

June 22<sup>nd</sup> - 24<sup>th</sup> 2015 Clermont-Ferrand, France

# INVESTIGATING THE STRAIN RATE-DEPENDENT COMPRESSIVE PROPERTIES OF FIBER-REINFORCED SOY-BASED POLYURETHANE FOAMS

N.Obaid<sup>1</sup>, M. Kortschot<sup>1</sup>\*, M. Sain<sup>2,3</sup>

<sup>1</sup> Department of Chemical Engineering, University of Toronto, Toronto, Canada M5S 3E5 <sup>2</sup> Faculty of Forestry, University of Toronto, Toronto, Canada M5S 3B3 <sup>3</sup> Adjunct, KAU, Jeddah, Saudi Arabia

\*Corresponding author; e-mail: <u>mark.kortschot@utoronto.ca</u>

### Abstract

Although conventional polyurethane foams are used in several applications; they are produced from non-renewable constituents. An alternative polyurethane foam can be produced by replacing petroleum-based polyol with one that is derived from soybean oil. Polyurethane foams are often used as the core material for sandwich panels in structural applications and as energy absorption materials in car bumpers and other applications. In order to maintain structural integrity, these foams must display acceptable properties over a wide range of strain rates. Deformation of materials at higher strain rates can be important in impact loading, and in designing for regions of seismic activity, high wind speeds, and areas prone to other natural disasters. In viscoelastic polymers, compressive modulus varies with strain rate. Although the modulus of foams can be improved by the addition of glass fibers, the effect of these fibers on strain rate-dependence is not well understood. This study investigates the effect of strain-rate on the modulus of glass fibre-reinforced polyurethane foams by comparing the results at quasistatic and dynamic compression.

#### Keywords:

Polymer Composites; Biopolymers; Biofoams; Crushing; Viscoelasticity

### **1 INTRODUCTION**

The versatile properties of polyurethane foam make it suitable for various applications including packaging, cushioning, insulation, and as core material of sandwich panels. Despite their desirable properties, the polyurethane foams have adverse effects on the environment due to their lack of biodegradability. [Ashida, 2007] Several groups have investigated the use of soy-based polyol as an alternative to conventional petroleum-based polyols in order to improve the biodegradability of polyurethane foams. The ester bonds in soy-based polyol are more susceptible to fungal attack, resulting in improved biodegradability. [Oprea, 2011]

Foam properties are dependent on two main factors: the solid material from which the foam was derived, and the architectural structure. The compressive behavior of foams was extensively investigated by Ashby and Gibson who modeled the behavior using a cubic lattice model [Gibson, 1997]. This model considers the foam to be a uniform array of hollow cubes, where the beams are made of the solid material from which the foam was derived. The properties are then dependent on the properties of the cell wall material and the density of the foam. Upon the application of a compressive load on a foam, the shape of a generalized stress-strain curve is shown in Fig. 1 below. Fig. 2 shows the shape of the deformed cells, corresponding to each region in Fig. 1.

At low strains, the horizontal cell struts begin to bend, resulting in a linear relationship between stress and strain. The foam modulus is related to the modulus of the cell wall material. During the next stage, the vertical struts begin to buckle, and the plateau stress is related to the modulus and yield strength of the solid wall material. The buckling of the struts continues until the third region, where the vertical and horizontal struts start to interact in the densification region. In this region, the closing of these voids results in a modulus that eventually approaches the modulus of the solid material. Due to the high modulus, the energy absorbed in the densification region is negligible compared to the first and second regions.

The mechanical properties of foam can be enhanced by the addition of reinforcing fillers. Composite literature has shown that if fibres are well-bonded to the matrix, load transfer can occur via interfacial shearing. [Piggott, 1980] In foams, fibre reinforcement depends on the relative size of fibres. Short fibres remain embedded in the cell struts, changing the cell wall material from a solid polymer to a polymer-fibre composite, improving its modulus and yield strength. As mentioned previously, the properties of the foam are based on the solid material from which it was derived. Thus, improvements in the solid material can result in an increase in the foam modulus and plateau stress.

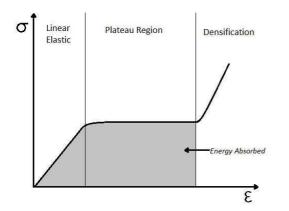


Fig. 1: Generalized stress-strain curve obtained during the compressive loading of a foam

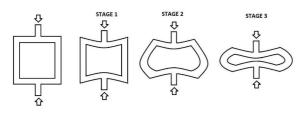


Fig. 2: Cellular structure of neat foam, as observed under a scanning electron microscope.

