Development of High Density Syntactic TPU Foam by Incorporation of Expancel through Extrusion

Linghong Li, Wanqiao Wang, Ali Anwer, Muhammad Anwer, Qinping Guo, Andrew Kenny and Hani Naguib

Department of Mechanical and Industrial Engineering, University of Toronto, 5 Kings College Cr., Toronto, Canada, M5S 3G8

Department of Materials Science and Engineering, University of Toronto, 184 College St., Toronto, Canada, M5S 3E4

Institute of Biomaterials and Biomedical Engineering, University of Toronto, 164 College St., Toronto, Canada, M5S 3G9

EHC Global Inc., 1287 Boundary Rd., Oshawa, Canada, L1J 8P8

*equally contributed

**corresponding Author: naguib@mie.utoronto.ca

Abstract

Extrusion was used to produce thermoplastic polyurethane foams using Expancel microspheres as a blowing agent. Few studies have looked into syntactic thermoplastic polyurethane foams by extrusion, making it a topic worth exploring. The density of the foams is reported in terms of cell size and cell density using 0.05wt%, 0.1wt%, 0.3wt%, 0.4wt%, 0.5wt%, 0.8wt%, and 1wt% of Expancel. The resulting foams were characterized mechanically in terms of tensile modulus. In general, specific gravity and tensile modulus decrease with increasing addition of foaming agent.

Introduction

With the rising awareness of environmental concerns such as greenhouse gases (GHGs), initiatives pertaining to the reduction of the use of petrol-based chemicals, has gathered much interest. One such chemical is thermoplastic polyurethane (TPU), displaying a global market weightage of 496,000 tons in 2015. [1] It is predicted that the global polyurethane production volume will reach 77 million tons in 2020.[2] Due to its excellent mechanical properties and wear resistance, TPU has long been chosen for a wide range of market applications where high structural integrity is required. Foaming can be used to achieve weight reduction in TPU, lower materials cost, and flexible transportation.

Thermoplastic polyurethane (TPU) is a popular and widely used thermoplastic elastomer consisting of a linear segmented block copolymer composed of hard and soft segments. Introduced by Bayer in 1937, TPU was synthesized via a polyaddition reaction of diisocyanates with diols. [3] The polymer’s final resin structure is composed of linear polymeric chains of amorphous, flexible soft segments and crystalline, rigid hard segments. The soft blocks enhance the elasticity and flexibility of the polymer, while the hard blocks provide the strength and rigidity. There are no chemical cross-links in the thermoplastic elastomer. The physical cross-links in TPU make it thermally reversible. [4] TPU can be mainly categorized into three groups based on the composition of the soft segments: polyester based TPUs, polyether-based TPUs, and polycaprolactone TPUs. Polyester based TPU provides excellent abrasion resistance and mechanical properties. Polyether-based TPU provides low-temperature flexibility and hydrolysis resistance. [5] Polycaprolactone TPUs have the similar toughness and resistance as polyester-based TPUs, but feature good low-temperature performance and a relatively high resistance to hydrolysis. [6] A polyester TPU is used for this study.

A polymeric foam is a two-phase material wherein gas is dispersed in a solid polymer matrix. Due to the rapid combination of two phases, bubbles or voids are formed and incorporate themselves in the solid matrix. Based on cell morphology, polymeric foams are categorized as either open cell or closed cell. Open cell foams tend to be more flexible, with cells partially connected by broken cell walls. Closed cell foams tend to be more rigid, with cells separated and enclosed by complete, well-connected cell walls. [7] According to size, foams can be categorized into macrocellular (>100 μ m), microcellular (1-100 μ m), ultramicrocellular (0.1 – 1 μ m) and nanocellular (0.1 – 100 nm) foams. [8] The uniformity of the polymer-gas mixture depends on the spatial distribution profile of the system’s pressure, temperature, and gas diffusion in the polymer matrix. Therefore, the system pressure must be greater than the solubility pressure to avoid the formation of undissolved gas pockets and to speed up the process. [9]

