COMBINING FOAMING TECHNIQUES TO ATTAIN TPU POROUS HETEROSTRUCTURES

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Abstract

The production of porous thermoplastic polyurethane (TPU) heterostructures was achieved by combining physical gas foaming with fused deposition modeling (FDM). The choice of combining these two techniques lies in the possibility of creating a macrostructure by FDM and a microstructure by foaming. The thermal stability and rheological properties of the polymer were investigated prior to foaming. Three different foaming processes are proposed: Pressure Quench (PQ), Temperature Rise (TR) and 3D Foam Printing (3DFP). The morphologies of the foams were evaluated by SEM and the expanded structures were thermally and mechanically characterized to highlight the differences between these process methods. The results presented in this paper open up the possibility of producing objects with complex geometry and porosity avoiding the traditional processes of material removal.

Introduction

The potential in design the fine structure is of great importance to improve and tune properties of a material for each technological application.

According to IUPAC association, porous materials can be classified into three categories based on the pore size: macroporous (size >50nm), mesoporous (2<size<50 nm) and microporous (size<2 nm). Porous heterostructures display a composition of macro and micropores, whose distribution can be controlled by synthesis and manufacturing. They represent an interesting material in the field of the light structures and have many industrial applications thanks to their mechanical, thermal and sound insulating properties [1].

Thermoplastic polyurethanes (TPUs) are a class of thermoplastic elastomers. They are linear block copolymers of soft and hard segments. Such a structure gives to TPU high tensile strength and a wide elastic region [2, 3, 4]. Due to these properties, TPUs are polymers with versatile performances and a wide range of applications including foaming and Fused Deposition Modeling (FDM) [5, 6, 7].

Physical foaming using Carbon Dioxide (CO₂) as blowing agent has environmental, economic and technical advantages and produces foams with lower density and uniform cell morphology[8]. TPU-based foams have high flexibility, light weight structure and good impact properties but high shrinkage ratio and low mechanical strength could limit their applications. Moreover, due to random cell formation mechanism, gas foaming is not a satisfactory processing method to finely locate pores in the material. Then, coupling physical foaming to a processing technique able to control pore location and to increase mechanical strength of foams represents a way to enlarge the range of applications.

FDM is a solvent free additive manufacturing method where the filament is extruded from the nozzle and stacked layer-by-layer following a predetermined model. The advantage in processing materials by FDM is to reduce manufacturing costs and obtain hierarchical structure on a large scale with improved design flexibility. The resolution of FDM is nowadays of about 100µm which is not suitable and time consuming for the design of a microporous structure.

Since gas foaming can form micrometer-sized cells, the combination of these two processing methods is exploited in this research to finely design the porous architecture at a dual scale and create a TPU-based macrostructure via FDM and a microstructure via physical foaming. The comparison of three processes, Pressure Quench (PQ), Temperature Rise (TR) and 3D Foam Printing (3DFP) is reported, to gain a deep understanding in mechanical properties of manufactures obtained by coupling gas foaming and FDM.

Materials and Methods

Materials

A commercial TPU with shore of 55D, a diameter of 1.75mm and a density of 1.25 g / cm³ was purchased by FILOALFA (Italy) and used as received.

Methods

For additive manufacturing, The Original Prusa I3 MK3S 3D printer was used.

Foaming process was conducted in a batch autoclave with a volume of 0.3L [9].
The macrostructure of the samples reproduces the Gibson & Ashby model \[10\]. This model is used to simulate the mechanical behavior of the internal cells of the foams.

**Characterization**

To fine-tune the processing conditions and pre-treatment requirements, thermal and rheological analyses were conducted.

A Perkin Elmer Diamond TGA was used for the thermogravimetric analysis. Samples were prepared with a weight of approximately 5 mg. The dried samples were placed in an oven at 60°C overnight. The test was carried out both in air and in nitrogen with a ramp of 20°C/min from 30°C to 800°C with a flow of 30 mL/min.

The thermal properties of the samples were investigated using a Perkin-Elmer Pyris Diamond DSC, equipped with an Intracooler II. The samples were heated from -50°C to 240°C at a rate of 100°C/min.

In order to measure the viscoelastic properties of the TPU samples with different hard segment contents, rheological measurements were made with an angular frequency between 0.1 and 100 rad/s at 200-210-220-230°C. A rotational ARES II rheometer from TA Instruments was implemented for measurement using a parallel plate of 25mm in diameter with a gap of 1mm. A dynamic temperature ramp test at a constant rate of 10°C/min was also performed to investigate the thermal dependence of the viscoelastic properties between 190 and 230°C.

The compression properties were tested in displacement control, using a universal electromechanical machine (INSTRON mod. 4325y234, AL, USA), with a head speed of 5 mm/min with a load cell of 0.1 KN.

