PREPARATION AND CHARACTERIZATION OF THERMOPLASTIC POLYURETHANE (TPU) FOAMS WITH A LARGE VARIETY OF CELL SIZES

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Abstract

In this study, thermoplastic polyurethane (TPU) foams were fabricated by batch foaming using supercritical carbon dioxide (ScCO\(_2\)) at different foaming temperatures and saturation pressures. Experimental results revealed that lower saturation pressures would increase the sensitivity of cell sizes to varying foaming temperatures due to the different crystallization behaviours of TPU at different saturation pressures. As a result, lower saturation pressure seemed to provide more flexibility for researchers to develop multifunctional TPU composite foams by taking advantage of foaming-assisted alignment of fillers along their cell walls.

Introduction

Over the past decades, the applications of polymers have grown enormously due to properties that have made them attractive for different applications, namely being inexpensive to manufacture, corrosive resistant, and lightweight. Yet their low thermal conductivity, poor mechanical properties and electrical conductivity are the main challenges in emerging sectors such as electronics, energy, and aerospace. Therefore, more attention has been given to the idea of tailoring polymers’ properties by adding fillers to polymer matrices such as metal [1], ceramic[2], and carbon-based fillers [3]. However, high filler loading can also lead to negative effects on cost, weight, and processability of polymer composites. As reducing cost can be achieved by reducing the density of the material, foaming has attracted significant attention as a way to decrease the cost and increase the applications of polymers. Therefore, incorporating foaming process and functional fillers can be a potential route to develop novel lightweight polymer composites.

Recently, many studies have been conducted on application of foaming to induce filler alignment in polymer matrix [4-6]. Ding et al. [4] showed that foaming is the potential way to assist filler alignment and filler network which enhance thermal conductivity of polymer material systems. In a similar way, Yan et al. [7] fabricated electrically conductive PU foams with a low electrical percolation threshold by only 1.2 wt.% carbon nanotubes loading. This was achieved by controlling the filler dispersion in the cell walls, which resulted in the formation of electrically conductive pathways. Ling et al. [8] have recently fabricated lightweight polyetherimide (PEI) composites for EMI shielding by combining foaming with a small amount of graphene. It was observed that microcellular foaming induced perfect orientation of graphene along the cell walls. This resulted in creating an effective electrically conductive graphene path at lower graphene loadings (i.e., 0.18 vol.%).

Thermoplastic polyurethanes (TPUs) are unique polymeric materials exhibiting a wide range of physical and chemical properties. They are a commercially important class of thermoplastics that can be tailored to meet the manufacturing challenges of a fast-changing world [9]. Embedding different types of filler into TPU matrix can tailor TPU’s multifunctional properties while maintaining its uniquely high compliance. Therefore, many studies have been conducted to develop TPU composites. Improved mechanical and adhesive properties by incorporation of nanosilica were reported in literature [10]. While the uses of carbon nanotubes (CNT) have been limited because of the difficulties to uniformly disperse CNT within the TPU matrix, extensive studies have been conducted to study TPU/CNT nanocomposites. Bilotti et al. [11] studied the electrical and mechanical properties of TPU fibers containing multi-walled carbon nanotubes (MWCNTs). They were able to achieve electrical conductivity of ~3 S m\(^{-1}\) with 3 wt.% of CNT loading.

In addition to TPU composites and nanocomposites, many studies on TPU foams have been reported. Nemati et al. [12] studied microcellular TPU foams by using butane as the blowing agent. It was demonstrated that the plasticizing effect of butane induced a wide range of HS crystalline domains. As a result, the presence of HS crystalline domain enhanced cell nucleation over a wide range of saturation temperatures ranging from 150°C to 170°C at a saturation pressure of 55 bar. Shu-kai et al. [13] studied four types of polymer foams and revealed that TPU foams was the most promising one due to the possibility to achieve extremely high cell population density and small cell size. Moreover, they investigated the effect of nanoclay as nucleation agent on the TPU foams’ morphology. However, limited research has been conducted to develop conformable multifunctional TPU composite foams by taking advantage of foaming-assisted filler alignment in TPU matrices. With continuous development of flexible and wearable electronics, multifunctional materials with good conformability would...
represent an emerging family of engineering materials in different economic sectors.

In this context, the main goal of this research is to investigate the foaming behaviours of TPU foams in order to identify appropriate processing windows that would offer flexibility for researchers to develop multifunctional TPU composite and nanocomposite foams. While TPU foams usually yield extremely high cell population density and small cell size, this work aims to identify the processing conditions that would yield a wide range of cell sizes. Consequently, these conditions can be used to investigate the foaming-assisted filler alignment in TPU composite and nanocomposite foams for tailoring their multifunctional properties.