Syntactic foam is a type of polymeric foam and is composed of two components: expandable particles that function as a filler, and a resin system, which functions as a binder. With the addition of filler content in the foam matrix, the system’s moduli and fracture properties often improve. [10] It differs from the ordinary plastic foams since they have a tertiary system due to the different material used for filler and binder. [11] For this study, Expancel, manufactured and commercialized by AkzoNobel, was used as the filler. Expancel is a type of microsphere which has been widely applied as additives in
thermoplastic, coating, paper, and textile industries. These unexpanded microspheres are thermoplastic shells enclosing a droplet of volatile saturated hydrocarbon which vaporizes upon heating. The sphere shells are made of copolymers, each with a different glass transition temperatures. Upon reaching these temperatures, the gas pressure, resulting from the vaporized hydrocarbons within the spheres, cause shell expansion. The microspheres are fabricated through suspension polymerization, which splits the monomer into tiny droplets by mechanical agitation in a liquid phase. The droplets would then be stabilized by the addition of surfactants such as silica particles and \( Mg(OH)_2 \), to prevent agglomeration and coalescence of droplets. The size of the expanded Expancel ranges from 20 – 150 µm, and the density is reduced from 1000 Kg/m³ to 30 g/m³ upon expansion. These transformations mostly take place between 80 – 190 °C. [12] When heating up Expancel, both the evaporation of the hydrocarbon, and the gas pressure, will soften the thermoplastic shell, leading to the expansion of the sphere. The shell will then harden, stabilizing and retaining the shape upon cooling. The Expancel spheres are commercially available in two forms, expanded and unexpanded. The expanded Expancel serves as a filler in plastics and elastomers, while the unexpanded version is applied as blowing agent in foaming by extrusion and injection molding. [13]

Extrusion is widely used of foaming for polymers due to its better flexibility, low cost and after extrusion alterations. [14] During extrusion, a uniform mixture is first formed with the matrix and filler. The mixture is then pushed through the slit or capillary die. At the bubble inflation position, foaming commences. The pressure is maintained at a high-level. As the distance from the die entrance increases, pressure along the die axis decreases. The formation of gas bubbles strongly affects the shear stress. [15]

The long-term objective of this study is to reduce the material usage of TPU by extrusion without compromising much of the structural integrity and mechanical performance of the material in comparison to the pure solid TPU. The whole process is mainly comprised of experimental development, characterization of foam morphology, and mechanical properties testing, through which the underlying structure-properties relation between Expancel and TPU can be determined.

**Materials**

Thermoplastic Polyurethane was obtained in pellet form, serving as the foam matrix, with a specific gravity of 1.2. The foaming agent used is Expancel Master Batch, 950 MB 80 purchased from AkzoNobel NV. The specific gravity is 0.4 – 0.5 kg/L, and particle size ranges from 20 to 40 um. From the thermomechanical analysis, the microspheres reach its maximum volume at 210°C.

**Experimental**

TPU pellets were dried in vacuum at a pressure of less than -20in.Hg for more than 4 hours. The TPU syntactic foam is produced by a single-screw extruder (Harrel Geartruder) with three identical exit dies attached to the extruder. The extruder barrel temperature was kept at 185°C and the expanded TPU was processed with a screw speed of 5RPM. Two temperature profiles at the die section were chosen. For the lower temperature setting, die 1 was kept at 165°C, die 2 was at 150°C and die 3 at 140°C, and the elevated temperature profile was kept at die 1 at 180°C, die 2 at 170°C, and die 3 at 160°C. The Expancel microspheres are loaded from a side feeder and the designated weight percentage is achieved by an automatic feeding system synchronized with the main feeder. Pure TPU was fabricated for a comparison study. The foam strips have a diameter ranging from 5 to 7 mm, and are water cooled at ambient temperature.

