of foams [11 30, 31]. The cell wall contribution is valid for foams containing thin cell walls ($\delta <$ 30 µm, around 2 µm in our foams), and includes the hypothetical extinction coefficient for a uniform material which occupies the entire volume of the foam, whose attenuation is the same to those of thin cell walls. The value of the extinction coefficient of the solid polymer (K_W =600 cm^{-1}) was obtained from the literature [7].

The values of the Glicksman extinction coefficients (K_G) calculated using equation 6 are presented in Figure 7. These data show an increase of the extinction coefficient for foams with fillers, being higher for those with lower cell sizes (systems with T and DE), what implies a reduction of the radiation contribution to the thermal conductivity (equation 4). Therefore, the improvement of the thermal properties observed for the different materials with particles at initial times could be due to the decrease of the radiation contribution, assuming a constant gas concentration just after production.

Study of thermal conductivity of gas mixture evolution (λ_g)

The conduction through the gas phase (λ_g) is the most significant contribution to the final value of the thermal conductivity. Thus, the variations of the thermal conductivity of the gas mixture (λ_g) modify the total thermal conductivity, as can be observed in Figure 4. As explained previously, the gas inside the cells changes from CO_2 (14.5 mW/m•K) and CP (12 mW/m•K) to atmospheric air (25.3 mW/m•K), due to the diffusion through the PU matrix. Assuming that the conduction through the solid (λ_s) and the radiation contribution (λ_r) are time independent,

the conduction through the gas contribution (λg) can be calculated using the thermal conductivity model (equation 1) by subtracting the solid phase and the radiation contributions from the experimental values of the thermal conductivity. The contribution of the thermal conductivity of the gas mixture (λ_g) with time can be also calculated by using the thermal conductivity model (equation 2). Figure 8 shows the evolution of the thermal conductivity of gas mixture with time for the all the systems studied. The initial value calculated for the gas conductivity of each foam is between 13 and 16 mW/m•K, which implies that a mixture of CO_2 and CP is present in the cells (Figure 8. A). However, these initial values increase in different ways depending on how gas diffusion occurs for each material. Clearly, the slope of the gas mixture thermal conductivity shown in Figure 8 follows a similar trend than those of the slopes of the thermal conductivities shown in Figure 4. Thus, those foams that presented a fast thermal conductivity evolution display also a fast thermal conductivity evolution of the gas mixture (such as the systems with 1.5%T, 1%DE, 3%DE or 0.2%NPS). Nevertheless, the rest of the foams present a slightly increase of both the thermal conductivity of gas mixture and of the total thermal conductivity.

On the other hand, the value of the thermal conductivity of the gas mixture calculated after 900 days is between 20 and 25 mW/m•K, what indicates that the gas diffusion has not finished yet (Figure 8. A). The foam containing 0.2 wt% NPS presents the highest open cell content, and has the highest thermal conductivity of the gas mixture (around 25 mW/m•K), which means that the exchange of gases (almost all the gas inside the cells is air, whose conductivity at 20°C is 25.6 mW/m•K [32]) has practically finished.

Prediction of the thermal conductivity at stationary state

The thermal conductivity has been measured for 900 days, but the foams have not yet reached a stationary state at this time, as discussed in the previous section. In this section, we present a prediction of the thermal conductivity evolution supposing that the stationary state has been reached, that is, considering that all the gas inside the cells is atmospheric air. This would allow to know how the different particles added to the PU matrix affect the total thermal conductivity. Figure 9 collects the thermal conductivity values calculated using the thermal conductivity model (equation 1). Clearly, the thermal properties of the foam would be