**Experimental**

**Materials**

Commercially available TPU (Estane® 2103-70A TPU, Lubrizol) was used as the base polymer. Carbon dioxide (CO$_2$) of 99.8% purity (Linde Gas Inc.) was used as the physical blowing agent for the batch foaming of TPU. The physical properties of TPU is summarized in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Density</td>
<td>1060</td>
<td>kg·m$^{-3}$</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>171-181</td>
<td>°C</td>
</tr>
<tr>
<td>Softening temperature</td>
<td>75</td>
<td>°C</td>
</tr>
<tr>
<td>Shore hardness</td>
<td>72</td>
<td>A</td>
</tr>
</tbody>
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**Compression Molding of TPU Films**

TPU pellets were ground into fine powders with particle sizes ranging from 250 µm to 500 µm by a mill freezer (SPLEX SamplePrep Group, model 6770, Freezer/Mill). Calculated amounts of TPU powders were weighed. The materials were then compression-molded into circular disc samples of 120 mm in diameter and 500 µm in thickness by the following procedures:

Step 1. TPU powders were charged into a circular disc mold and loaded into a compression molding machine (Craver Press, 4386 CH) preset at 210°C.

Step 2. The sample and the mold were equilibrated at the preset temperature for 1 min while contacting the heating platens to completely melt the TPU powders.

Step 3. The sample and the mold were pressurized gradually to 30 MPa to compression mold the materials into thin-disc samples.

Step 4. The heaters of the compression molding machine were turned off samples while the molded sample was solidified under pressure.

**Batch Foaming of TPU Using Supercritical CO$_2$**

The fabrication of TPU foams was performed by supercritical carbon dioxide (ScCO$_2$) foaming. All samples were pre-cut into square-shaped samples of 1 cm by 1 cm before being foamed. First, the samples were loaded into a high pressure/high temperature vessel. Once the vessel was heated to the preset temperature, it was then saturated with CO$_2$ at elevated pressure and temperature for one hour. The saturation time had been selected to ensure sufficient time to saturate the TPU with CO$_2$. After that, the pressure of the vessel was rapidly decreased by releasing the ScCO$_2$ from the vessel. This would lead to thermodynamic instability in the saturated sample. The cell structure of foamed TPU was stabilized by submerging it under an ice bath. Key parameters used in the foaming experiments are summarized in Table 2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation Pressure</td>
<td>1200, 1600, 2000</td>
<td>psi</td>
</tr>
<tr>
<td>Saturation Time</td>
<td>1</td>
<td>hr</td>
</tr>
<tr>
<td>Foaming Temp.</td>
<td>60, 80, 100, 120</td>
<td>°C</td>
</tr>
</tbody>
</table>

**Sample Characterization**

The apparent density of TPU foam samples were determined in accordance to ASTM D792. After measuring their weights in air and in water, the apparent density ($\rho$) and the volume expansion ratio ($\phi$) can be determined by Equations (1) and (2), respectively.

$$\rho = \frac{m_{\text{air}}\rho_{\text{water}}}{m_{\text{air}} - m_{\text{water}}}$$

where $\rho$ is the apparent density of a sample, $m_{\text{air}}$ and $m_{\text{water}}$ are the sample’s weights measured in air and water, respectively, and $\rho_{\text{water}}$ is the density of water.

$$\phi = \frac{\rho_s}{\rho_f}$$

where $\rho_s$ and $\rho_f$ are the densities of solid and the foam samples.

The foam morphology of TPU foams was characterized by scanning electron microscopy (FEI Company Quanta 3D FEG). The cross-sections of all samples were exposed by cryo-fracturing the samples under liquid nitrogen. The fractured surfaces were sputter-coated with gold (Denton Vacuum, Desk V Sputter Coater). The cell size and cell population density were obtained by analyzing the SEM micrographs of the foams.
The cell population density \((N_0)\) with respect to the unfoamed volume was determined by Equation (3).

\[
N_0 = \left( \frac{nM^2}{A} \right)^{\frac{1}{3}} \times \phi
\]  

(3)

where \(n\) is the number of cells in the SEM micrograph, \(M\) is the magnification factor, and \(A\) is the area of the micrograph.

Differential scanning calorimetry (DSC, TA Instruments Q2000) were used to investigate the thermal properties and crystallization behaviour of TPU. Thermal analysis was conducted in a temperature range of 50°C to 200°C at a heating rate of 10°C/min.

**Results and Discussion**

**DSC Thermal Analysis of TPU**

Figure 1 shows the DSC thermogram of the compression-molded TPU sample before undergoing ScCO\(_2\) foaming. It can be observed that multiple melting peaks were present in the thermogram due to the existence of high segment (HS) crystals with different levels of perfection, which is consistent with the results reported by Nemat et al. [8]. The onset of the broad melting peak was at approximately 100°C. It is expected that the plasticizing effect of ScCO\(_2\) during foaming process would enhance the melting of HS crystals and shift the melting peak to lower temperature. It should be noted that the broad melting peak spans over the range of foaming temperatures being investigated in this study. Therefore, the influences of the presence of HS crystals to the foam morphology of TPU were expected. It would be interesting to elucidate the how this would affect the foam morphology so that potential processing windows can be identified to fabricate TPU composite and nanocomposite foams with the appropriate foam morphology to tailor the filler networking within the polymer matrix.

