

In-situ thermal aging of biobased and conventional rigid polyurethane foams nanostructured with bacterial nanocellulose

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Abstract

The incorporation of nanofillers and the use of biobased polyols might have a deleterious effect on the aging performance of rigid polyurethane foams (RPUFs) applied in the insulation and marine industries. To study this, RPUFs obtained from petroleum based (RPUF) and castor oil (RPUF_{RIC}) polyols were nanostructured with bacterial nanocellulose (BNC) up to 0.3 wt%. Water immersion experiments revealed that the normalized water absorption (NWA) at the steady state was not affected by lower BNC contents (<0.2 wt%). Higher BNC contents caused a complex effect on post-cure and foaming, generating cell size expansion as well as shrinkage. In-situ DMA aging analysis revealed that the specific storage modulus (E'_{sp}) under flexural conditions of the RPUF_{RIC} and RPUF decreased by a maximum amount of 7.27% and 6.19%, respectively. The effect of BNC on the E'_{sp} was negligible, except for the case of the RPUF, where higher BNC concentrations (>0.2 wt%) caused a decrease of up to 13.69%. The previous results reinforce the hypothesis that the incorporation of BNC in both conventional and biobased polyurethane systems do not cause significant changes on the aging performance of the resulting foams, provided that low BNC concentrations are employed.

KEYWORDS

ageing, biopolymers and renewable polymers, cellulose and other wood products, mechanical properties, polyurethane

1 | INTRODUCTION

Rigid polyurethane foams (RPUFs) are one of the most relevant materials within the thermal insulation industry. A key property of this material is its low thermal conductivity, which is produced by small closed cells which retain specific gases denominated as physical blowing agents. For this reason, the integrity of the cells during service is a key aspect to maintain low thermal conductivity as well as its thermomechanical properties. The widespread application of RPUFs in industrialized

building systems (IBS) such as insulation and sandwich panels, spray-up and insulated pipes creates the necessity to understand the in-service behavior of those materials caused by several environmental factors, such as elevated temperatures, water absorption and UV irradiation. In addition, these materials are widely applied in underwater environments, such as buoyant in boat hulls and as a core in structural sandwich structures.^{1,2}

Nowadays, isocyanates and polyols are mostly produced from non-renewable resources, an aspect which has a negative impact in the sustainability of this

industry.³ To ameliorate this disadvantage, several studies have led to the development of bio-based polyols.^{4–7} Within the Americas, castor oil as well as soy-based polyols are very important renewable materials.⁷ Another key aspect in this discussion is the introduction of nanoparticles (NPs) in the polyurethane network. Most of the scientific studies have incorporated NPs as a soft segment,^{8–12} giving rise to improvements of thermomechanical properties but with a limited effect in actually improving the specific properties.¹³ Our group has addressed this important issue by using the NPs as a hard segment. Using this technique, it is possible to increase significantly specific thermomechanical properties while also increasing sustainability.¹⁴ However, a key aspect towards the implementation of nanostructured RPUFs in industry relies on the impact of such NPs on the stability and mechanical properties of the RPUFs in service. Among all the NPs available, the ones obtained from lignocellulosic precursors represent the most promising candidates.^{15,16} Its renewable nature and almost non-existent toxicity has been recently recognized as key aspects for future materials.^{17–19} However, bacterial nanocellulose (BNC) has a high hydrophilic character.²⁰ Such functionality might raise concerns in the development of RPUFs due to the probable increase of water absorption and its impact in service life.

As already noticed by a recent study,²¹ the influence of environmental factors on the thermomechanical properties of RPUFs has not been extensively studied. Most previous research^{22–24} have focus on how the gases permeate out of the foam, giving rise to changes of the thermal conductivity but assuming that no other fluid might have an interaction with the foam. Barszczewska-Rybarek et al.²¹ showed that RPUFs presented post-cure when aged in an aqueous environment. This study emphasized on the concept that the foams used in industry are not fully cured, hence, thermal aging might induce both degradation and chemical conversion. A similar result was obtained by Davies et al.²⁵ where RPUFs were immersed in marine environments for up to 2 years at 50°C. On the other hand, literature regarding biobased polyurethane foams is very scarce. Silva et al.²⁶ studied the incorporation of rubber powder waste in a RPUF obtained from castor oil. They found that the increase of filler content caused a substantial increase of water absorption but the mechanical properties of the aged specimens were not reported. Zhou et al.²⁷ studied the aging of polyurethane foams obtained from palm-oil reinforced with cellulose nanocrystals (CNCs). They found a substantial increase of water uptake of the nano-reinforced foams but its consequences on mechanical properties were also not reported. Other studies have dealt with the aging of thermoplastic

polyurethanes,²⁸ thermosetting polyurethanes,²⁹ coatings³⁰ as well as classical studies regarding changes of thermal conductivity caused by aging.^{31–33} These last publications presented results which are not the focus of the present work.

As far as the authors are concerned, no other study has dealt with the aging of RPUFs obtained from conventional resources as well as castor oil nanostructured with BNC. These results are very important for the successful implementation of nanostructured polyurethane foams in the insulation and marine industries. Our group has published several works related to the development of nanocomposites from BNC encompassing DSC and TGA analyses.^{7,34–36} Nonetheless, this is the first work which has thermal aging as the main scope.

This work will focus on in-situ studies of the thermal aging under aqueous immersion of RPUFs obtained from conventional and castor-oil polyols and its BNC nanostructured counterparts. Our experimental design is centered on in-situ dynamical mechanical thermal analysis (DMTA), where the samples were submerged in distilled water while measuring the changes of thermomechanical properties. We have correlated these results with the traditional water immersion experiments, obtaining kinetic parameters in simultaneous with the specific elastic modulus of the foams. The main variables of the analysis where foam type (conventional or biobased), temperature, time and BNC content. Further characterization techniques involved the measurement of cell size with SEM, apparent density and thermal conductivity of air-aged samples.

2 | MATERIALS AND METHODS

2.1 | Materials

A Polymeric Methylene Diphenyldiisocyanate (commercial name Suprasec 5005) with a functionality of 2.70 and a NCO number of 31.0 was used as received, corroborating this last value using the ASTM D2572 standard.

The conventional RPUF was formulated using a commercially available polyether polyol, denominated Rubitherm LP18497 (Huntsman). HCFC141 was used as the physical blowing agent and the formulation of the polyol component consisted of 100 parts by weight (pbw) of the polyol, 2 pbw of catalyst (Dimethylcyclohexylamine) and 14 pbw of HCFC141. Due to the fact that this blowing agent (BA) is being phased out, future research will use BAs with lower ODP. Finally, the isocyanate and polyol mixture was intensively mixed using a weight relationship of 160 and 100 parts of the isocyanate and polyols, respectively. The isocyanate index ($\text{NCO}_{\text{index}}$) was 1.05.

The polyurethane foam obtained from castor oil was formulated using the same isocyanate but with a polyol based on castor oil (Eiffel industries, cosmetic grade). The hydroxyl value (OH#) of the castor oil was determined by acetylation using acetic anhydride according to the ASTM D4274-99 test method A. An average value of 157 ± 3.2 mg KOH/mg was found for the castor oil used in this work. Due to the fact that the main objective of this work was to prepare RPUFs, alcoholysis of the castor oil polyol was performed using triethanolamine and lithium hydroxide as catalyst.³⁷ A weight relationship of 3:1 of castor oil:triethanolamine was able to produce a polyol with an OH# of 451 ± 2.2 mg KOH/mg. The RPUF obtained from castor oil (RPUF_{RIC}) was then obtained intensively mixing the isocyanate at 192 pbw and the castor oil at 100 pbw previously mixed with DI water at 1 pbw.

Measurement of NCO number was achieved following the ASTM D2572 standard using A.C.S grade chemicals such as dry toluene (Biopack), diisobutylamine (Sigma-Aldrich), isopropyl alcohol (Biopack) and hydrogen chloride (Biopack).

2.2 | BNC preparation procedure

BNC was produced by a static bacterial fermentation process carried out at 28°C for 14 days, with *Gluconacetobacter xylinus* (syn. *Komagataeibacter xylinus*) NRRL B-42 gently provided by Dr. Luis Lelpi (Fundación Instituto Leloir, Buenos Aires, Argentina). The production medium was the traditional Hestrin and Schramm medium³⁸ modified by replacing D-glucose (2% m/v) by the same concentration of glycerol (Biopack), maintaining a ratio “volume flask: volume medium” of 5:1 in the fermenters. The BNC membranes obtained, from now on denominated BNC mat, were removed from the bioreactors, and purified in few and simple steps. First, they were washed with water and then boiled in a water bath with a 2% wt/vol NaOH solution for 1 h, to remove the culture medium and the bacterial cells trapped in the BNC mat, respectively. Finally, they were rinsed with distilled water until a neutral pH was reached.

2.3 | Sample preparation procedures

The incorporation of BNC in the polyurethane foam derived from a conventional polyol (RPUF) and castor oil (RPUF_{RIC}) was performed using the “polmix” route described in previous works of our group.^{14,39} It is important to highlight that the BNC had to be lyophilized and subsequently dispersed in the polyol, giving rise to a colloidal dispersion. For the case of the RPUF, concentrations of 0.1, 0.2, and 0.3 wt% with respect to the polyol

were implemented. On the other hand, for the RPUF_{RIC}, a single concentration of 0.2 wt% was implemented.

For both cases, the polyol and the isocyanate were finally mixed in a HDPE cylindrical mold (internal diameter of 70 mm) equipped with an in-situ temperature thermocouple. The dispersion was performed using a Cowles agitator at 2000 rpm for 30". To ensure reproducibility, at least three samples were prepared. After the foam was prepared, cubic samples were cut from the main polyurethane block using a struers rotational cutter equipped with a diamond disc and obtaining cubes with sides of approximately 3 cm in length.