enhanced by the addition of particles. This is mainly due to the decrease of the cell size, which increases the extinction coefficient (Figure 7), and therefore reduces the radiative contribution to the thermal conductivity. The foam containing 1.5 wt% T, which has the smallest cell size (307 µm) compared with that of reference material (608 µm), would present the highest radiative contribution reduction, and therefore the lowest thermal conductivity (around 5% lower that of the reference foam). Among the systems containing DE, the materials with 3% and with 5%DE have smaller cell sizes (331 and 340 µm respectively) than that with 1%DE (409 µm). However, a high thermal conductivity reduction (around 5%) is predicted for the foam with 5%DE in comparison to that with 3%DE because of the higher anisotropy of the later (Table 1). The foams containing NPS would have a small improvement of the thermal conductivity (around 2.7 % of reduction) because their cell sizes do not decrease significantly in comparison to that of the rest of the foams with fillers (Table 1). Therefore, these samples present lower extinction coefficient values (Figure 7).

Regarding the densities of the samples, these are verysimilar to reference foam and thus this parameter does not have a signifcant influence on the thermal conductivity. Only the foam containing 1.5%T with a higher density (4 kg/m^3 more than the reference foam) could present an increase in the thermal conductivity of solid phase. However, this foam has the lowest thermal conductivity of Figure 9, which suggest that the reduction of the radiative contribution has a more important influence on the predicted thermal conductivity.

CONCLUSIONS

The effect of different types of particles (Talc (T), diatomaceous earth (DE) and non-porous silica (NPS)) on the thermal conductivity of the rigid polyurethane (RPU) foams with cyclopentane (CP) and water as blowing agents have been here investigated along three years of aging. The initial measurements show an improvement of the thermal conductivities due to the presence of particles into the RPU matrix, because they decrease the cell size, and thus also decrease the radiation contribution. However, the thermal conductivities evolve differently in each system, due to the variations of the gas composition inside cells with time, what in many cases leads to the loss of this first improvement of the thermal conductivity measured at initial times. We have found for the first time, a relationship between the thermal

conductivity slope at initial times and the foaming temperatures reached during the foams formation. Thus, foams reaching higher foaming temperatures (systems with 1.5% T, 1%DE, 3%DE or 0.2%NPS) generate a high pressure difference between the inside and the outside of the foam cells once the material is cooled down, and consequently a very quick diffusion of the gasses out the cells. As expected, slow diffusion of gases is observed for those foams reaching lower temperatures during their formation (systems with 5% DE, 0.05%NPS or 0.1%NPS) and as a consequence a slower rate of thermal conductivity increase vs time. Modelling the thermal conductivity of the foams allows calculating the evolution of the thermal conductivity of the gas mixture (λ_g) with time, which follows a similar trend to those of the slopes of the thermal conductivities experimentally measured. Moreover, the thermal conductivity model allows predicting the thermal conductivity values when the foams reach a stationary state (once all the gas inside the foam is air). The foams with a higher decrease of the cell size would give rise to higher extinction coefficients, and therefore to higher thermal conductivity reductions. The best systems from this point of view are T and DE.

The findings of this paper are important in the development of filled RPU foams with improved thermal conductivities. The filler has to be useful to reduce the cell size but at the same time it is needed that is does not affect the temperature of the system or the increase of temperature associated to the addition of the filler has to be compensated by modifications of the formulation.

REFERENCES

1. Oertel, G., *Polyurethane Handbook* 2nd ed.; Hanser Publishers: Munich, 1993.
2. Hopmann, C.; Wagner, R.; Fischer, K.; Böttcher, A. *Cellular Polymers* **2017,** 36, (3).
3. Choi, S. W.; Jung, J. M.; Yoo, H. M.; Kim, S. H.; Lee, W. I. *Journal of Thermal Analysis and Calorimetry* **2018,** 132, (2), 1253-1262.

4.   Zhang, H.; Fang, W.-Z.; Li, Y.-M.; Tao, W.-Q. *Applied Thermal Engineering* **2017,** 115, 528-538.

5.   Santiago-Calvo, M.; Tirado-Mediavilla, J.; Rauhe, J. C.; Jensen, L. R.; Ruiz-Herrero, J. L.; Villafañe, F.; Rodríguez-Pérez, M. Á. *European Polymer Journal* **2018,** 108, 98-106.

