Supplementary Materials

Section S1

Characterization

1.1. Characterization of the foams

The bulk density of the foams (ρ_f) was obtained from the ratio between its weight (W_f) and volume (V_f) calculated by its width (W), length (L) and thickness (l) measured by a digital caliper (Mastercraft, USA). The measurements were taken at four random positions to calculate the average. The bulk density was obtained as:

$$\rho_f = \frac{W_f}{V_f} = \frac{W_f}{L\,W\,l} \tag{1}$$

Then, the porosity (P) was obtained from:

$$P = \frac{\rho_l - \rho_f}{\rho_l - \rho_a}(100\%) \tag{2}$$

where ρ_a and ρ_l is the density of air (1.225 kg/m^3) and unfoamed PP (910 kg/m^3), respectively. The unfoamed PP volume (V_l) was determined as:

$$V_l = \frac{\rho_f - \rho_a}{\rho_l - \rho_a}V_f \tag{3}$$

while the gas phase (air) occupies a volume of:

$$V_a = P\,V_f \tag{4}$$

The samples were then immersed in ethanol for 3 days. The ethanol volume absorbed (V_e) was associated with the weight gained (W_e), while its density (ρ_e) is 789 kg/m^3 to combine with the matrix mass ($V_l\rho_l$) to give:

$$V_e = \frac{W_e - V_l\rho_l}{\rho_e} \tag{5}$$

The open cell content (OCC) was calculated as the ratio between the volume of ethanol and air as:

$$OCC = \frac{V_e}{V_a}(100\%) \tag{6}$$

1.2. Foam morphology

The cell dimensions were obtained via scanning electron microscope (SEM) using a Zeiss Crossbeam 540 FIB/SEM (Carl Zeiss, Germany). The cross-sections were exposed by cutting 1.5 mm thick slices before coating (Au/Pd). The images were then quantitatively analyzed (morphology analysis) to get the cell diameters via the Image J software (National Institutes of Health, USA).

1.3. Poisson's ratio

The Poisson's ratios were determined under tension and compression. Tensile measurements were performed using a dynamic mechanical analyzer (DMA) model RSA 3 from TA Instruments (USA). On the other hand, compressive measurements were done on a model 5565 from Instron (USA). The deformation rate was fixed at 1.2 mm/min and the deformations were determined using a high-resolution video camera (FDR-AX53, SONY, Japan) in two perpendicular directions. Then, ImageJ was again selected to perform image analyses after dimensions calibration. The Poisson's ratio (v) was obtained as the negative ratio between the transverse (ε_y or ε_z) and axial (ε_x) deformations as[1]:

$$v = -\frac{\varepsilon y}{\varepsilon x} \; or \; -\frac{\varepsilon z}{\varepsilon x}$$

(8)

1.4. Mechanical properties

The tensile and compressive stress-strain data were obtained by both the RSA 3 and Instron 5565. The tests were done at 1.2 mm/min for both tension and compression and the modulus was determined by the slope in the linear region of the stress-strain curves (below 5% deformation). The samples dimensions were about 3 mm x 5 mm x 30 mm (tension) and 45 mm x 45 mm x 25 mm (compression). Toughness was determined as the area below the stress-strain curve up to failure as:

$$Toughness = \int_{0}^{\varepsilon_f} \sigma(\varepsilon)d_\varepsilon$$

(9)

where σ is the stress (MPa or N/mm²), ε is the strain (unitless), and ε_f is the strain at failure. Finally, the elastic limit represents the maximum stress without permanent (plastic) deformation. Once a material goes over this limit, it will not return to its original shape when the stress is

removed. This is a parameter of importance for long term use of materials in terms of dimensional and mechanical stability.