2.4 | Sample characterization techniques

The thermal conductivity was measured using the transient method developed by Harikrishnan et al.⁴⁰ A thermometrics epoxy-coated thermistor (RL503) was implemented to this effect. The calibration of the thermistor consisted in measuring its resistance (Proskit MT1860) as a function of temperature immersing the thermistor in a thermostatically controlled (Lauda ECO gold) water bath. Then, a plot of resistance versus temperature was obtained and the R_{25} and the β values were linearly correlated, giving values of $2046.8 \pm 2.5 \Omega$ and 3863.5 ± 1.2 K, respectively. The implementation of the transient method consisted in the application of a pulse of 1 s duration and the subsequent measurement of the evolution of resistance as a function of time. The pulse was specified to give a temperature excursion of approximately 2°C, in agreement with the experiments performed by Harikrishnan.⁴⁰ In contrast to this work, the system implemented in our studies was controlled by an Atmega 328 microprocessor, giving rise to a precise control of pulse duration. The thermal conductivity was then obtained using the following equation,

$$T(t) = \frac{(\rho c)^{0.5} P}{4\pi^{1.5} k^{1.5}} \left[(t - t_p)^{-0.5} - t^{-0.5} \right] \quad (1)$$

where ρ was the density of the foam (kg/m^3), c was the specific heat capacity of the foam ($\text{J kg}^{-1} \text{K}^{-1}$), P was the applied power (W), k the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$) and t_p the pulse time duration (seconds). In a typical experiment, the curve $T(t)$ is obtained. Then, using a non-linear correlation method, the k -value is obtained using Equation (1). Calibration of this system was achieved using previously known mediums, such as glycerin, water and air.

Water absorption tests were performed following the guidelines of Zhou et al.²⁷ The samples consisted of cubes with sides of 3 cm in length. Then, the cubes were

completely submerged in a thermostatically controlled bath (Velp Scientifica) ensuring that all sides of the cubes were exposed to the medium. Isothermal experiments at 25, 50, and 60°C were performed. The selection of these temperatures was based on preliminary experiments performed within this temperature range. Weight uptake measurements were performed with a frequency of 30 minutes for a total experimental time of 4 h. Weight was measured (Ohaus Adventurer) removing the sample from the water bath and by carefully drying the water excess using paper cloth. Then, it was submerged until the final measurement was performed. The weight measurements were normalized taking into account the exposed area using the following equation,

$$\text{NWA (\%/cm)} = 100 \frac{W_f - W_o}{W_o} \cdot \frac{1}{AR} \quad (2)$$

where W_f and W_o represented the initial and final weight and AR was the aspect ratio, defined as the area per unit volume of the cubes used in this work. To avoid the effect of temperature changes in the isothermal measurements the samples were previously conditioned at 25, 50, and 60°C in a convection oven, respectively.

DMTA tests were carried out with a Perkin & Elmer DMA 8000 equipped with an immersion bath. A single cantilever flexural mode was used, implementing two superimposed oscillation frequencies of 1.0 and 10 Hz and an amplitude of 0.01 mm. The selection of the flexural mode was associated to the fact that the sample expansion during the experiment did not affect the measurement, as already noticed by our previous work.³⁴ The thermal scan started at 25°C and went up to 180°C at a scan rate of 2°C/min. Sample dimensions were 30 mm in length by 10.0 mm in width and 4.0 mm in thickness. The sample was cut so as that foam growth was aligned to the longitudinal direction. Two sets of experiments were performed. The first set consisted in using air as immersion medium while the second used DI water. For these last experiments, the samples were previously conditioned at the specific isothermal temperatures (25, 50, and 60°C) using a convection oven.

Micrographs of the cell size and dimensions were taken using a Phenomworld ProX SEM at a voltage of 5 kV, giving magnifications of 150×. Before the analysis, the samples were gold sputtered. The statistical analysis consisted of obtaining 30 measurements of cell dimensions in both the longitudinal (L) and transverse (T) growth direction for each sample type. These measurements were obtained from three randomly selected samples. It is important to highlight that the L direction represented the direction where the foam growth was not

constricted by a wall, whereas the T direction was limited by the wall of the cylindrical PEAD mold.

Regarding nomenclature, RPUF will refer generally to a RPUF. The RPUF obtained from castor oil polyol will be denoted as RPUF_{RIC}. The RPUF obtained from conventional petroleum based polyols shall be termed as RPUF. If any foam in this work was nanostructured with BNC, then, the nomenclature will be RPUF-BNC x %, whereas the specific x value represents the weight percent of BNC with respect to the total amount of components present in the formulation of the polyurethane foam.

3 | RESULTS AND DISCUSSION

3.1 | Water absorption tests

The normalized water absorption (NWA) spectrum as a function of time for the RPUF prepared with incremental amounts of BNC and also for the three isothermal experiments are depicted in Figure 1. In a similar way, the NWA for the RPUF_{RIC} are also depicted in Figure 2.

As it can be deduced from Figures 1 and 2, the NWA evolution as a function of time followed Fick's law. Each of the curves presented had a gradual increase of the NWA up to a steady state, where the maximum water absorption was achieved. The effect of increasing the temperature had an identical effect on all the samples, it reduced the time necessary to reach the steady state and caused a simultaneous increase of the absolute NWA value at the steady state. To further analyze the effect of BNC content and polyurethane type, we have modeled the results using the following equations,

$$\text{NWA}_M(t) = y_0 \left(1 - e^{-\frac{t}{\tau}}\right) \quad (3)$$

$$y_0 = A e^{-\frac{E_a}{T}} \quad (4)$$

where y_0 represented the NWA at the steady state, τ represented the time constant and A and E_a were the pre-exponential factor and the activation energy of the Arrhenius dependence of NWA with respect to temperature, respectively. The fitted parameters are reported in Table 1. It should be noted that, in all cases, the correlation factor was above 0.99. Our discussion will focus on the engineering parameters τ and y_0 .

The variation of y_0 as a function of temperature and polyurethane type is depicted in Figure 3a. The graph is divided into three regions, where each region represents the y_0 values associated to a specific isothermal experiment as a function of polyurethane type. The first logical deduction from this graph is that, in all cases, the y_0

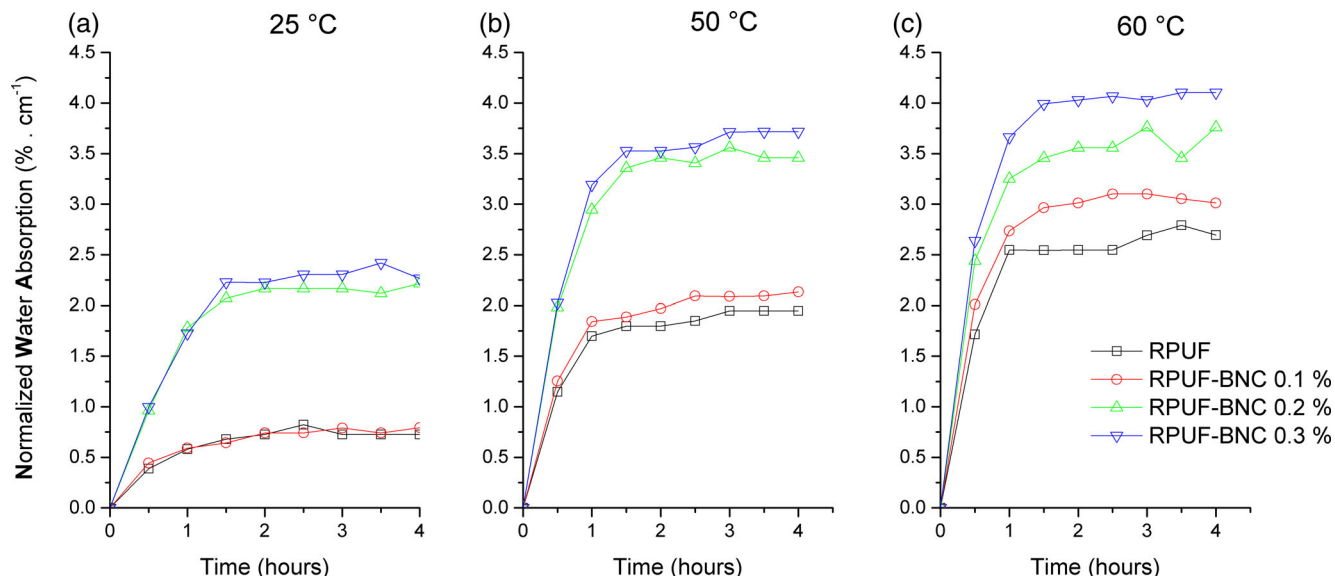


FIGURE 1 Normalized water absorption of the RPUF, RPUF-BNC 0.1%, RPUF-BNC 0.2% and RPUF-BNC 0.3% at the isothermal temperatures of (a) 25°C, (b) 50°C, and (c) 60°C |