Several studies have found short fibre reinforcement to improve the compressive properties of foam. One study found an increase in the elastic modulus of polyurethane foam upon the addition of glass fibres under quasistatic compression. [Hussain, 2015] Another study showed that low contents of nanocellulose can improve the compressive modulus of foam. [Li, 2010] This was explained by an increase in the bending strength of the cell struts. Other studies have also shown an improvement in the compressive properties upon addition of titanium oxide and carbon nanopowder. [Uddin, 2005]

Although compressive properties for foam have been studied at low strain rates, the behavior of composite foams at high strain rates is not well understood. Strain rate is an important variable influencing the properties of polymeric foams, as they are derived from viscoelastic materials. In the utilization of polyurethanes as a core material for sandwich panels for building applications, investigating the behavior at various strain rates can be quite important. Building materials are often designed to take into consideration various environmental factors such as natural disasters, impact from precipitation, and high wind speeds.

Several studies have investigated the strain rate effect in foams. One study observed that an increase in the strain rate resulted in an increase in the elastic modulus and plateau stress of foams; however, the maximum strain to fracture decreases. [Subhash, 2006] Several studies have observed that the strain rate-sensitivity increases at higher foam densities. [Chen, 2002; Luong, 2013; Linuel, 2013] Although these studies have investigated the effect of strain rate on the properties of foams, there are few investigations into the strain rate-effect in composite foams.

The purpose of this study is to investigate composite foams for changes in their compressive properties such as modulus, plateau stress, and energy absorption, at various strain rates. The study will examine the effect of strain rate on the compressive properties of soy-based polyurethane foams with various fiber contents.

# 2 EXPERIMENTAL

### 2.1 Materials

Polyurethane foams were prepared using soy-based polyol and isocyanate using water as the blowing agent. Two surfactants and a catalyst were also added in the system. Various content of glass fibers was added to act as reinforcement. The formulation for these foams is shown in Tab. 1 below.

Chemical	Commercial Name & Supplier	Content
Polyol	BiOH-X005 by Cargill	100
Isocyanate	Rubinate by Huntsman	85
DI water		1.3
Catalyst	Polycat 9	0.3
Catalyst	33LV	2.0
Surfactant	DC5357	1.5
Glass Fibers	9907D by Fibertech	Variable

### 2.2 Sample Preparation

Polyurethane (PU) foams were prepared by mixing soy-polyol with glass fibers for approximately 10 min. Next, all remaining chemicals, excluding isocyanate, were added and mixed at ambient conditions for 20 min. The isocyanate was then added for 1 min or until a color change was observed. The mixture was then poured into an aluminum mold and allowed to cure at room temperature. For samples without fibers (neat PU), the first step was eliminated.

# 2.3 Foam Density Calculation

The average density of neat foams was calculated by measuring the mass and volume for five replicate samples.

For fibre-reinforced foams, the density calculation was more complicated. The presence of fibres results in changes to the foam density due to increased heterogeneous nucleation and increased viscosity. The foam density is a critical parameter that changes the properties of foam. As a result, any improvement in properties of fibre-reinforced foams compared to neat foams can be attributed to a combined effect of the presence of fibers as well as changes in the density. In order to isolate the effect of reinforcement only, the properties of reinforced foam must be compared to an equivalent neat foam with the same polymer density. An additional parameter called the equivalent neat foam density (ENF) must then be calculated by removing the mass of the fibers from the total mass of the reinforced foams. This will then isolate the mass of the polymer matrix, which can be used to calculate the density of an equivalent neat foam.

#### 2.4 Visual Characterization

Gold sputtered foam samples were examined via scanning electron microscopy (SEM) analysis using a Hitachi S-2500 microscope at a voltage of 15 kV.

#### 2.5 Compression Testing

Uniaxial compression testing was performed in accordance with ASTM D1621-10 using a Sintech 20. The displacement was applied at a fixed rate, producing strain rates of  $1.67E-2 \text{ s}^{-1}$  and  $2.78E-1 \text{ s}^{-1}$ . At higher strain rates, compression testing was conducted using a modified Instron Dynatup tester, producing a strain rate of  $1.12E+5 \text{ s}^{-1}$ .