To minimize the instabilities caused by printing, the specimens were rotated by 90° with respect to the printing axis.

Density measurements were performed according to the ASTM D792 standard, using an analytical balance (Mettler Toledo, Columbus, OH). Ans two procedures were used to evaluate density:

1) Locally, analyzing a piece of the structure:
   \[
   \rho_{\text{strut}} = \frac{m_A}{(m_A - m_{H_2O})} \tag{1}
   \]
   where \(m_A\) and \(m_{H_2O}\) are the masses of the polymer in air and water respectively.

2) Considering the structure as a solid:
   \[
   \rho_{\text{app}} = \frac{V}{m} \tag{2}
   \]
   Where \(V\) is the volume and \(m\) mass of the structure.

The cellular structure of the foams was studied using a scanning electron microscope (TM3000 TableTop). The specimens were first sectioned with a blade and then coated with gold and palladium.

**Processing methods**

**Pressure Quench (3P)**

The model is printed at a speed of 20mm/s, with a layer height of 0.3mm, printing temperature of 230°C and a nozzle of 0.4mm. Then the model was placed in the autoclave preheated to a temperature of about 175°C, the vacuum is applied for 10 min, until reaching 180°C. CO\(_2\) was injected at a pressure of 120 bar and the sorption occurred for 10 minutes, then CO\(_2\) was released through the ball valve.

The foaming conditions have been set to avoid TPU degradation and achieve controlled expansion.

**Temperature Rise (3T)**

The models printed with the same protocol used for 3P were saturated with CO\(_2\) at a pressure of 40 bar at room temperature for about 1 hour in the autoclave. In the meantime, a diathermic oil (ThermoFischer Scientific synth 260) was heated to a temperature of 120°C. After extracting the saturated models from the autoclave, they were immersed in hot oil for 10s and then cooled to room temperature.

**3D Foam Printing (F3)**

The samples were foamed in one process. The filament was saturated with CO\(_2\) at a pressure of 50 bar at room temperature for 1 hour before printing step. Then the filament is removed from the autoclave for the printing step and about 10 minutes passed before the filament was inserted into the printer.

The model was printed at a speed of 20 mm/s with a temperature of 215°C, just enough to melt the polymer and start the simultaneous foaming.

Lower temperatures were used than previous prints, to better control foaming and adhesion between layers by exploiting the CO\(_2\) plasticization effect. In this process, the speed of the extrusion cooling fan must be adjusted to ensure that the layer cools down enough not to collapse the structure but not too much to prevent the next layer from sticking. In our case a fan speed of 20% was used.

**Results**

**Material characterization**

Rheological tests were performed on the TPU filament in order to evaluate the optimal temperature for 3D printing.
Figure 1 reports the storage ($G'$) and loss ($G''$) moduli as functions of frequency at different temperatures.

![Graphs showing $G'$ and $G''$ over frequency at different temperatures.]

At 200°C (Figure 1.A) the polymer is a soft solid, being $G' > G''$. While at 210°C, 220°C and 230°C (Figures 1 B-D) it is a purely viscous fluid, with $G'' \gg G'$ and with a unit slope with respect to the frequency. Deviations of the slope of $G'$ from the terminal slope of 2 might be attributed either to incoming crystallization or to low sensitivity of the instrument.

Thermal Ramps from 190 to 230°C (and back) at 10°C/min were also carried to identify possible phase transitions. From Figure 2, it is evident that the polymer liquefies between 200°C and 210 °C. In the return ramp, there is no transition, probably due to the degradation of the polymer at high temperature. Then, the optimal printing temperature is greater than 210 °C. Temperatures higher than 230°C would induce thermal degradation which would negatively affect the printing process.

![Graph showing TPU ramp from 190°C to 230°C.]

From these results it was evident that it was not necessary to carry out an oven treatment before printing.

**Morphologies**

The resulting structures are visible in Figure 4. The samples after the foaming process have maintained the printed macrostructure.

![Morphology images: A) 3P; B) 3T; C) F3.]

The internal morphologies reported in Figure 5, were analyzed by SEM at different magnifications.

![SEM images of the structure obtained for A) 3P; B) 3T; C) F3.]

Sample 3P shows the most homogeneous morphology (cell size approx. 400 μm), while foaming 3T produces the smaller cells (less than 200 μm). Sample F3 displays an uneven cells spatial distribution and cells have a slightly elongated shape due to the stretching of the expanded
filament during the printing process. Furthermore, in the foam produced by F3, the space between the layers is no longer visible due to the extreme adhesion between the layers.

**Density**

Table 1 reports all the calculated densities.