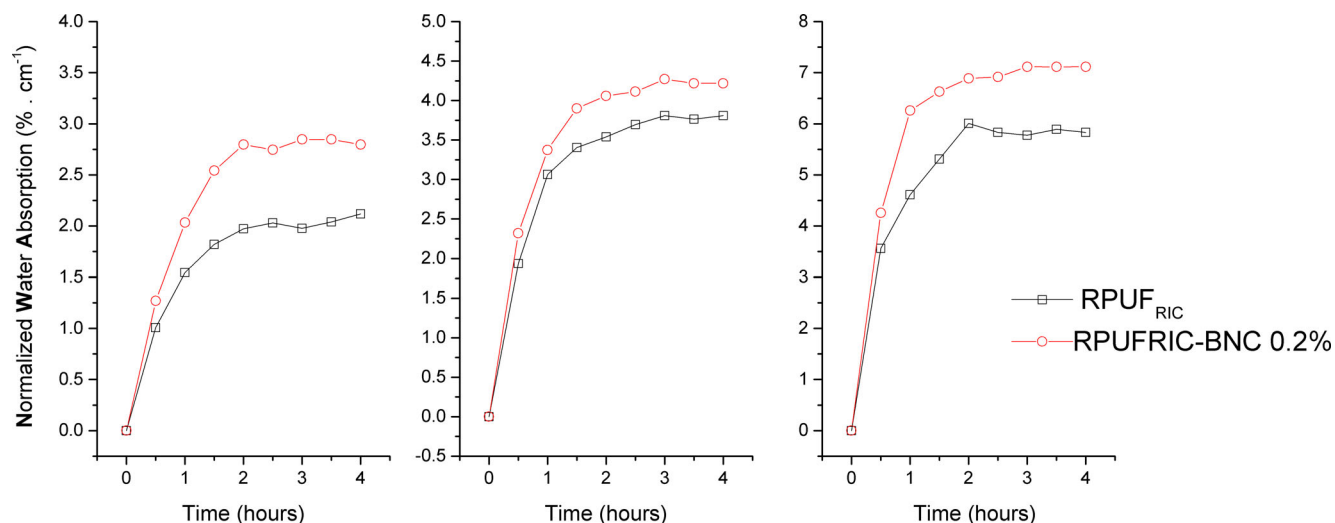


FIGURE 2 Normalized water absorption of the RPUF_{RIC} and RPUF_{RIC}-BNC 0.2% at the isothermal temperatures of (a) 25°C, (b) 50°C, and (c) 60°C |

increased as a function of increasing temperature. Hence, an increase in temperature was translated into a higher water absorption capacity at the steady state. The lowest value was measured for the RPUF at 25°C (0.757%/m) while the highest value was measured for the RPUFRIC-BNC 0.2% (7.102%/m) at 60°C. As far as the polyurethane type is concerned, similar tendencies were found at each isothermal experiment. For example, at any temperature, the y_0 of the RPUF was always lower than the RPUF_{RIC}. This was expected due to the fact that the foams prepared with castor oil had a higher open cell content (as reflected by SEM micrographs, see Sections 3.2 and 3.3) as well as a higher cell volume. This observation

should not be considered as a detrimental aspect of castor oil based foams. The formulation of the foam dictates the cell size and open cell content. Another formulation would be able to achieve similar values with respect to the RPUF, as already noticed by previous studies.^{4,34,38,41–45}

The effect of BNC content had a similar effect in all the samples analyzed. It generally increased the y_0 values as a function of increasing BNC content, both for the RPUF as well as the RPUFRIC. However, it is important to emphasize that for the lowest BNC contents, particularly at 0.1%, the variation of the y_0 was found to be negligible. This is a clear indication that the foams with lower

TABLE 1 Kinetic parameters obtained from the water absorption tests

Polyurethane type	Immersion T ($^{\circ}\text{C}$)	y_0 (%/m)	τ (hour)	E_a (kJ/mol)
RPUF	25	$7.57.10^{-1} \pm 1.20.10^{-2}$	$6.62.10^{-1} \pm 7.36.10^{-3}$	$3.10.10^1 \pm 8.96.10^{-1}$
RPUF	50	$1.92.10^0 \pm 1.15.10^{-2}$	$5.26.10^{-1} \pm 8.24.10^{-3}$	
RPUF	60	$2.68.10^0 \pm 2.1.10^{-2}$	$4.50.10^{-1} \pm 9.14.10^{-3}$	
RPUF-BNC 0.1%	25	$7.69.10^{-1} \pm 7.1.10^{-3}$	$6.68.10^{-1} \pm 5.370.10^{-3}$	$3.43.10^1 \pm 7.32.10^{-1}$
RPUF-BNC 0.1%	50	$2.09.10^0 \pm 1.01.10^{-2}$	$5.37.10^{-1} \pm 9.32.10^{-3}$	
RPUF-BNC 0.1%	60	$3.07.10^0 \pm 1.67.10^{-2}$	$4.63.10^{-1} \pm 7.98.10^{-3}$	
RPUF-BNC 0.2%	25	$2.23.10^0 \pm 1.34.10^{-2}$	$6.86.10^{-1} \pm 8.25.10^{-3}$	$1.23.10^1 \pm 1.89.10^{-1}$
RPUF-BNC 0.2%	50	$3.52.10^0 \pm 1.78.10^{-2}$	$5.64.10^{-1} \pm 9.89.10^{-3}$	
RPUF-BNC 0.2%	60	$3.63.10^0 \pm 3.10.10^{-2}$	$4.50.10^{-1} \pm 7.89.10^{-3}$	
RPUF-BNC 0.3%	25	$2.39.10^0 \pm 1.43.10^{-2}$	$7.62.10^{-1} \pm 8.34.10^{-3}$	$1.43.10^1 \pm 9.30.10^{-1}$
RPUF-BNC 0.3%	50	$3.71.10^0 \pm 1.76.10^{-2}$	$5.73.10^{-1} \pm 2.28.10^{-3}$	
RPUF-BNC 0.3%	60	$4.09.10^0 \pm 1.29.10^{-2}$	$4.67.10^{-1} \pm 9.55.10^{-3}$	
RPUF _{RIC}	25	$2.07.10^0 \pm 1.54.10^{-2}$	$7.44.10^{-1} \pm 9.44.10^{-3}$	$2.40.10^1 \pm 2.30.10^{-1}$
RPUF _{RIC}	50	$3.82.10^0 \pm 2.30.10^{-2}$	$6.64.10^{-1} \pm 1.15.10^{-2}$	
RPUF _{RIC}	60	$5.94.10^0 \pm 2.15.10^{-2}$	$6.14.10^{-1} \pm 1.06.10^{-2}$	
RPUF _{RIC} -BNC 0.2%	25	$2.90.10^0 \pm 3.27.10^{-2}$	$7.68.10^{-1} \pm 4.98.10^{-3}$	$2.57.10^1 \pm 5.84.10^{-1}$
RPUF _{RIC} -BNC 0.2%	50	$4.24.10^0 \pm 1.17.10^{-2}$	$6.24.10^{-1} \pm 4.75.10^{-3}$	
RPUF _{RIC} -BNC 0.2%	60	$7.10.10^0 \pm 7.20.10^{-3}$	$5.01.10^{-1} \pm 7.48.10^{-3}$	

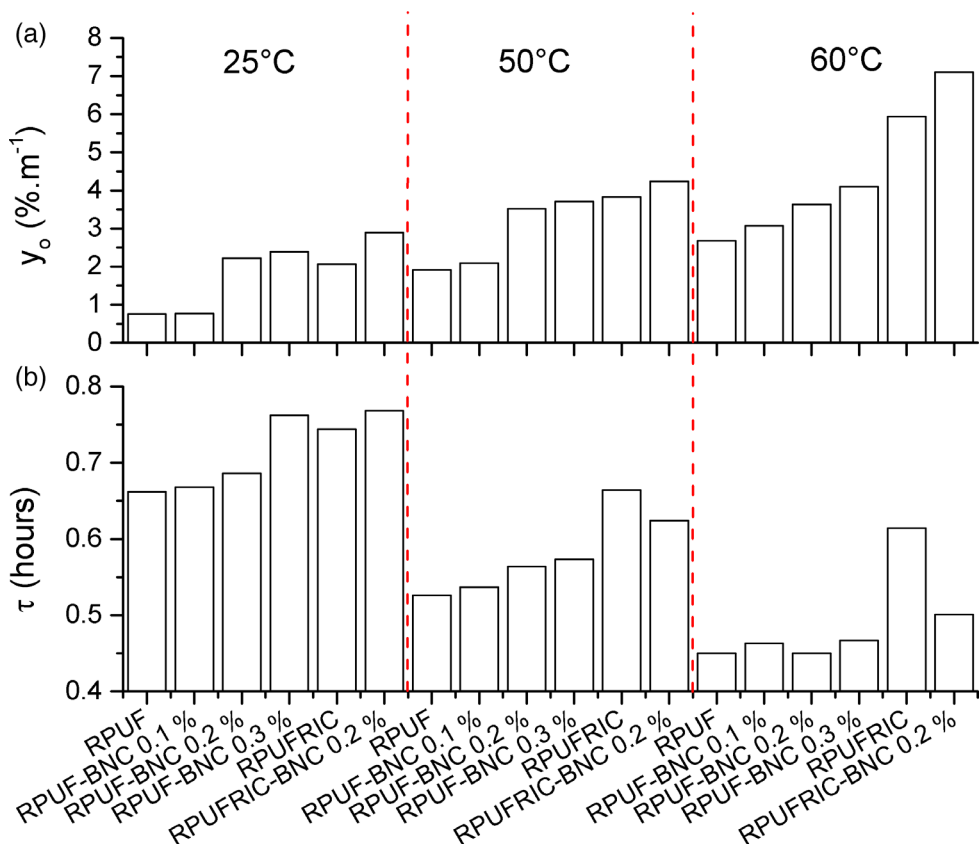


FIGURE 3 Immersion constants as a function of polyurethane type and temperature. (a) Normalized water absorption at the steady state (y_0) and (b) time constant (τ)

BNC content had more closed cells, indicating that the alteration of the blowing and expansion process was not as severe for the lower BNC concentrations. As a matter

of fact, the increase in the y_0 value at 25°C for the RPUF without BNC compared to that with 0.3% was 216% while the same comparison with respect to RPUF-BNC 0.1%

was negligible. Another observation was that the effect that the BNC had in the RPUF_{RIC} y_0 's values was much less severe. For example, at 25°C and at a 0.2% BNC content, the y_0 increase for the RPUF was 194% while for the RPUF_{RIC} was only 40%. This indicated that the foams prepared with castor oil retained more its geometrical integrity as a function of increasing BNC content.