# **3 RESULTS AND DISCUSSION**

### 3.1 Foam Morphology

Fibre addition has two competing effects on foam morphology. On one hand, the fibres can provide additional surface area with reduced surface energy, promoting heterogeneous nucleation. Conversely, the presence of fibres can also disrupt the cell growth mechanisms, increasing cell coalescence and cell rupture. The balance between these two competing phenomenon can result in changes to cell size as well as foam density. The resulting foam densities are summarized in Tab. 2 below.

Tab. 2: Effect of fibre content on foam morphology

Fibre Weight Fraction	ENF Density	
0%	0.107 ± 0.004	
3%	0.102 ± 0.001	
5%	0.062 ± 0.001	
8%	0.108 ± 0.001	
10%	0.109 ± 0.006	

The addition of fibres resulted in a statistically negligible change in the density of the foam, based on a 95% confidence interval, with the exception of foams prepared with 3% and 5% fibre contents, which displayed decreased foam density. This may be due to increased heterogeneous nucleation at lower fibre contents; however, higher fibre contents may result in increased viscosity preventing cell growth. However, the effect of fibre addition on foam density needs further investigation. The foams were visually inspected using SEM analysis, and the results are shown in Fig. 3 and Fig. 4. Both foams indicated isotropy in the shape of the cells.

An increase in cell size was observed upon the addition of glass fibres. This may be attributed to increased cell coalescence and cell rupture as a result of high fibre content, resulting in an increase in the cell size. [17] The cells were also observed to contain thin membranes, which were not disrupted by the presence of fibres.

In order to ensure that fibres act as effective reinforcement, they must be encapsulated by the polymer matrix in which they are contained. In addition, short fibres must be contained within the cell struts rather than spanning multiple cells. Fig. 5 shows encapsulation of fibres by the matrix.

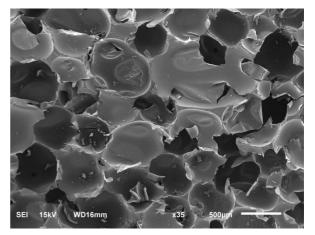


Fig. 3: Cellular structure of neat foam, as observed under an SEM.

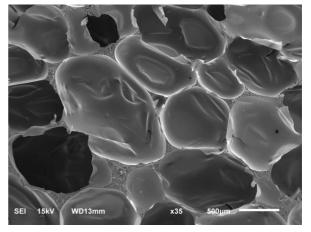


Fig. 4: Cellular structure of foam containing 11% glass fibres, as observed under an SEM.

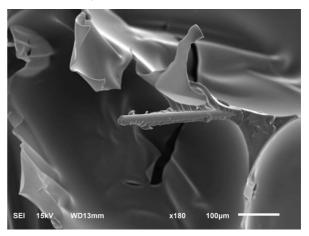


Fig. 5: The glass fibres were observed to exist in the cell struts and did not span multiple cells. The fractured surface above shows the presence of residual polymer covering the glass fibres. This indicated the fibres to be well-bonded to the polymer matrix.

### 3.2 Elastic Modulus

During each test, the foams were compressed until strains beyond the start of the densification regime. This ensured that a complete stress-strain curve was used in determining the modulus and plateau stress.

The compressive modulus of the foams was determined at three different strain rates:  $1.67E-2 \text{ s}^{-1}$ ,  $2.78E-1 \text{ s}^{-1}$ , and  $1.12E+05 \text{ s}^{-1}$ . As mentioned previously, in order to isolate the effect of fibre

reinforcement, an appropriate baseline must be established to remove the effect of density. This can be done by calculating the theoretical properties of a neat foam with the same density as that of the fibrereinforced foam. To do so, the equivalent neat foam densities from Tab. 2 can be used with the Ashby and Gibson model to calculate the elastic modulus of a neat foam at a particular density, as indicated in Equation (1).

$$E_{foam} = E_{solid} \left( \frac{\rho_{foam}}{\rho_{solid}} \right)^2 \tag{1}$$

In order to isolate the effectiveness of fibre reinforcement, the experimental modulus of the composite foam can then be compared to the predicted modulus of the neat foam with the same density. This calculation (Equation 2) produces a "reinforcement factor" (RF),

$$RF = \frac{\overline{E}_{compositor foam}}{\overline{E}_{aquitvalent near foam}}$$
(2)

Fig. 6 below shows the elastic modulus obtained for foams with various fibre contents. The predictions from the Ashby and Gibson calculations are also shown in this graph. The reinforcement factor is plotted in Fig. 7 below.