6.   Gama, N. V.; Ferreira, A.; Barros-Timmons, A. *Materials* **2018,** 11, (10).

7.   Glicksman, L., *Low Density Cellular Plastics: Physical Basis of Behaviour*. Springer Netherlands: London, 1994.

8.   Hasanzadeh, R.; Azdast, T.; Doniavi, A.; Lee, R. E. *Thermal Science and Engineering Progress* **2019,** 9, 21-29.

9.   A.G.Ostrogorsky; L.R.Glicksman; D.W.Reitz. *International Journal of Heat and Mass Transfer* **1986,** 29, (8), 1169-1176.

10.   Santiago-Calvo, M.; Tirado-Mediavilla, J.; Ruiz-Herrero, J. L.; Rodríguez-Pérez, M. Á.; Villafañe, F. *Polymer* **2018,** 150, 138-149.

11.   Estravís, S.; Tirado-Mediavilla, J.; Santiago-Calvo, M.; Ruiz-Herrero, J. L.; Villafañe, F.; Rodríguez-Pérez, M. A. *European Polymer Journal* **2016,** 80, 1–15.

12.   Wilkes, K. E.; Yarbrough, D. W.; Nelson, G. E.; Booth, J. R. *Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels — Four-Year Results with Third-Generation Blowing Agents*; The Earth Technologies Forum. Washington, DC, 2003.

13.   Wilkes, K. E.; Gabbard, W. A.; Weaver, F. J. *Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels — One-Year Results with Third-Generation Blowing Agents*; The Earth Technologies Forum, Washington, DC, 1999.

14.   Wilkes, K. E.; Gabbard, W. A.; Weaver, F. J.; Booth, J. R. *Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels — Two-Year Results with Third-Generation Blowing Agents*; 2000.

15.   Modesti, M.; Lorenzetti, A.; Dall'Acqua, C. *Polymer Engineering and Science* **2004,** 44, (12), 2229-2239.

16.   Modesti, M.; Lorenzetti, A.; Dall'Acqua, C. *Polymer Engineering & Science* **2005,** 45, (3), 260-270.

17.   Marrucho, I. M.; Santos, F.; Oliveira, N. S.; Dohrn, R. *Journal of Cellular Plastics* **2005,** 41, (3), 207-224.

18.   Murphy, J. *Cellular Polymers* **2010,** 29, (5), 313-326.

19.   Kuranska, M.; Prociak, A.; Michalowski, S.; Zawadzinska, K. *Polimery* **2018,** 63, (10), 672-678.

20.   Modesti, M.; Lorenzetti, A.; Besco, S. *Polymer Engineering & Science* **2007,** 47, (9), 1351-1358.

21.   Harikrishnan, G.; Singh, S. N.; Kiesel, E.; Macosko, C. W. *Polymer* **2010,** 51, (15), 3349-3353.

22.   Lorenzetti, A.; Roso, M.; Bruschetta, A.; Boaretti, C.; Modesti, M. *Polymers for Advanced Technologies* **2016,** 27, (3), 303-307.

23.   Sen, D.; Garcia, A. P.; Buehler, M. J. *Journal of Nanomechanics and Micromechanics* **2011,** 1, (4), 112-118.

24.   ASTM D1622-08: Standard Test Method for Apparent Density of Rigid Cellular Plastics.

25.   ASTM D6226-10: Standard Test Method for Open Cell Content of Rigid Cellular Plastics.

26.   Pinto, J.; Solorzano, E.; Rodriguez-Perez, M. A.; de Saja, J. A. *Journal of Cellular Plastics* **2013,** 49, (6), 555–575.

27.   UNE-EN 12667:2002. Thermal performance of building materials and products. Determination of thermal resistance by means of guarded hot plate and heat flow meter methods. Products of high and medium thermal resistance.