The variation of τ as a function of temperature and polyurethane type is depicted in Figure 3b. As a remainder, the time constant (τ) represents the water absorption velocity of the foams. A lower time constant indicates that a higher water absorption velocity was attained. Indeed, comparing the results depicted in Figure 3b as a function of increasing temperature, the τ decreased significantly. However, it is important to highlight how τ changed as a function of polyurethane type and BNC content. Comparing the RPUF with respect to the RPUF_{RIC} , the time constant of the former was 12.4% lower with respect to the latter (at 25°C). In addition, the experiment performed at 60°C increased this value up to 36.4%. These values clearly indicated that the water absorption velocity of the RPUF_{RIC} was significantly lower with respect to the RPUF, and more importantly, an increase in temperature had a less detriment impact in biobased foams. It can be argued that, even though the open cell content and geometry caused a higher y_0 , the fact that the time constant was higher indicated that the RPUF_{RIC} is more effective in preventing an inwards water diffusion. The effect of BNC content on τ was significantly dependent on polyurethane type. For the case of RPUF, the time constant remained constant or slightly increased, regardless of the temperature of the aging experiment. This clearly indicated that the velocity of water absorption was not reduced, which meant that BNC changed the absorption kinetics. On the other hand, the incorporation of BNC in the RPUF_{RIC} caused a reduction of the time constant which was more pronounced for higher aging temperatures. Then, it can be deduced that for the case of biobased polyurethanes, the incorporation of BNC in the microstructure caused an increase of the velocity of water absorption.

It is important to compare the results with what has been published before. However, as already noticed above, this is the first work which is focus on the aging of RPUF nanostructured with BNC. A recent study by Barszczewska-Rybarek²¹ reported that weight absorption of RPUF in seawater were the order of 15%–25%. Normalizing these values with respect to the AR leaves the range at 1.73–2.89%/cm. These values are similar to the ones reported in Table 1. However, it is important to emphasize that the NWA values reported by this study were obtained from sprayed up foam samples. In contrast, our work consisted on molded foams. For the case of the RPUF_{RIC} , Silva

et al.²⁶ reported that castor-oil based foams with an apparent density of 36.5 kg/m³ had a water absorption at 25°C of 1%. Normalizing this result with respect to the AR gives a value of 0.625%/cm. Unfortunately, we cannot compare the effect of BNC on weight absorption because no other published paper has performed this measurement. A similar work based on palm-oil polyurethane foams reinforced with nanocellulose was published by Zhou et al.²⁷ The reported NWA of the foams was 10.7%/cm for the pristine material and up to 22.7%/cm for a foam nanostructured with 8 parts per hundred resin of nanocellulose. Then, the incorporation of nanocellulose caused an increase of the NWA at the steady state of +112%. In a similar way, the work of Silva et al.²⁶ found that adding 20 wt% of rubber powder caused an increase of 58% of the NWA at the steady state.

3.2 | Cell size and apparent density

The apparent density of the RPUFs developed in this work using both conventional petroleum based polyol and castor oil as a function of BNC content are reported in Table 2. The pristine RPUF presented an apparent density of 38.4 ± 4.7 kg/m³. It showed negligible changes as a function of BNC concentration, having a slight nucleation effect (−6.7%) at a 0.2% of BNC concentration. On the other hand, the RPUF_{RIC} presented an apparent density of 72.6 ± 4.7 kg/m³ having also an insignificant change as a function of BNC concentration. It is important to highlight that the RPUF used in this work was formulated using conventional petroleum based components in conjunction with physical blowing agents. This lead to the development of foams which had apparent densities in the range of 40 kg/m³. These are the typical values used for insulation applications, taking into account the fact that the foams were molded in cylindrical foams. On the other hand, the RPUF_{RIC} were of a much higher apparent density. The main reason of this substantial change had to do with the absence of physical blowing agents in the formulation of the castor oil polyol. Taking into account that the solubility of this polyol with the physical blowing agent used in this work was very low, it was decided not to use it so as to avoid having to deal with foaming heterogeneities. It is important to notice that the development of physical blowing agents is a very active research field. As we have already pointed out in a previous publication,⁷ the physical blowing agents allowed in each country should be used to study its effect on the thermomechanical properties of the resulting foams.

The statistical analysis of cell size in both the longitudinal growth direction (L) and transverse one (T) are

TABLE 2 Cell size in the L and T directions and apparent density of the polyurethane foams studied in this work

Polyurethane type	Immersion T (°C)	Cell size L (μm)	Cell size T (μm)	Apparent density (kg/m^3)
RPUF	Pristine	$4.99.10^2 \pm 1.03.10^2$	$3.65.10^2 \pm 6.43.10^1$	$3.84.10^1 \pm 4.20.10^0$
RPUF	25	$4.71.10^2 \pm 9.30.10^1$	$3.27.10^2 \pm 5.01.10^1$	
RPUF	50	$5.95.10^2 \pm 8.20.10^1$	$4.12.10^2 \pm 7.80.10^1$	
RPUF	60	$4.85.10^2 \pm 6.42.10^1$	$3.26.10^2 \pm 4.80.10^1$	
RPUF-BNC 0.1%	Pristine	$4.27.10^2 \pm 1.01.10^2$	$3.05.10^2 \pm 7.63.10^1$	$4.11.10^1 \pm 3.80.10^0$
RPUF-BNC 0.1%	25	$4.70.10^2 \pm 8.42.10^1$	$3.16.10^2 \pm 5.64.10^1$	
RPUF-BNC 0.1%	50	$4.23.10^2 \pm 1.33.10^2$	$2.72.10^2 \pm 6.84.10^1$	
RPUF-BNC 0.1%	60	$4.47.10^2 \pm 8.89.10^1$	$3.16.10^2 \pm 3.96.10^1$	
RPUF-BNC 0.2%	Pristine	$4.59.10^2 \pm 1.24.10^2$	$2.96.10^2 \pm 6.81.10^1$	$3.58.10^1 \pm 4.50.10^0$
RPUF-BNC 0.2%	25	$5.21.10^2 \pm 1.52.10^2$	$2.94.10^2 \pm 9.07.10^1$	
RPUF-BNC 0.2%	50	$5.89.10^2 \pm 2.41.10^2$	$2.95.10^2 \pm 7.49.10^1$	
RPUF-BNC 0.2%	60	$5.09.10^2 \pm 1.43.10^2$	$2.74.10^2 \pm 6.10.10^1$	
RPUF-BNC 0.3%	Pristine	$4.02.10^2 \pm 1.14.10^2$	$2.83.10^2 \pm 7.83.10^1$	$4.32.10^1 \pm 3.50.10^0$
RPUF-BNC 0.3%	25	$5.89.10^2 \pm 2.73.10^2$	$2.51.10^2 \pm 7.96.10^1$	
RPUF-BNC 0.3%	50	$5.28.10^2 \pm 1.20.10^2$	$3.08.10^2 \pm 5.34.10^1$	
RPUF-BNC 0.3%	60	$4.61.10^2 \pm 1.19.10^2$	$1.19.10^2 \pm 2.35.10^2$	
RPUF _{RIC}	Pristine	$5.42.10^2 \pm 1.12.10^2$	$3.21.10^2 \pm 6.19.10^1$	$7.26.10^1 \pm 2.60.10^0$
RPUF _{RIC}	25	$4.72.10^2 \pm 7.72.10^1$	$2.63.10^2 \pm 4.90.10^1$	
RPUF _{RIC}	50	$5.36.10^2 \pm 1.05.10^2$	$2.84.10^2 \pm 5.95.10^1$	
RPUF _{RIC}	60	$5.31.10^2 \pm 8.52.10^1$	$2.90.10^2 \pm 4.45.10^1$	
RPUF _{RIC} -BNC 0.2%	Pristine	$4.70.10^2 \pm 8.22.10^1$	$2.57.10^2 \pm 8.03.10^1$	$7.02.10^1 \pm 3.70.10^0$
RPUF _{RIC} -BNC 0.2%	25	$4.15.10^2 \pm 1.02.10^2$	$2.17.10^2 \pm 5.34.10^1$	
RPUF _{RIC} -BNC 0.2%	50	$4.89.10^2 \pm 1.68.10^2$	$2.83.10^2 \pm 9.12.10^1$	
RPUF _{RIC} -BNC 0.2%	60	$4.90.10^2 \pm 1.48.10^2$	$2.53.10^2 \pm 7.90.10^1$	

reported in Table 2. The analysis covers the study of the effect of growth direction, polyurethane type and immersion temperature. To understand better the results reported in Table 2, Figure 4 can be consulted. In this figure, we have summarized the effect of the previously mentioned variables. It is important to emphasize the relevance of measuring cell size in both the L and T directions. In most research studies, molded foams are employed, hence, there's one direction in which the foam can freely grow (denoted L in this work). This analysis is usually underestimated in literature, giving rise to inaccurate conclusions due to fact that the anisotropy of the foam has not been taken into account. There are two key aspects when discussing cell size of RPUFs, that is, anisotropy and cell size *SD*. Anisotropy is always present in all types of polyurethane foams, regardless of the foaming technology employed to manufacture it.³ In addition, the incorporation of NPs in the formulation of foams can also interact or change the anisotropic behavior of the foam. In fact, our group and other researchers have already measured and published this relevant aspect

in previous studies.^{4,34,36,46–49} On the other hand, the cell size *SD* is associated to how processing or formulation changes affect the cell size distribution within a foam. For example, in Figure 4 we can elucidate that, in some cases, the *SD* of cell size is remarkably high, but, in other cases, it's much lower. However, as we have emphasized in several previous publications, it is normal to have significant variations in cell size as well as its *SD*. An increase in the latter does not indicate that the foam has been poorly manufactured, but, rather, that the specific formulation and processing conditions have led to such results. We will further discuss this important aspect below.