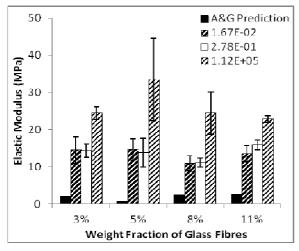


Fig. 6: Elastic modulus of fibre-reinforced foams at various strain rates.

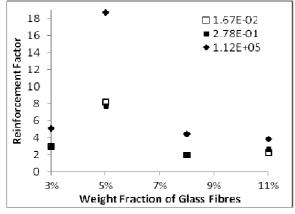


Fig. 7: Reinforcement Factors of fibre-reinforced foams at various fibre contents and strain rates.

It was observed that the addition of fibres resulted in an increase in the elastic modulus at all fibre contents when compared to the Ashby and Gibson model predictions. The reinforcement factors indicated the existence of an optimal fibre content at which the maximum reinforcement occurs. It was also observed that compression at higher strain rates resulted in a dramatic increase in the compressive modulus of the foam. The polyurethane matrix is a viscoelastic material, and is therefore sensitive to changes in strain rate. At higher strain rates, the material is more elastic, leading to an increase in the compressive modulus.

The effect of strain rate on the modulus; however, was observed to diminish at higher fibre contents. The addition of elastic glass fibres appears to have resulted in an increase in the net elastic character of the viscoelastic foams.

It may be inferred that the decreased strain ratedependence of composite foams with higher fibre content may lead to more consistent properties at various strain rates. Further studies are required to investigate the effect of elastic fibres on the viscoelasticity of polyurethane foams.

### 3.3 Plateau Stress

The next stage in foam deformation is a plateau region, where the cell struts continue to buckle until the foam has collapsed. The plateau stress can be dependent on both the elastic modulus and the yield stress of the cell wall material. The presence of fibres in the cell walls changes the material from solid polyurethane to a polyurethane-glass fibre composite. The presence of these fibres can thus increase the plateau stress of the material. The results are summarized in Fig. 8 below.

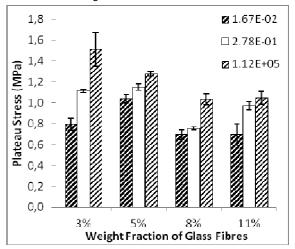


Fig. 8: Effect of fibre content and strain rate on the plateau stress of composite polyurethane foams.

As expected of viscoelastic materials, an increase in the plateau stress was observed at increasing strain rates. The plateau stress appeared to be more sensitive to incremental changes in strain rate compared to the elastic modulus. The elastic modulus did not change upon increasing the strain rate from  $1.67E-2 \text{ s}^{-1}$  to  $2.78E-1 \text{ s}^{-1}$ ; however, the plateau stress changes with small changes in strain rate.

The foam with the lowest fibre content was more sensitive to changes in strain rate; however, at higher fibre contents, the strain rate-effect decreased. This shows that polyurethane-glass fibre composite foams maintain the viscoelastic characteristic of solid polyurethane. However, the addition of an elastic glass fibre resulted in a decrease in the strain ratedependence of composite foams.

#### 3.4 Energy Absorption

Energy absorption is another important characteristic of foams. The total energy absorbed can be quantified as the work done during the elastic and the plateau regions. Any energy absorbed during densification is often deemed negligible in comparison to the first two regions. The addition of fibres can also have an impact on the energy absorption (Fig. 9).

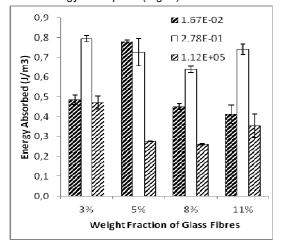


Fig. 9: Effect of fibre content and strain rate on the energy absorption of composite polyurethane foams.