28.   Gibson, L.; Ashby, M., *Cellular solids: structure and properties*. Pergamon Press: Oxford, 1988.

29.   Glicksman, L. R. *Cellular polymers* **1991,** 10, (4), 276-293.

30.   Pardo-Alonso, S.; Solórzano, E.; Brabant, L.; Vanderniepen, P.; Dierick, M.; Van Hoorebeke, L.; Rodríguez-Pérez, M. A. *European Polymer Journal* **2013,** 49, (5), 999–1006.

31.   Pérez-Tamarit, S.; Solórzano, E.; Hilger, A.; Manke, I.; Rodríguez-Pérez, M. A. *European Polymer Journal* **2018,** 109, 169-178.

32.   Howell, J. R.; Siegel, R.; Mengu, M. P., *Thermal radiation heat transfer*. 5th ed.; CRC press: 2010.

TABLES

Table 1. Density, open cell content (OC), mean cell size (Φ_{3D}), standard deviation (SD), normalized standard deviation (NSD) and anisotropy (AR) for each foam obtained.

Material	Density (Kg/m^3)	OC (%)	Φ_{3D} (μm)	SD	NSD	AR
Reference	31.19±1.69	8.1±1.9	608	68	0.11	1.11±0.29
1.5%Talc	35.55±1.16	9.5±3.1	307	98	0.32	1.27±0.27
1%DE	31.15±0.36	8.1±0.4	409	120	0.29	1.05±0.21
3%DE	31.81±0.07	9.2±0.8	331	102	0.31	1.69±0.44
5%DE	31.46±0.60	9.0±1.0	340	105	0.31	1.18±0.25
0.05%NPS	30.70±0.39	9.0±1.0	410	110	0.27	1.39±0.31
0.1%NPS	31.55±0.43	9.4±0.8	499	110	0.22	1.05±0.19
0.2%NPS	30.27±1.24	13.0±3.8	454	117	0.26	1.14±0.21

Table 2. The average foaming temperatures reached for the foams under study.

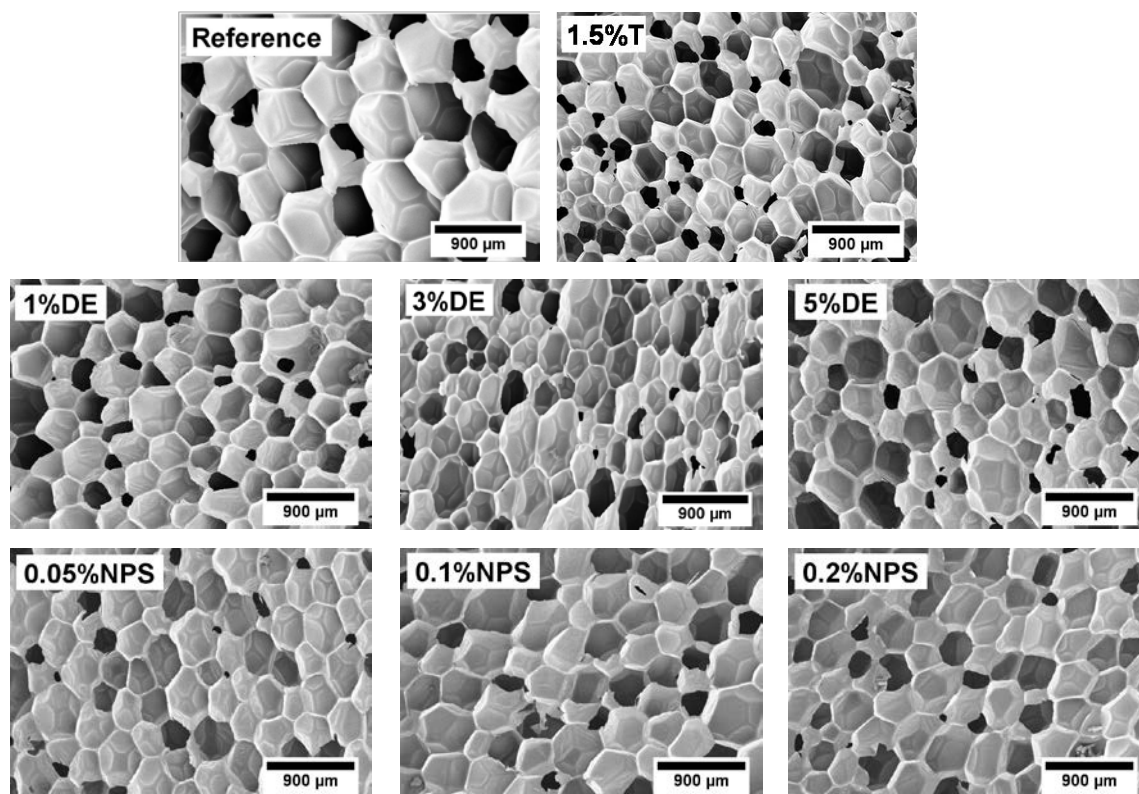| Material	Foaming temperature (°C)
Reference	105.9
1.5%Talc	121.9
1%DE	120.1
3%DE	120.6
5%DE	116.4
0.05%NPS	117.5
0.1%NPS	116.3
0.2%NPS	119.0