The cell size dimensions in the L and T direction can be found the left and right column of Figure 4, respectively. It is important to emphasize that the scale of both columns is different, then, taking into account this remark, we can elucidate that while the average cell dimension in the L direction was, roughly, 500 μm and, instead, in the T direction it was 300 μm . On the other hand, each row in Figure 4 represents the cell sizes of the

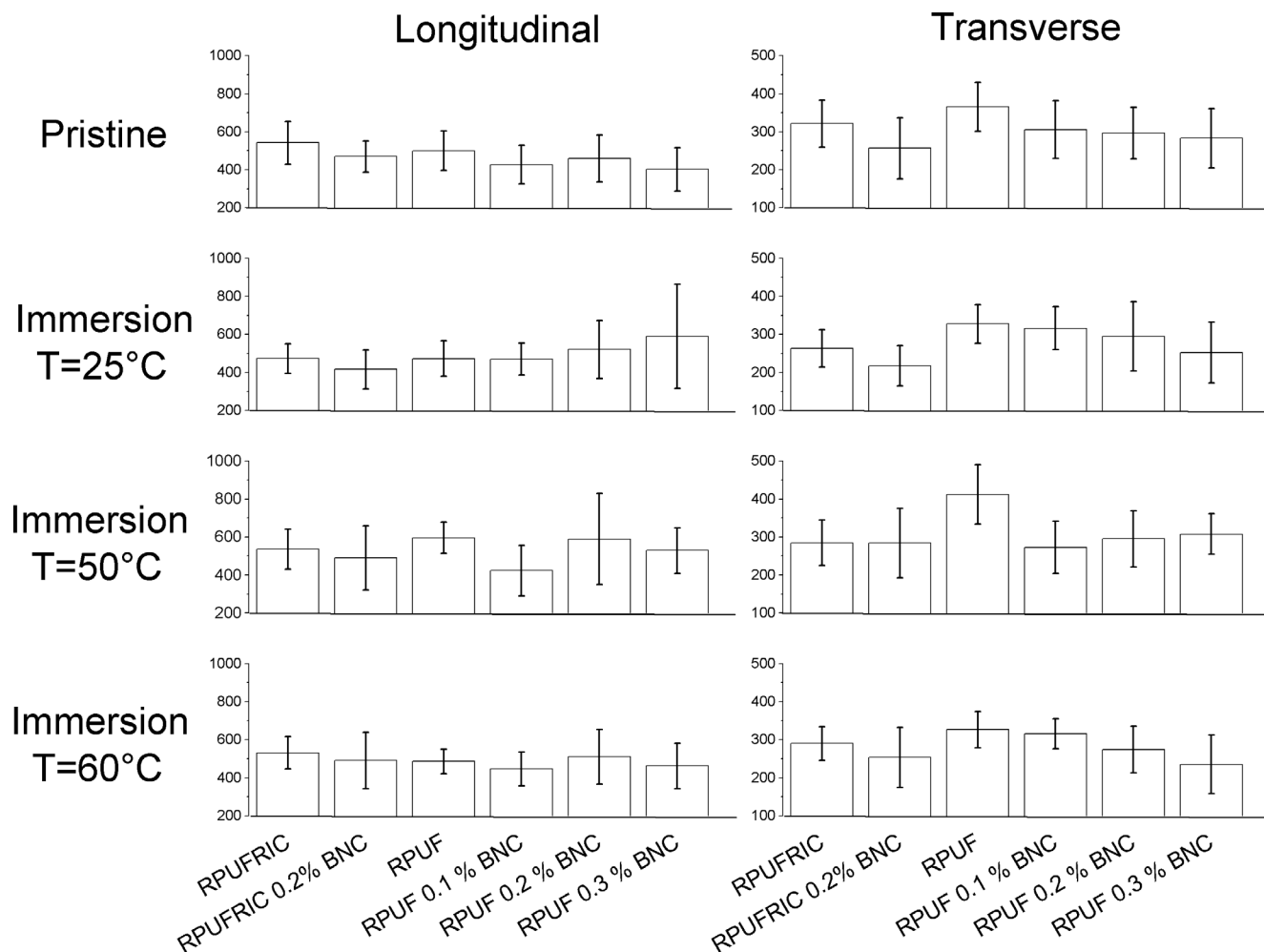


FIGURE 4 Cell size in the longitudinal (L) and transverse (T) direction for the pristine and aged foams as a function of immersion temperature, polyurethane type and BNC concentration

pristine foams (no aging) and after immersion at 25, 50 and 60°C, respectively. The sample dimensions were taken after reaching the steady state.

Let us focus first on the cell sizes of the RPUF_{RIC}. The values are represented by the first two column bars of either the left and right column depicted in Figure 4. For the case of the pristine foams, we can deduce from Figure 4 that BNC acted as a nucleation agent, decreasing cell size in both L (−13.3%) and T (−20.2%) directions. However, the SD in both cases indicated that no significant nucleation effect was taking place. The similarity between the changes observed in the L and T direction prevented any further conclusion towards the selectivity of BNC in foam growth (anisotropy). If immersion is taken into account into the analysis (aging), then, it is important first to clarify which were the phenomena that could take place under those conditions. One phenomena which took place was foam cure. As already noticed above and in previous study of our group,¹⁴ RPUFs can have post-foaming cure, causing either an increase in cell

size due to further reaction of remnant isocyanate with humidity or, in the other hand, shrinkage due to foam cell collapse.³ In addition to these effects, the permeation of water into the cells further complicates the analysis. The constant permeation of water into the cells can cause also cell expansion due to density changes but also for its reaction with remnant isocyanate. Taking into account that several phenomena were occurring simultaneously, it is difficult to ascertain which specific mechanism was preponderant. After considering this important comment, let us focus on the effect on immersion on the cell size of the foams prepared from castor oil (RPUF_{RIC}). As it can be deduced from Figure 4, the cell size in both the L and T direction did not increase as a function of immersion. Instead, the general tendency was towards further shrinkage as a function of immersion. Taking into account that the highest shrinkage measurements were in the order of 18.4% in the T direction and 12.7% in the L direction, it can be argued that no significant changes took place in the foams prepared from castor oil. If the

analysis is extended to take into account the combined effect of BNC and immersion, similar conclusions can be drawn. Then, it can be concluded that, from a cell size and anisotropy point of view, the incorporation of BNC and aging did not produce significant changes, only a slight nucleation effect caused by it was measured.

On the other hand, a completely different scenario was present for the case of the RPUF. First, let us focus on how the cell size changed for the foams prepared without BNC (third column bar of the L and T graphs represented in Figure 4). The cell size in the L direction ranged at an average of 499 μm , while in the T direction it was 365 μm . The *SD* of these measurements indicated that the foam size cell distribution ranged from values starting at approximately 265 μm going up to 563 μm . The cell distribution in the L direction and the T direction barely overlapped, indicating clearly that the L direction was effectively where the foam could freely grow. Continuing with the analysis, the effect of aging had a profound impact on cell size. As it can be deduced from Table 2, the values indicated that the foams presented either a net reduction of cell size as well as an increase of cell size in both the L and T directions. The maximum increase in cell size in both the L and T directions was measured at an immersion temperature of 50°C while the maximum decrease in cell size (L and T) was measured for an immersion temperature of 25°C. It is important to emphasize that a simple explanation of this behavior cannot be easily deduced. As already explained above, several phenomena were taking place simultaneously and the relative weight of each cannot be a priori deduced. In this case, it might be argued that aging at 25°C triggered mostly the shrinkage caused by post-cure (without additional foaming) associated to the further reaction of hydroxide and isocyanate groups, as well as the formation of a polyurea network. On the other hand, at 50°C, foaming was triggered due to the increased kinetics of foaming reaction coupled with a decrease in the elastic modulus of the foam during the aging process.

Focusing now on the effect of BNC on the RPUFs, the most relevant deduction that can be made from Figure 4 is how BNC interacted in changing the anisotropy of foam growth. Let us focus first on the pristine foams (first row in Figure 4). The effect of increasing BNC content had a completely different effect in the L and T directions. In the former, the statistical variation of cell size indicated that almost no changes of cell size dimensions were present. However, this was not the case for the T direction. Indeed, in this direction, an increase in BNC content caused a monotonous decrease of cell size of up to 22.5% for the RPUF-BNC 0.3%. This result clearly indicated that BNC was changing the foam growth stage, inhibiting the growth velocity and causing nucleation

effect in the T direction. Thus, the resulting foam will have a higher anisotropic behavior as a function of increasing BNC content. If we add into the analysis the effect of immersion, we can deduce a similar effect, where the BNC still acted as a nucleation agent and growth inhibitor in the T direction but not in the L direction. In fact, for the case of immersion at 25°C, we can observe that increasing contents of BNC caused a monotonous increase of cell size in the L direction, which was the exactly opposite case in the T direction. These results reinforce the hypothesis that BNC was increasing the anisotropic behavior of the foams,¹⁴ causing more heterogeneity in the variation of cell size.

The authors would like to compare these results with previous studies, however, no other previous work has dealt with the effect of BNC on cell size and anisotropy of RPUFs. It is important to emphasize that several studies report cell size in the L direction, while the T direction is usually disregarded. The anisotropic behavior of RPUF has already been extensively studied from an experimental as well as modeling point of view. A recent study of Andersons et al.⁵⁰ proposed a modified Kelvin cell model to obtain estimates of foam stiffness and strength as well as the effect of cellulose microfibrils.⁸ In particular, the elongated kelvin cell model can be applied to predict the role of anisotropy on the mechanical properties of RPUFs. Hamilton et al.⁵¹ studied the effect of milled glass fibers and montmorillonite-carbon hybrid NPs under tensile, compressive and shear states of stress. A relevant result reported in this work indicated that the normalized moduli of the composite foams increased by 4%–26% in the L direction while decreased by approximately 40% in the T direction. Other studies have also reported the effect of anisotropy on the mechanical properties of RPUFs.^{52–54}

3.3 | Fractured surface analysis

The fractured surface of the foams studied in this work are depicted in Figure 5. To emphasize on the geometry of the cells, its orientation as well as specific features, the micrographs depicted in Figure 5 are presented at low magnifications (150 $\times$). The first two columns were associated to the foams prepared from castor oil (RPUF_{RIC}), whereas the other columns represented the foams obtained from conventional petroleum based polyols. The first row in Figure 5 represented the micrographs of the foams in pristine conditions, while the micrographs of the fracture surface of the foams which were aged can be found in the subsequent rows. Finally, the growth direction is signaled in each micrograph with a green arrow. The most relevant feature of the micrographs was