**Parametric Studies of Foaming Conditions on TPU Foams’ Morphology**

Parametric studies were conducted on various key processing parameters that govern the foaming process, including the saturation pressure (i.e., 1200, 1600, and 2000 psi) and foaming temperature (i.e., 60, 80, 100, and 120°C). Figures 2 through 4 show the SEM micrographs of the foam morphology of TPU foams fabricated at different combinations of saturation pressure and temperature. Regardless of the saturation pressure, it can be observed that an optimal temperature existed to promote the cell population density of the TPU foams blown by ScCO\(_2\). Furthermore, it is also apparent that the dependence of TPU foams’ morphology prepared at a saturation pressure of 1200 psi was different from those prepared at a higher saturation pressure. When the saturation temperature changed from 80°C to 100°C, TPU foams prepared at 1200 psi demonstrated dramatic changes in the cell structures while such behaviours did not exhibit for foams prepared at higher saturation pressures.

![Figure 1. DSC thermogram of compression-molded TPU sample](image)

![Figure 2. SEM micrographs of TPU foams prepared at 1200 psi and different foaming temperatures: (a) 60°C, (b) 80°C, (c) 100°C, and (d) 120°C](image)
with the increased CO$_2$ content within the polymer matrix. Experimental results revealed that cell population density decreased as the foaming temperature increased for all saturation pressures. However, the sensitivity of the cell population density on varying foaming temperatures was more pronounced when the TPU foams were prepared at a saturation pressure of 1200 psi. In contrast, the average cell size increased with foaming temperatures from 60°C to 100°C at all saturation pressures, with the effect to be more dramatic again for the foams prepared at 1200 psi. When the foaming temperature further increased to 120°C, the average cell size decreased. As the foaming temperature increased, the surge in CO$_2$ diffusivity would promote the cell expansion. However, as the temperature continued to increase, the excessive gas loss would eventually lead to smaller cell size.

In the TPU-CO$_2$ system, the mobility of HS chains within the HS crystalline domains was enhanced due to the plasticizing effect of ScCO$_2$ on the TPU matrix [12]. As the saturation pressure increased, the amount of HS crystalline domains would be promoted even at higher foaming temperatures. This would lead to the release of CO$_2$ in the surrounding area and increased the degree of supersaturation for nucleation. Furthermore, the local stress fluctuation caused by the restriction of the molecular chain mobility in the soft segments (SS) of TPU would also contribute to the surge in nucleating power of the polymer-gas system [12]. However, when the saturation pressure was 1200 psi, it is believed that the small level of plasticizing effect caused by lower dissolved CO$_2$ content was in sufficient to compensate the melting of the HS crystalline domains with lower degrees of perfection. This led to the decrease in the number density of heterogeneous nucleating sites in the matrix, and thereby resulted in a dramatic decrease in TPU foam’s cell population density as the foaming temperature increased beyond 80°C.
expansion ratio. Such observation was consistent with the typical observation in extrusion foaming of thermoplastic.

Figure 6. Effect of foaming temperature and pressure on TPU foam’s average cell size

Figure 7. Effect of foaming temperature and pressure on TPU foam’s volume expansion

Overall, it is observed that a wider range of cell size could be achieved by varying the foaming temperature when the TPU-CO$_2$ system was saturated at a lower saturation pressure (i.e., 1200 psi). As the enhancement of foaming-assisted filler alignment along the cell walls required an appropriate level of cell expansion, it can be concluded that such processing condition would be beneficial to the fabrication of TPU composite foams filled with functional filler in order to enhance their multifunctional properties (e.g., mechanical, thermal, and electrical).

Conclusions

This paper reports the fabrication of thermoplastic polyurethane (TPU) foams by batch foaming using supercritical carbon dioxide (ScCO$_2$). The effects of foaming temperature and pressure on TPU foam’s morphology were studied. It was found that the foaming behaviours at lower saturation pressure (i.e., 1200 psi) and those at higher saturation pressure (i.e., 1600 psi and 2000 psi) were different due to the variation in crystallization behaviours of TPU under different processing conditions. In particular, a lower saturation pressure would yield higher sensitivity of cell expansion to varying foaming temperatures. Such observation suggested that foaming-assisted filler alignment in TPU composite foams would be beneficial to be conducted in such processing windows so that it would provide researchers more flexibility to identify the optimal cell size to promote specific multifunctional properties of TPU composite or nanocomposite foams.

References