Figure 1. SEM micrographs of the foams under study showing the cell morphology.
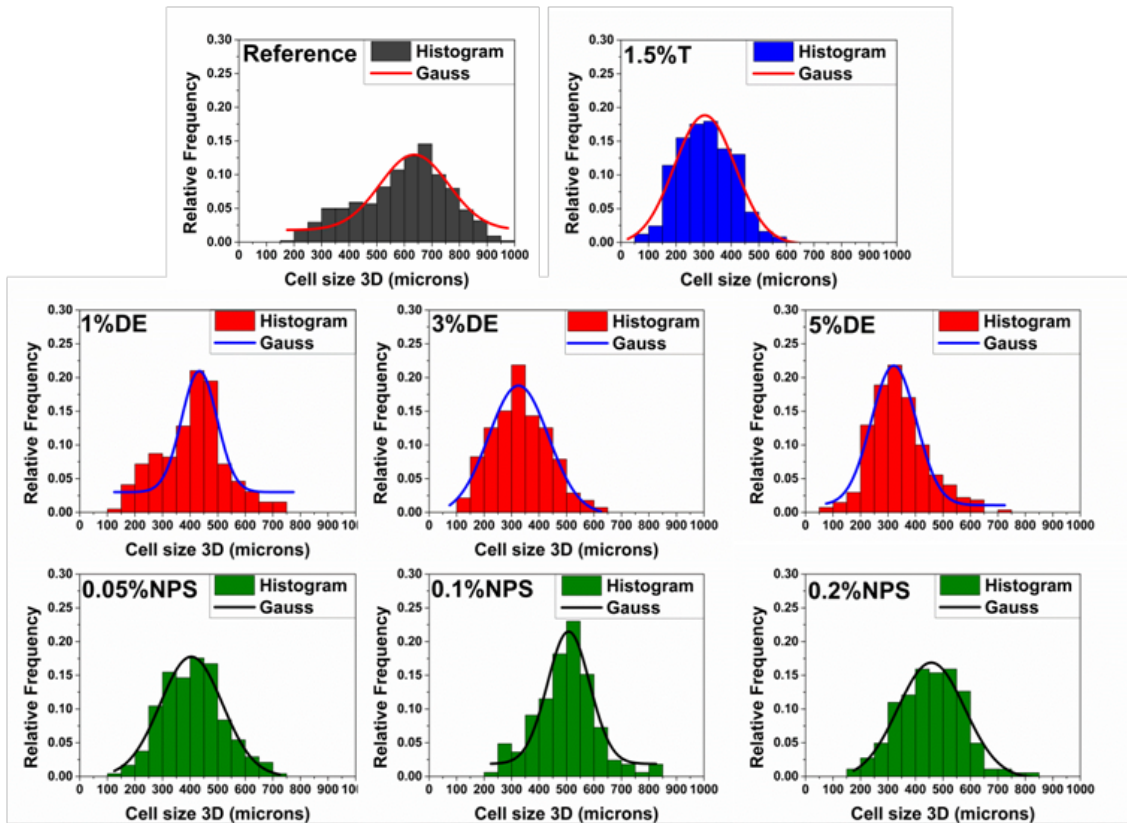
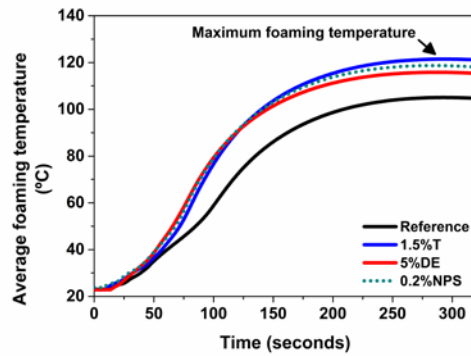Figure 2. Cell size distribution for the foams.