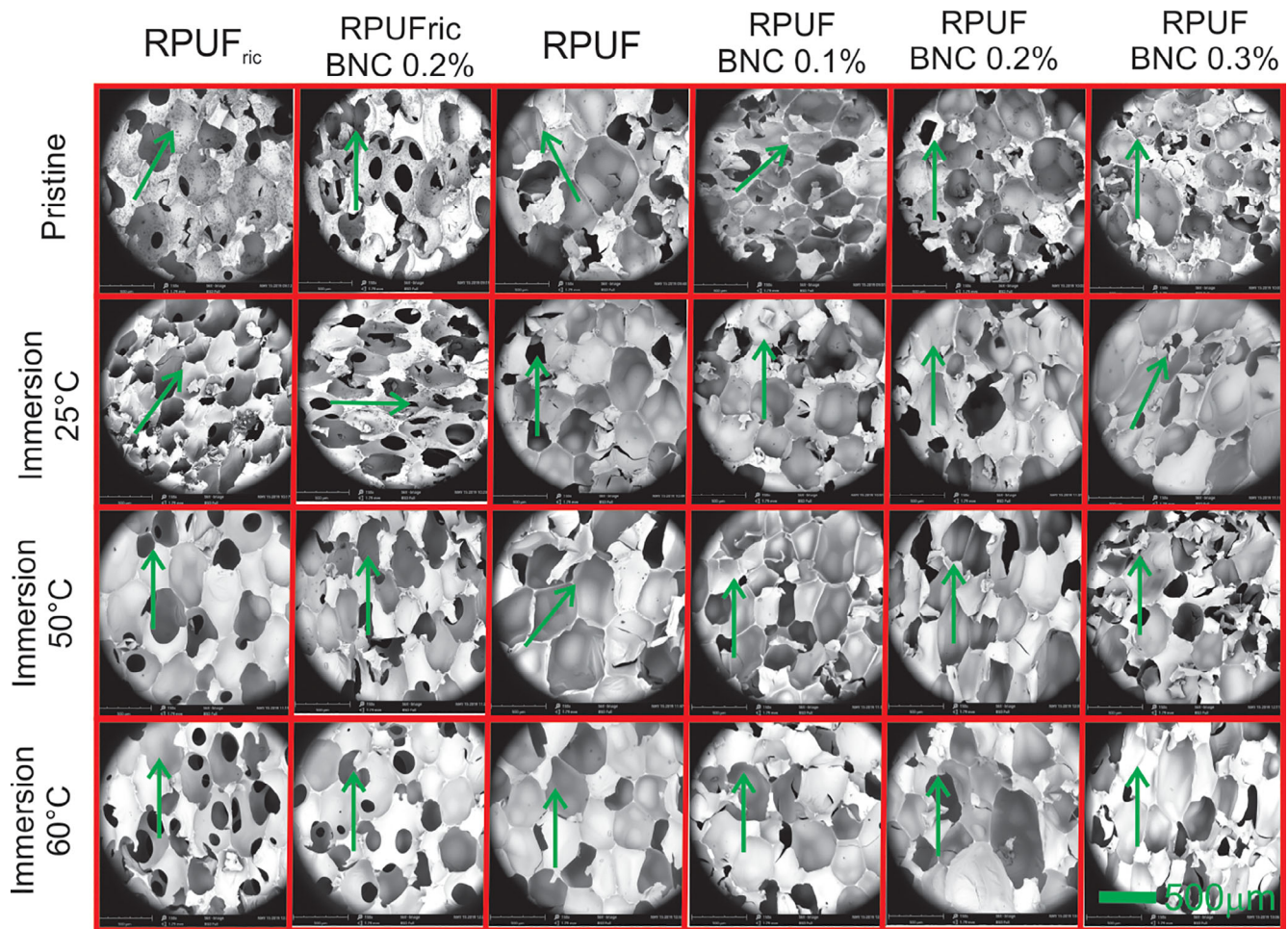


FIGURE 5 SEM micrographs as a function of polyurethane type and BNC content. The green arrows indicate the L direction

related to the presence of open cells, cell wall wrinkles and deformation. As it can be deduced from Figure 5, the higher population of open cells were associated mostly to the foams prepared with BNC. It is important to highlight that, in all cases, water immersion produced and increased amount of open cells, but, the observation of the micrographs of the pristine foams clearly indicated that BNC acted as a cell opener. Such result were completely logical and it has already been observed by our group as well as other researchers.^{14,35,55,56} Nowadays, it is known that BNC has a substantial role in the formation and rupture of cell windows during foaming and this aspect is clearly affected by the insertion route.^{14,39} Taking into account that in this work we have dispersed the BNC in the polyol component, then, it will certainly act as a nucleation agent and cell opener. The development of insertion routes which do not produce cell opening have already been studied by our group and can be consulted elsewhere.¹⁴ Another relevant feature of the micrographs depicted in Figure 5 is cell wall wrinkles. Wrinkling was mostly detected on aged samples,

particularly from RPUFs at 50°C. Taking into account that aging at such temperatures can cause a significant decrease of the elastic modulus of the polymeric cell wall, it was logical to observe such features. Indeed, it is also believed that such wrinkles can be the starting point of a cell rupture, particularly in aged foams at the highest temperatures. A final feature which was also encountered was excessive cell deformation. Such feature was particularly present for the RPUFs aged at 25°C. An interesting aspect of the cell deformation was its shape. As it can be deduced from Figure 5, the shape of the deformation indicated that the origin of such deformation was probably due to gas permeation. The combination of a low elastic modulus and unreacted isocyanate component probably caused additional foaming during aging.

3.4 | Thermal conductivity

The thermal conductivity (λ) as a function of polyurethane type and aging is depicted in Figure 6. It is

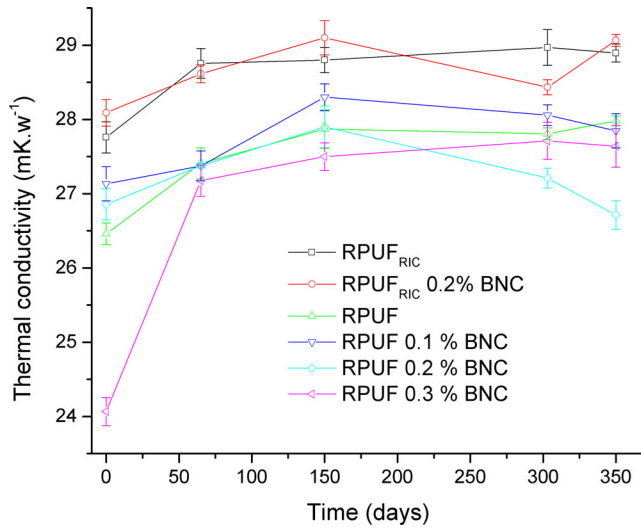


FIGURE 6 Thermal conductivity at ambient conditions as a function of time for the polyurethane foams prepared from castor oil, conventional polyols, and nanostructured with BNC

important to highlight that, only in this section, aging was associated to the exposure of the foams at ambient conditions (air, not water). So as to have an idea of the range of values the typical λ -value for RPUFs⁷ oscillate in the range $24\text{--}28 \cdot 10^{-0.3} \text{ W/(m K)}$. The first deduction than can be made from Figure 6 has to do with the fact that the λ -value of the RPUF_{RIC} was always higher than all the RPUF. Such result was expected because the foams prepared from castor oil did not have foaming physical agents within its formulation. For the case of the RPUF_{RIC}, the incorporation of BNC in the formulation had a negligible effect on both the initial λ -value as well as a function of aging, indicating that BNC did not have a substantial change on this property. On the other hand, for the case of the RPUF, the λ -value were also similar as a function of aging, but the initial values (pristine or without aging) indicated that BNC caused a decrease of the thermal conductivity in the order of 11.1%.

To understand the previously stated results, it has to be noticed that the thermal conductivity of a polymeric foam is mainly associated to the contribution of the radiative, solid, gas and convective components.³ Of all these, the most relevant is associated to the thermal conductivity of the retained gases within the cells. According to Estravís et al.,⁵⁷ the contribution of λ_{gas} in the overall thermal conductivity of the foam is in the order of 71%. Then, the discussion of how thermal conductivity changes as a function of specific variables has to be centered in this issue. Indeed, in our work we have measured that the thermal conductivity of the RPUF_{RIC} was indeed higher than the one associated to the RPUF,

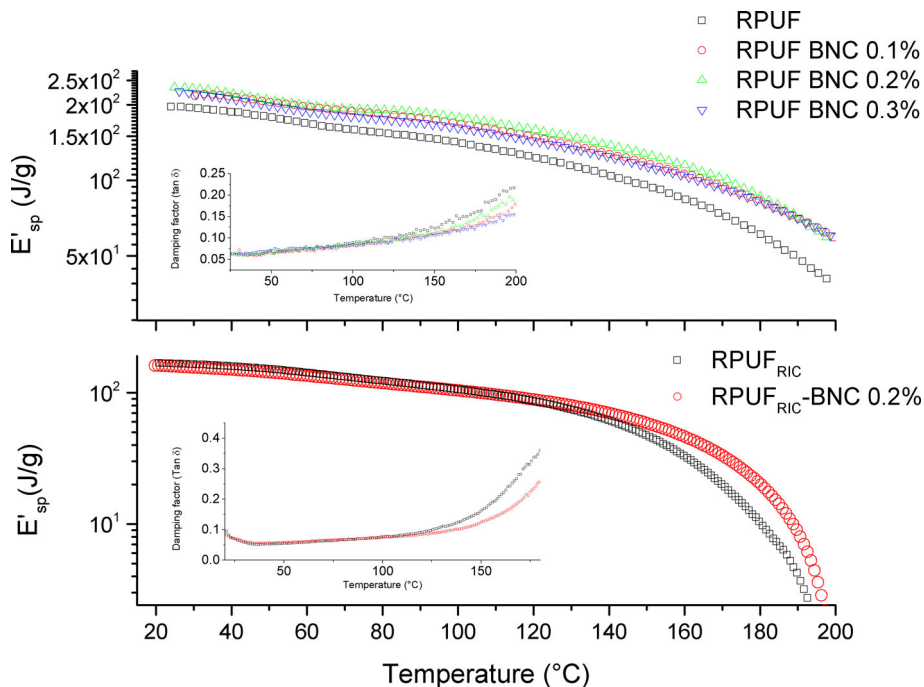
regardless of aging, processing condition as well as BNC content. This clearly indicates the relevance of the gases retained in the cells and that the values presented in Figure 6 clearly reflected that the physical blowing agent used in the formulation of the RPUF was retained within the cells. On the other hand, only $\text{CO}_2(\text{g})$ was present for the case of the RPUF_{RIC}. Taking into account that this gas easily permeates out of the cells, then, the only plausible gas retained in the cell was certainly air. The effect of BNC on the thermal conductivity was also highly correlated to the open cell content of the specimen under analysis. Processing conditions and the foam formulation (selection of surfactant) play a very relevant role in this regard. Finally, there has been several works which have already studied in depth the thermal conductivity of RPUFs as well as its aging effects.^{32,33,58,59} For this reason, our discussion in this work will be centered on the water immersion experiments.