At the same strain rate, varying the fibre content resulted in negligible change in energy absorption. The highest energy was absorbed by foams with 5% glass fibres at a strain rate of 1.67E-2 s<sup>-1</sup>. This foam also had the highest reinforcement factor with respect to elastic modulus. With the exception of foams with a 5% fibre content, the energy absorption increased at a rate of 2.78E-2 s<sup>-1</sup> and decreased at 1.12E+5 s<sup>-1</sup> for all foams. At low strain rates, the modulus and plateau stress is lower, resulting in lower energy absorption. On the other hand, at strain rates, although the modulus and plateau stress increase significantly, this is coupled with a decrease in the maximum strain, reducing energy absorption. As a result, at moderate strain rates, it might be possible to achieve an increase in the modulus and plateau stress without significant decrease in the maximum strain, resulting in higher energy absorption.

### **4 CONCLUSIONS**

This study investigated the effect of adding perfectly elastic glass fibres into a viscoelastic polyurethane matrix and evaluate the changes in morphology and compressive properties. The addition of fibres affected the structure of the foams, their basic mechanical properties, and their viscoelastic character. The fibres remained contained in the cell struts without rupture of the cell membranes. The composite foams had larger cells; however, the cells remained isotropic in shape. It was observed that although the addition of glass fibres improved the elastic modulus and plateau stress, the effect of fibres on energy absorption was much less pronounced. The optimal fibre content was determined to be 5% by weight; these foams resulted in the highest reinforcement factor and highest energy absorption at low strain rates.

The elastic modulus and plateau stress increased with increasing strain rate at all fibre contents; however, the plateau stress was more sensitive to strain rate. The energy absorption decreased significantly at very high strain rates. This can be attributed to a decrease in the densification strain.

It was evident that the properties varied with both fibre content and strain rate, indicating a coupling the two variables. It was also observed that the strain rateeffect diminished at higher fibre loadings. One possible explanation is that adding elastic fibres in the viscoelastic cell wall material resulted in an increase of its elastic character. Since the properties of foam are dependent on the solid cell wall material, the decreased viscoelasticity also resulted in a diminishing of the strain rate-effect at higher fibre loadings.

#### **5 ACKNOWLEDGMENTS**

The authors are grateful to the Automotive Partnership Canada (APC) NSERC program for their financial support. The authors also thank Cargill Industries, Huntsman, and Air Products and Chemicals Inc. for their donation of materials used in this study.

#### **6 REFERENCES**

Ashida K.; Polyurethane and Related Foams: Chemistry and Technology. Boca Raton, U.S.A., 2007. Chen W., Lu F., Winfree N.; High strain rate compressive behavior of a rigid polyurethane foam with various densities. Experimental Mechanics, 2002, 42, 1, 65-73.

Gibson L. J., Ashby M. F.; Cellular Solids: Structures and Properties. New York, U.S.A., 1997.

Hussain S., Kortschot M. T.; Polyurethane foam mechanical reinforcement by low-aspect ratio microcrystalline cellulose and glass fibres. Journal of Cellular Plastics, 2015, 51, 1, 59-73.

Khazabi M., Gu R., Sain M.; Fiber reinforced soybased polyurethane spray foam insulation. Part 2: thermal and mechanical properties. Bioresources, 2011, 6, 4, 3757-3774.

Li Y., Ren H., Ragauskas A.J.; Rigid polyurethane foam reinforced with cellulose nanowiskers: synthesis and characterization. Nano-micro Letters, 2010, 2, 89-94.

Linuel E., Marsavina, L., Voiconi T., Sadowski T.; Study of factors influencing the mechanical properties of polyurethane foams under dynamic compression. Journal of Physics: Conference Series, 2013, 451, 1-4.

Luong D. D., Pinisetty D., Gupta N.; Compressive properties of closed-cell polyvinyl chloride foams at low and high strain rates: experimental investigation and critical review of state of the art. Composites Part B, 2013, 44, 1, 403-416.

Oprea, S., Doroftei, F.; Biodegradation of polyurethane acrylate with acrylated epoxidized soybean oil blend elastomers by Chaetomium globosum. International Biodeterioration & Biodegradation, 2011, 65, 533-538.

Piggott M.R.; Load Bearing Fibre Composites. Willowdale, Canada, 1980.

Subhash G., Liu Q., Gao X.; Quasistaic and high strain rate uniaxial compressive response of polymeric structural foams. International Journal of Impact Engineering, 2006, 32, 7, 1113-1126.

Uddin M. F., Mahfuz H., Zainuddin S., Jeelani S.; Infusion of spherical and acicular nanoparticles into polyurethane foam and their influences on dynamic performances. SEM Annual Conference on Experimental Mechanics 2005, Portland, OR.