The storage modulus (E′) and tan δ of the auxetic PP foam in tension and compression were measured using a DMA (RSA-3, TA Instruments, USA). The temperature was increased from 30 to 100 °C (tension) and 30 to 140 °C (compression) at 10 °C/min, with a strain of 0.1% and a frequency of 1 Hz. The loss tangent (tan δ), defined as the ratio between the loss modulus and the storage modulus, was also determined via DMA as:

$$\tan \delta = \frac{E''}{E'}$$

(10)

Section S2

Poisson's ratio

2.1. Vacuum Time

Fig. S-1 presents the results for different vacuum periods (18, 24 and 48 h). When the foam is under vacuum for a specific time, the pressure inside the cells reaches equilibrium with the pressure outside the cells. When the oven returns to ambient pressure, the air pressure outside the foam cells exceeds the internal cell pressure. Higher imposed pressure compresses more the foam, leading to rapid shrinking and limited cell wall collapse generating a re-entrant structure. The morphology is locked in place after cooling down to room temperature. Thus, the driving force behind the formation of the re-entrant structure is the pressure differential between the outside and inside of the cells. In theory, longer vacuum periods make it easier to achieve this force.
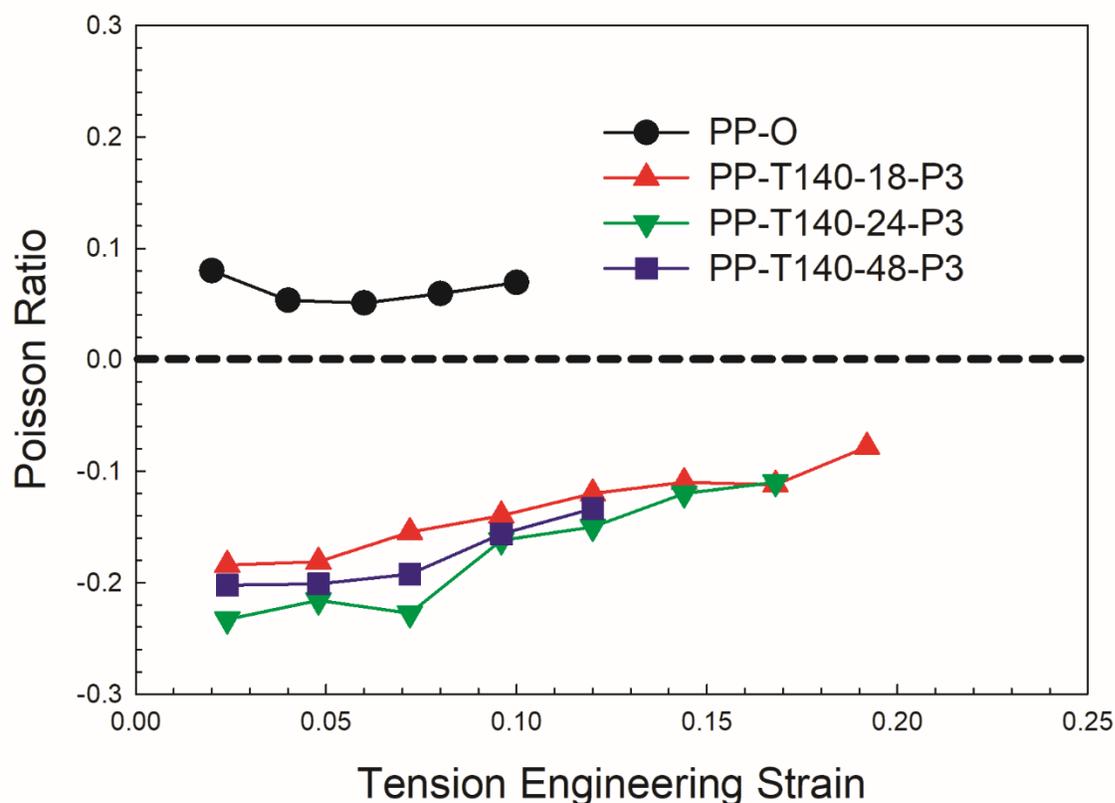
Figure S-1. Poisson's ratio as a function of engineering strain (tension) for auxetic foams treated for different time at 140 °C under vacuum (-0.88 bar) and mechanical pressure (3 kPa).