3.5 | Dynamical mechanical thermal analysis

3.5.1 | DMTA for the pristine specimens

The specific storage modulus (E'_{sp}) as well as the damping factor of the pristine RPUF and RPUF_{RIC} (non-aged) samples as a function of BNC content are depicted in Figure 7. The evolution of E'_{sp} as a function of temperature followed a monotonous decrease, reaching more than an order of magnitude at a temperature of around 200°C . After this temperature, the E'_{sp} of all samples were extremely small for the experiment to continue. The main difference between the evolution of E'_{sp} for the case of the RPUF versus the RPUF_{RIC} had to do with the fact that for the latter the E'_{sp} retained a higher value at higher temperatures ($>100^\circ\text{C}$). This observation can be justified based on the molecular structure of both polyurethane types. As already noticed in a previous work of our group,³⁴ the RPUF had a higher crosslinking degree, then, it was expected that the E'_{sp} should be retained up to higher temperatures. In addition, this tendency was also present at lower temperatures. For example, at approximately 30°C , the E'_{sp} of the RPUF_{RIC} was 28% lower with respect to the RPUF. On the other hand, the influence of BNC content had a different effect in each polyurethane type. For the case of the RPUF, all BNC concentrations caused an increase of the E'_{sp} , which was in the order of +15%. As already noticed in a previous work of our group, increasing BNC concentrations did not cause substantial improvements of the specific properties.³⁴ Small concentrations and better dispersion were the key to achieve improved mechanical properties. On

FIGURE 7 Specific storage modulus (E'_{sp}) and damping factor (inset) for the non-aged RPUF (up) and RPUF_{RIC} (down) as a function of temperature



the other hand, for the case of the RPUF_{RIC}, the E'_{sp} retained its E'_{sp} as a function of BNC content. Taking into account that the values presented in Figure 7 represented averages of several samples, it can be argued that cell anisotropy played a very important role in this case. It is important to highlight the fact that the samples were obtained cutting along the L and T directions. However, these directions were previously associated to the molded foam growth experiment. That is, the L direction was ascribed to the physical direction where the foam was able to freely expand. Taking into account what has been explained in Sections 3.2 and 3.3, it can be deduced that BNC caused higher anisotropy in this last case.

The damping factor ($\tan \delta$) as a function of temperature for the RPUF and RPUF_{RIC} is depicted in the inset of Figure 7. The evolution of $\tan \delta$ reflected the behavior previously measured by our group and other studies.^{14,34,60–62} In this regard, a wide temperature transition was measured which started at room temperature all the way up to the highest temperature of the experiment, indicating that the transition temperature was probably higher than the maximum measured temperature (200°C). This result was logical and in accordance to crosslinked polymeric structures. Even though the maximum value of $\tan \delta$ was not measured, it can be clearly discerned that the maximum changed its position as a function of BNC content. In fact, for all the foams nanostructured with BNC and regardless of polyurethane type, the extrapolated damping factor indicated a lower absolute value, which can be associated to an improvement of

viscoelastic mechanical response, giving an improved toughness.

3.5.2 | In-situ DMTA aging experiments

The results of the in-situ DMTA experiments under water immersion are depicted in Figure 8. The specific storage modulus as a function of time (E'_{sp}), absorption and polyurethane type for the RPUF_{RIC} are depicted in Figure 8d–f. In these graphs, the experiments were divided into three columns which corresponded to each isothermal experiment, that is, at 25, 50, and 60°C, respectively. First, it is important to contrast how the results changed as a function of time and also as a function of absorption. For example, in Figure 8a, the lower plot depicts the evolution of E'_{sp} as a function of time. As it can be seen, the E'_{sp} decreased monotonously as a function of time. In contrast, the evolution of E'_{sp} for the same experiment but expressed as a function of absorption had a dissimilar pattern. Indeed, from Figure 8a it can be deduced that the E'_{sp} only decreased significantly when the steady state was achieved. These results are completely logical because significant changes on the mechanical properties are usually ascribed to a significant amount of water content within the cells. However, the results also reflect an important fact which is directly associated to the geometry of the specimens. Indeed, the results which are reported as a function of time should be highly dependent on specimen geometry. If the area exposed to the immersion medium increases, then, the

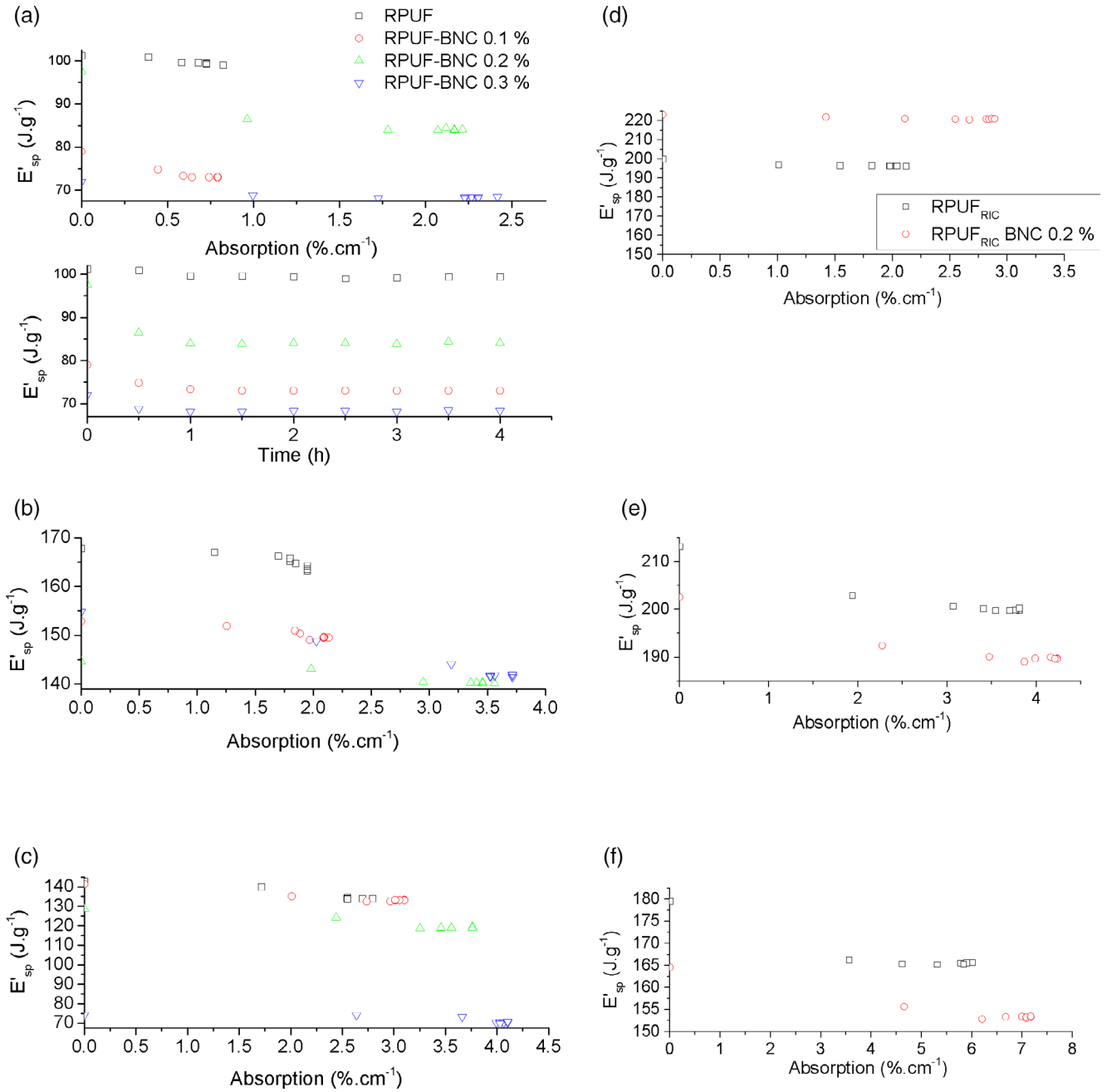


FIGURE 8 Specific storage modulus (E'_{sp}) as a function of time (only a) and absorption for the RPUF, RPUF_{RIC} and the nanostructured counterparts at immersion temperatures of (a) 25°C, (b) 50°C, (c) 60°C, (d) 25°C, (e) 50°C, and (f) 60°C

time to reach the steady state should decrease. For this important reason, our analysis will focus on the evolution of E'_{sp} as a function of normalized absorption.

To perform a quantitative analysis of the results depicted in Figure 8, the percentage variation of both E'_{sp} ($\Delta E'$) and NWA (ΔNWA) are reported in Table 3. For example, at 25°C, the $\Delta E'$ of the RPUF_{RIC} was 1.73%. This meant that the E'_{sp} decreased by 1.73% from its initial non-aged state (null NWA) and to its final aged state (maximum NWA).