Table 1: ρ_{strut} and ρ_{app} of the foams produced

<table>
<thead>
<tr>
<th>Model</th>
<th>Printed</th>
<th>3P</th>
<th>3T</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ_{strut} (g/cm^3)</td>
<td>1.25</td>
<td>0.84</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>ρ_{app} (g/cm^3)</td>
<td>0.16</td>
<td>0.14</td>
<td>0.15</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The similarity of the ρ_{app} demonstrates the good control of the machining, while the similar ρ_{strut} is advantageous in the comparison of the mechanical properties.

**DSC**

The influence of thermal treatment and foaming process are evaluated via DSC.

Table 2. Melting Temperature (T_m) and Melting Enthalpy (ΔH_m) calculated by DSC curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_m (°C)</th>
<th>ΔH_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament</td>
<td>190.36</td>
<td>6</td>
</tr>
<tr>
<td>Printed</td>
<td>192.03</td>
<td>10.31</td>
</tr>
<tr>
<td>F3</td>
<td>190.68</td>
<td>9.10</td>
</tr>
<tr>
<td>3P</td>
<td>194.05</td>
<td>6.41</td>
</tr>
<tr>
<td>3T</td>
<td>212.5</td>
<td>19.08</td>
</tr>
</tbody>
</table>

CO₂ act as plasticizer for TPU, enhancing the chain mobility and promoting crystallization in the form of bigger and better packed crystals which have a higher melting temperature respect to smaller and less ordered crystals. This effect is clearly visible from results reported in Table 2. T_m displays the synergic effect of CO₂ coupled to treatment temperature. Increasing treatment temperature, i.e. from F3 to 3T sample, the melting temperature shifts to higher values due to the melting of crystals with a more uniform morphology formed during the solubilization of CO₂ at 180°C.[11]

**Compression Tests**

In Figure 6 an initial linear section is observed which represents the linear behavior of the material before instability occurs, then a sudden reduction in force to the critical load value is observed.

![Compression test results](image)

Figure 6: Compression test results

All models, after the compression test, have almost completely regained their original shape. The results were subsequently analyzed considering the model as if it were a full cube. Then the stress and strain were calculated from the data obtained from the compression tests:

\[ \sigma = F/A \]  
\[ \varepsilon = \Delta \delta/L \]

where σ is the stress, ε is the strain.

The Young’s modulus:

\[ E_e = \sigma/\varepsilon \]

With \( E_e \) the experimental elastic modulus of the model.

To calculate the theoretical Young’s modulus, the bulk density of the foam was calculated and it was related to the density of the polymer:

\[ \rho_{app} = \frac{M}{V} = \frac{\rho_{app}}{\rho_p} = \phi_{app} \]

\( \rho_{app} \) is the density of the macroscopic model, \( \rho_p \) is the density of TPU, \( \phi_{app} \) is the relative density of the macroscopic model.

Then:

\[ E_{Th} = K_1 E_{Bulk} \phi_{app}^2 \]

\( E_{Th} \) is the theoretical Young's modulus of the macroscopic model, \( K_1 \) is the proportionality constant and \( E_{Bulk} \) is the TPU Young’s modulus.

The experimental Young’s modulus was compared with the theoretical Young's modulus (Figure 7) and the respective ratio to calculate the constant \( K_1 \) (Figure 8).
Experimental data do not differ much from the theoretical data. From Figure 7 it is possible to see that the foam obtained for 3P displays the highest Young's modulus followed by the foam obtained for 3T.

The constant $K_1$ (Figure 8) includes all those uncertainties that are not easily determined, such as: residual stress from the printing process and foaming, anisotropy and CO$_2$ treatment. For Gibson and Ashby this constant is about 1.

**Conclusion**

A rapid production procedure has been developed, combining 3D printing and foaming, which can be proposed at an industrial level, for the production of complex porous structures. In this work, the morphological and process differences between the foaming techniques presented were highlighted. Furthermore, it has been noted that these two technologies, 3D printing and foaming, are compatible with each other by creating a macroporous structure with 3D printing and a microporous one foamed with a physical blowing agent, without altering the printed structure.

Compression tests have shown that the foams produced have good mechanical properties and good shape recovery. It has also been noted that the three processes produce three different foam morphologies, so it is possible to adopt the process that best meets the needs. Furthermore, by varying the solubilization pressure or temperatures, it is possible to increase or decrease the stiffness of the resulting foam. The technologies shown could have results in both industrial and biotechnology fields.

A use of more precise 3D printers allows to print any kind of object. This opens up the possibility of producing parts that have complex geometry hard to achieve using conventional material removal processes.

The main advantage of the proposed technology is that these processes are adjustable by tuning some steps: solubilization pressure and time, extrusion temperature and oil temperature to have the desired density and mechanical properties.

The use of these technologies could be of great value for many applications where foams are used today.

**References**