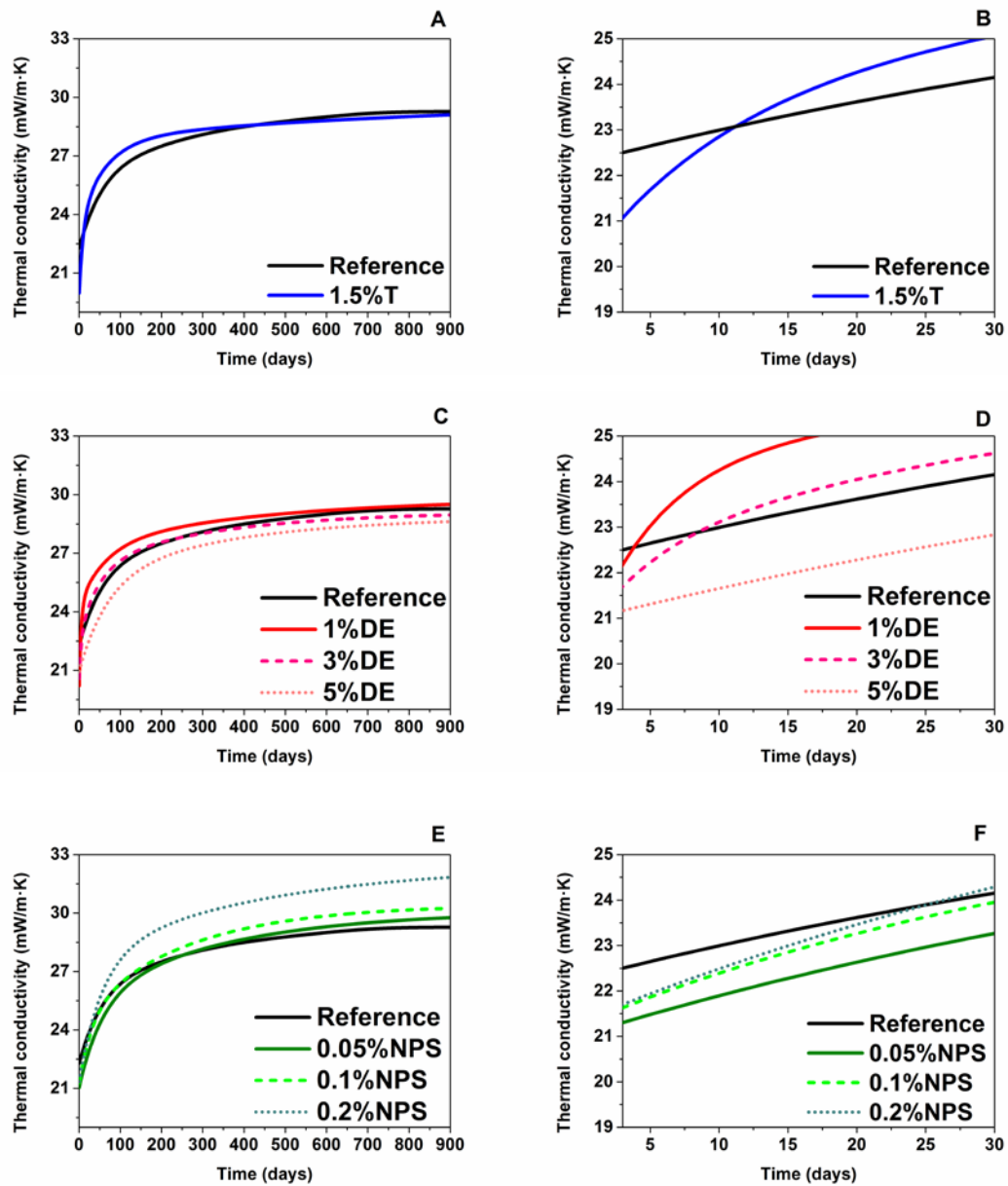Figure 3. Average maximum foaming temperatures for several materials.