Based on the results of Fig. S-1, it was observed that the NPR values were very close for 18, 24 and 48 h, with 24 h showing the most negative values. Therefore, 24 h was selected as the optimal vacuum time for the subsequent steps, as it represents an equilibrium between an effective re-entrant structure formation and limited experimental time. This period likely allows for optimal pore alignment and structural reconfiguration, ensuring that the auxetic foam achieves a stable and well-formed re-entrant structure.

To improve the NPR value, the processing conditions were optimized. During this process, the maximum vacuum level (-0.88 bar) was applied for all experiments. From our previous study [2], a temperature of 140 °C was selected. However, it was necessary to control the other parameters,

namely vacuum time and mechanical pressure (Table 1). The effect of each parameter is described next.

2.2. Mechanical Pressure

Applying mechanical pressure induces more deformation to help create the re-entrant structure. This also generates higher final densities. Nevertheless, excessive pressure leads to cell collapse, destroying the structure produced as reported in our previous investigations [2-4].

To determine the best mechanical pressure, four levels (0, 3, 5 and 9 kPa) were selected using the maximum vacuum available (-0.88 bar) for a duration of 24 h at a temperature of 140 °C. Figure S-2 presents the Poisson's ratio as a function of tensile engineering strain for the different mechanical pressures applied. A comparison between P3, P5 and P9 shows similar trends leading to the same minimum PR (-0.23, -0.22 and -0.18, respectively), but different than that of P0 (-0.12). So 3 kPa was used to minimize the applied force, while generating the best NPR.
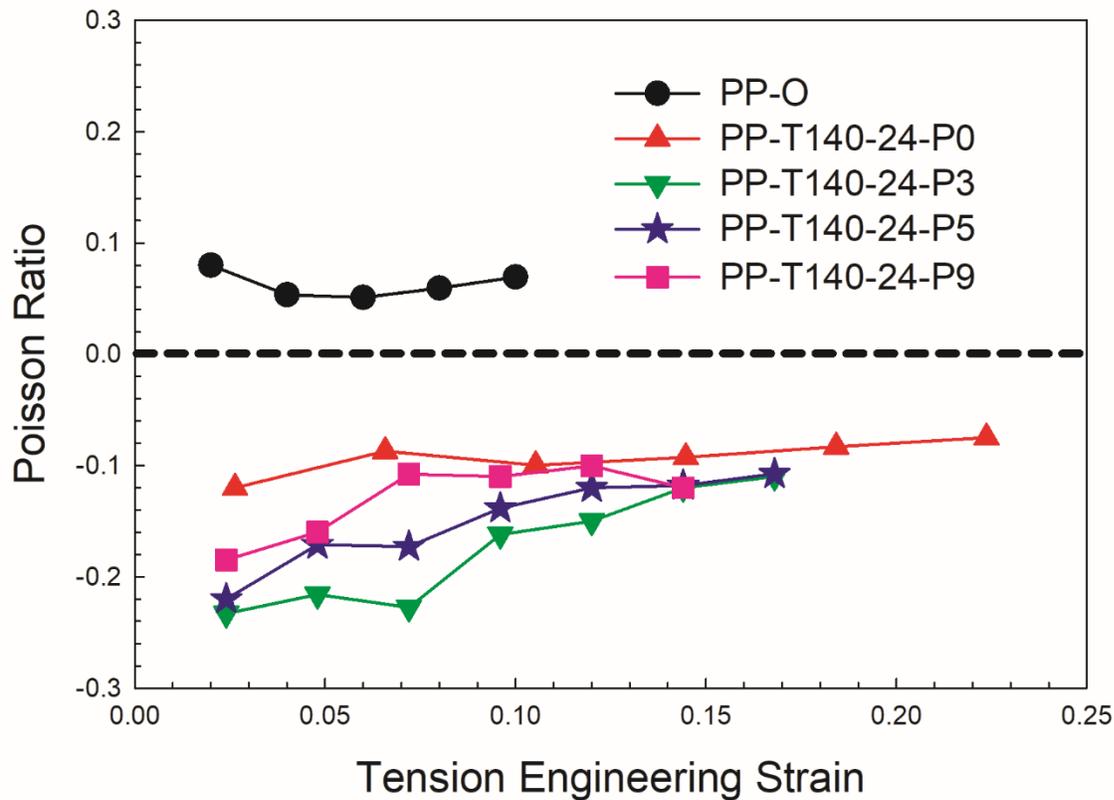
Figure S-2. Poisson's ratio as a function of engineering strain (tension) for auxetic foams treated under different mechanical pressure at 140 °C for 24 h of vacuum (-0.88 bar).