Prior to fabrication, differential scanning calorimetry (DSC Q200, TA Instrument) was conducted on pure TPU to access its crystallization point. The pure TPU also underwent rheology tests to study its viscoelastic behaviour in Figure 5. (TA Instrument, ARES) The density of the foam strips was measured using the buoyancy method (METTLER TOLEDO). The strips were cut into cylindrical discs with a height of 5mm, for density measurement. The modulus of elasticity was obtained through tensile testing (Instron 5848 Microtester, TA Instrument), which was conducted on 9cm-long test specimens with a strain rate of 500mm/min and maximum load of 500N. The cell distribution and morphology was studied through Scanning electron microscopy images (JSM 6060, JEOL Inc.). Prior to imaging, the samples were sputter coated with Platinum for 1 min.

**Figure 1 – Schematic of Extrusion process**
Results and Discussion

The results of the measured specific gravity in relation to the weight percentage of Expancel microspheres are shown in Figure 2. Density tests were conducted on TPU foam samples with Expancel addition of 0.05wt%, 0.1wt%, 0.3wt%, 0.4wt%, 0.5wt%, 0.8wt%, and 1wt%. Two sets of data were acquired from two temperature profiles, respectively. Decreasing trends can be seen using the moving average trend line from both temperature profiles with the increase of the amount of foaming agent added. In general, the difference in die temperature does not play a significant role in weight reduction.

![Figure 2. Specific gravity behavior with foaming agent content](image)

The correlation between the modulus and weight percentage is exhibited in Figure 3. Results were acquired from expanded TPU with 0.3wt%, 0.4wt%, 0.5wt%, and 0.8wt% and 1wt% of Expancel content. Once again, descending trends with Expancel addition can be observed, as expected, in both temperature settings. A noticeably sharper decrease in tensile modulus can be seen in expanded TPU samples with lower die temperature settings. At the die exit section, the temperature of the Expancel microsphere walls decrease, resulting from convection at the die and isentropic gas expansion. In addition, the cell wall thickness decreases due to cell growth, leading to higher rate of gas escape at elevating die temperature. The foam expansion is dependent on gas loss and polymer crystallization. When Expancel content is high (>0.5 wt%), with higher die temperature, the polymer matrix requires more solidification time, gas retained in the microsphere shell is more likely to escape, limiting the eventual foam expansion. When Expancel content is low (<0.5 wt%), at lower die temperature, the polymer matrix solidifies faster, leaving less time for full cell expansion. Consequently, volume expansion of the extruded foam is restricted.

![Figure 3. Tensile modulus behavior with foaming agent content](image)
Figure 4. 100X SEM of 0.3wt%, 0.5wt%, and 1wt% Expancel/TPU at 160/150/140C (Left), 180/170/160C (Right)

For demonstrative purpose, SEM images of 3 compositions are chosen to be shown in Figure 4. In general, the cells are well dispersed, and uniform cell size can be observed. At higher weight percentage, some cell wall rupture can be seen, and cell size distribution gets wider.

Figure 5- Rheological analysis was conducted on pure TPU using a parallel plate testing fixture; a) Strain sweep of pure TPU to determine strain % independent of frequency to use in frequency sweep test, b) Frequency sweep Test to verify the reduction in viscosity with increasing frequency to simulate rotatory RPM motion in extruder and c) Temperature sweep test to determine optimal melt temperature and verify shear thinning effect of TPU. [20]

Conclusions

Syntactic TPU foam has been successfully developed using Expancel microspheres by single screw extrusion. Expansion ratio, tensile properties, and cell morphology are studied at two extruder die temperature settings. Noticeable expansion can be seen in TPU foam with Expancel addition greater than 0.05wt%. Specific gravity and tensile properties decreases with increasing addition of foaming agent. Difference in tensile modulus is more visible between extruded foams with two die temperatures. Lower die temperature setting exhibits steeper decrease in tensile properties with Expancel addition.

References