Figure 4. Thermal conductivity evolution for the pure foam and for the foams with fillers: during the first 900 days (A, C and E); and during 30 days (B, D and F).
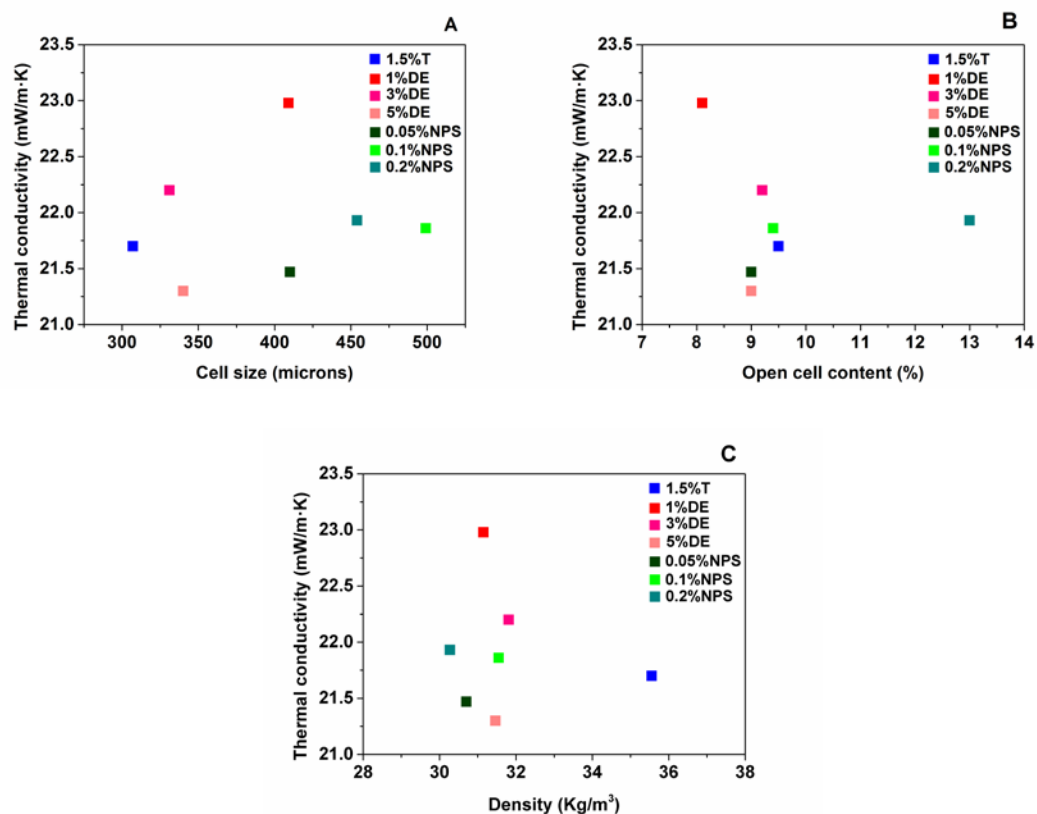
Figure 5. A) Thermal conductivity versus cell size after 5 days of the foam production; B) Thermal conductivity versus open cell content after 5 days of the foam production; C) Thermal conductivity versus density after 5 days of the foam production.
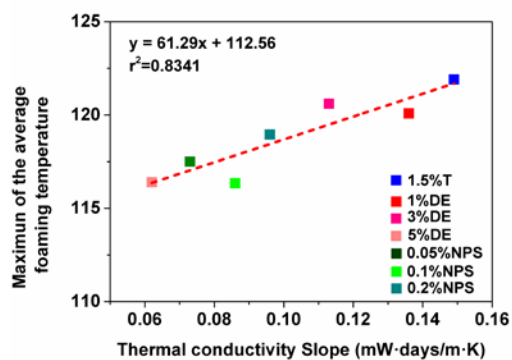