To complete the analysis, the Poisson's ratio (PR) as a function of compressive engineering strain was studied for both the original PP foam (PP-O) and auxetic foams treated with different mechanical pressures. Figure S-3 compares all the samples together.
In theory, applying higher mechanical pressure in the treatment should generate a more important force to create a re-entrant structure in the foam. However, applying too much pressure excessively compresses the foams, causing cell collapse, leading to higher density (Table 1) and a subsequent loss of the auxetic behavior.
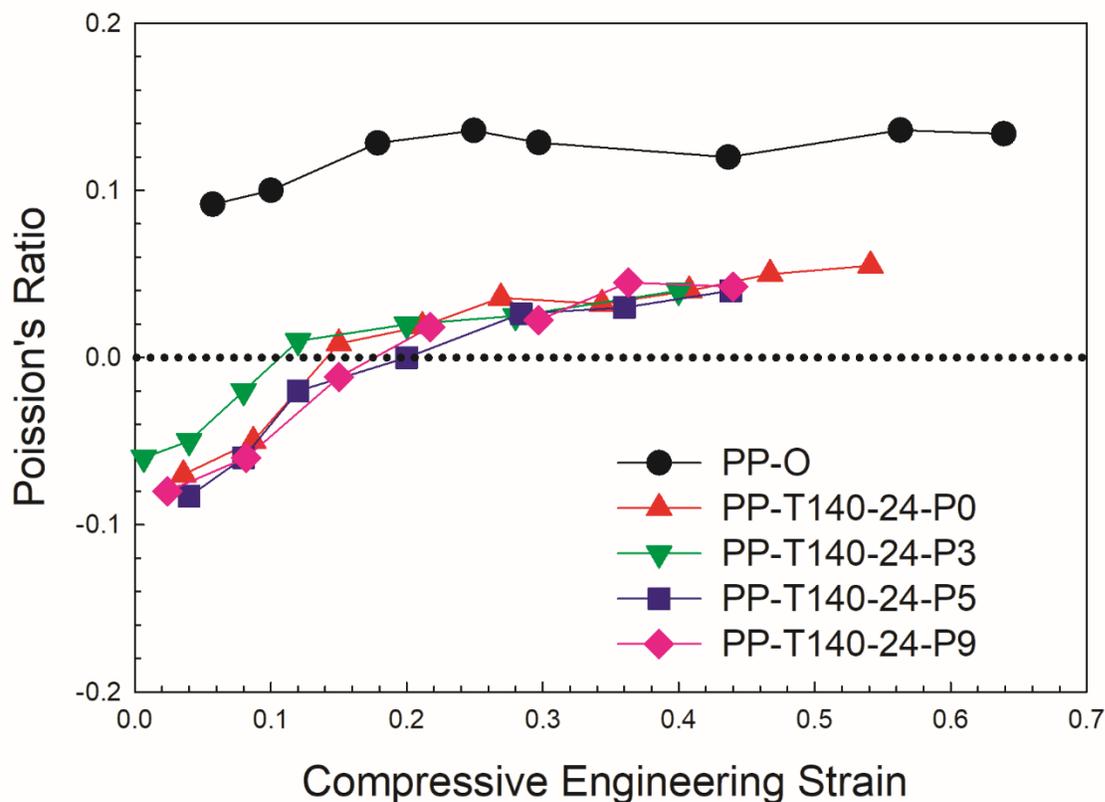

Figure S-3. Poisson's ratio as a function of engineering strain (compression) for PP-O and auxetic foams treated with different mechanical pressure at 140 °C for 24 h of vacuum (-0.88 bar).

References

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