For the case of the RPUF_{RIC}, the reduction of E'_{sp} as a function of aging (increasing NWA values) was relatively small. In fact, even at the highest immersion temperature analyzed (60°C), the E'_{sp} decreased by approximately 7.27%. Another relevant aspect can be deduced comparing the temporal and absorption evolution of E'_{sp} (Figure 8). For example, in Figure 8a, a significant change of E'_{sp} was measured after only 30' of aging (immersion). However, when the values are referred to NWA, a completely different scenario occurred. Indeed,

TABLE 3 Variation of specific storage modulus and normalized water absorption as a function of polyurethane type and aging temperature

Polyurethane type	Immersion T ($^{\circ}\text{C}$)	DE' (%)	ΔNWA (%)
RPUF	25	$-1.79.10^0$	$7.26.10^{-1}$
RPUF	50	$-2.22.10^0$	$1.95.10^0$
RPUF	60	$-6.20.10^0$	$2.74.10^0$
RPUF-BNC 0.1%	25	$-7.47.10^0$	$7.65.10^0$
RPUF-BNC 0.1%	50	$-2.22.10^0$	$2.11.10^0$
RPUF-BNC 0.1%	60	$-5.76.10^0$	$3.03.10^0$
RPUF-BNC 0.2%	25	$-1.37.10^1$	$2.16.10^0$
RPUF-BNC 0.2%	50	$-3.01.10^0$	$3.45.10^0$
RPUF-BNC 0.2%	60	$-5.94.10^0$	$3.61.10^0$
RPUF-BNC 0.3%	25	$-4.85.10^0$	$2.34.10^0$
RPUF-BNC 0.3%	50	$-8.49.10^0$	$3.72.10^0$
RPUF-BNC 0.3%	60	$-4.85.10^0$	$4.10.10^0$
RPUF _{RIC}	25	$-1.48.10^0$	$2.04.10^0$
RPUF _{RIC}	50	$-6.92.10^0$	$3.75.10^0$
RPUF _{RIC}	60	$-7.05.10^0$	$5.87.10^0$
RPUF _{RIC} -BNC 0.2%	25	$-2.00.10^0$	$2.84.10^0$
RPUF _{RIC} -BNC 0.2%	50	$-7.19.10^0$	$4.22.10^0$
RPUF _{RIC} -BNC 0.2%	60	$-7.28.10^0$	$7.12.10^0$

as it can be deduced from Figure 8, only at values very close to the steady state the changes of E'_{sp} ($\Delta E'$) were significant.

Continuing with the analysis, the role of BNC in the RPUF_{RIC} was not relevant, because the $\Delta E'$ values for the RPUF_{RIC} and its RPUF_{RIC} BNC counterparts were very similar. The only relevant effect was that the addition of BNC had only the effect of increasing the final ΔNWA by 21%, as already noticed in Section 3.1. The main cause of this variation has to do with the nature of BNC. It is known that BNC is highly hydrophilic,¹⁸ hence, it is logical to expect that a material which is nanostructured with pristine BNC should have a higher hydrophilic nature. Even though the RPUF_{RIC}-BNC absorbed more water at the steady state (see Figure 2), the final E'_{sp} did not decrease in proportion to what it should be expected if the values of the RPUF_{RIC} were extrapolated to higher NWA values. Hence, it can be understood that BNC was indeed producing a twofold effect on the physico-mechanical properties of the resulting foam. Indeed, one possible effect is that the incorporation of BNC caused a decrease of the closed cell content and a higher hydrophilic character. Both aspects should be considered detrimental to the properties of foams which are suited for insulation purposes, but not for foams which are tailored to other applications, such as absorption of heavy metals.³ The other effect is reflected on the resultant mechanical properties. Even though the BNC increased the mechanical properties of the RPUF_{RIC}, this increase

is hindered and attenuated by the first effect previously described. This tendency is present in all the foams studied in this work, and it can be deduced because most of the experimental points are concentrated at NWA values close to the steady state (see Figure 8).

For the case of the RPUF, the reduction of E'_{sp} as a function of aging is also reported in Table 3. The results indicated that the changes of E'_{sp} were very small as a function of aging. In fact, the maximum $\Delta E'$ was 6.19% for an experiment performed at 60°C. In contrast, the nanostructured RPUF had a different behavior, reaching $\Delta E'$ values of up to 13.69%. It is important to notice that the maximum $\Delta E'$ was measured for the RPUF-BNC 0.2% in an isothermal experiment performed at 25°C. In contrast, the aging experiments performed at both 50 and 60°C had much lower values. At first sight, this seems to represent a logical contradiction. In fact, it is expected that the $\Delta E'$ should increase monotonously as a function of aging temperature, as it was usually the case for all the other foams tested in this work. To further corroborate the results, we conducted additional experiments, finding values in agreement to what it is reported in Table 3. To explain this logical contradiction, we established the hypothesis that the foams prepared with BNC at concentrations higher than 0.1% had not been fully cured at room temperature. We based our hypothesis on a recent published paper where we found that the cure enthalpy of these foams were indeed affected for BNC concentrations above 0.1 wt%.¹⁴ This indicated that the foams were

not fully cured, hence, when the isothermal aging experiments were performed at higher temperatures, then, not only absorption and degradation of mechanical properties of the foam occurred, but also curing (enthalpic heat of reaction). This hypothesis explains why the relevant change of $\Delta E'$ was only measured at 25°C. Indeed, as it can be deduced from Table 3, the isothermal aging experiments performed at 50 and 60°C presented values similar to the RPUF. Then, what probably happened was that, at 25°C, the foams nanostructured with BNC were not properly cured, giving rise to poor mechanical properties and, consequently, severe aging. On the other hand, for higher temperatures, the foam was simultaneously curing and aging, giving an overall improved performance. To further support this hypothesis, we conducted additional experiments using RPUF-0.2% BNC samples which were previously cured in an oven at 50°C for 4 h. Then, the subsequent water immersion experiments were performed. The results of these experiments proved that the hypothesis was correct. Hence, it can be concluded that the RPUF nanostructured with BNC had to be post-cured at higher temperatures so as to ameliorate aging effects on mechanical properties. In this regard, it is relevant to notice that foams which are applied as insulation materials are not frequently post-cured. Then, this might represent a problem towards the practical application of RPUF nanostructured with BNC at higher loadings (>0.2%). To ameliorate this effect, a change in the catalyst formulation has to be performed to avoid this effect. Another possibility is to directly react the BNC with the isocyanate precursor. In a recent publication,¹⁴ we have developed a new BNC insertion route which is based on the reaction of BNC with the isocyanate precursor. By avoiding the conventional route of insertion which is based on the colloidal dispersion of BNC in the polyol component, our group has achieved substantial improvements of specific mechanical properties. As a remainder, in this work we have used the conventional dispersion method, whereas the BNC is colloiddally dispersed in the polyol component and later reacts with the isocyanate precursor giving rise to the polyurethane foam.

Taking into account that no other publication has dealt with the in-situ DMA aging of RPUF nanostructured with BNC produced with both petroleum-based polyols as well as castor oil, it is difficult to compare the results presented in this section with what has been published. However, similar studies have been published in this area. Most of it was focus on how the thermal conductivity changed as a function of time with very few works emphasizing on water immersion and its effect on thermomechanical properties. Zhou et al.²⁷ studied the effect of water immersion at ambient temperature on the

properties of semi-RPUFs obtained from palm-oil polyol and nanostructured with CNCs. They found that significant water uptake (up to 400%) was probable due to an increase of open cell content, but no results of the variation of mechanical properties as a function of immersion were reported. Davies et al.²⁵ studied the effect on mechanical properties after a long term (up to 5 years) immersion at sea. The results indicated that RPUF obtained from petroleum sources retained its mechanical properties after such long term exposure, in agreement to what we have found in this work. Recently, Liszkowska et al.^{63,64} studied the biodegradation and photodegradation of RPUF derived from sorbitol and modified by natural compounds of plant origin, such as cinnamon, green coffee extract and others. They found that the incorporation of such components increased biodegradation. On the other hand, Barszczewska-Rybarek et al.²¹ studied the effect of seawater immersion on the mechanical properties of RPUFs for temperatures within the range of 40–80°C. Similarly, to the results of this work, they found that post-cure of the foams caused an improvement of mechanical properties, particularly T_g . In addition, they found very small changes of flexural properties as a function of exposure, in agreement with the results we have presented above. Silva et al.²⁶ studied the incorporation of tire waste in a polyurethane foam derived from castor oil. Very small water uptake (in the order of 1.5 wt%) was measured after exposure at ambient temperature. The authors of this work did not focus on the variation of mechanical properties as a function of immersion conditions.

It is important to emphasize that polyurethanes cover several industries. In this work, the focus was on RPUFs. Other works have been published for polyurethane adhesives,^{65,66} thermoplastic polyurethanes,²⁸ flexible foams⁶⁷ as well as thermosetting polyurethanes.²⁹ However, those results cannot be compared with this work due to the fact that the microstructure as well as the chemical structure of the materials unable us to perform a valid comparison.

4 | CONCLUSIONS

The experiments conducted in this study reinforce the hypothesis that the incorporation of BNC as a nanofiller can have a negligible effect on the aging performance of petroleum based RPUFs as long as low BNC concentrations are employed. Taking into account the results of previous work performed by our group,^{6,18,40} it can be inferred that the nanostructured RPUFs can have both improved specific thermo-mechanical properties as well as aging performance. Then, it can be argued that the

application of these nanomaterials in the insulation and marine industries can lead to an improvement of the current state of the art properties. Special care needs to be taken to ensure that the foam is properly cured.

On the other hand, the substitution of a petroleum based polyol with castor-oil had a relevant effect in open cell content, increasing the normalized water absorption at the steady state with respect to the RPUF. Nonetheless, these measurements did not have a significant effect on the in-situ specific flexural modulus, indicating that the foam retained its mechanical properties after aging. In addition, the incorporation of BNC in the foam obtained from castor-oil had a reduced impact on aging performance, particularly when this effect is compared with petroleum based polyols. Then, the successful implementation of castor-oil based polyols in both the insulation and marine industry require the use of new formulations which enable the reduction of open cell content. The benefits of using BNC in castor-oil foams are the same as the ones described above for petroleum based polyols.

Future work in this area will focus on the aging of BNC based foams prepared using the iso-route described above. This is a key aspect for the development of nano-structured polyurethane foams which do not require complicated processing paths for the manufacture of the final product.

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DATA AVAILABILITY STATEMENT

Data available on request due to privacy/ethical restrictions.

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