Figure 6. Maximum of the average foaming temperature curves versus thermal conductivity slope between 0 and 30 days.
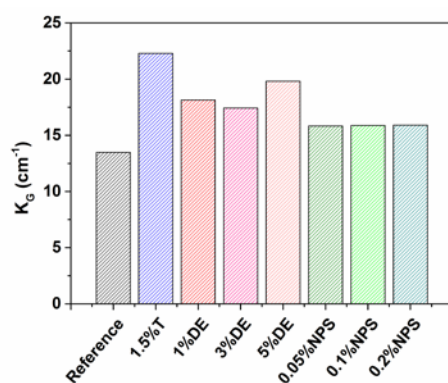
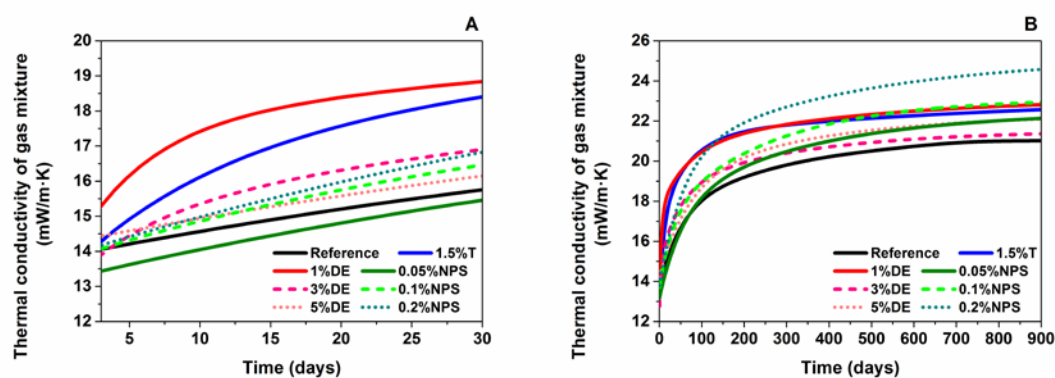Figure 7. Calcualted Glicksman extinction coefficient for the foams under study.

Figure 8. Thermal conductivity of the gas mixture as a function of time for all systems studied: A) during the first 30 days; B) during 900 days.
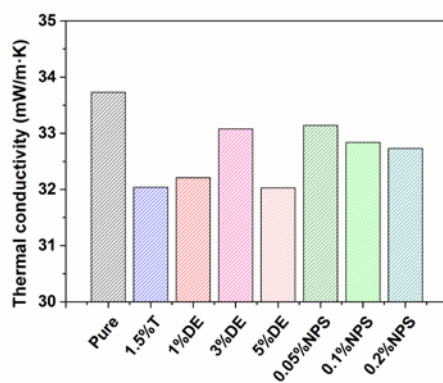
Figure 9. Thermal conductivity predicted using the thermal conductivity model assuming that air is the only gas inside the cells.