



# Research & Reviews On Polymer

*Full Paper*

RRPL, 6(1), 2015 [018-031]

## A study of the characteristics of hollow glass microspheres reinforced thermoplastic polyurethane composite foam

Fredrick Nzioka Mutua<sup>1\*</sup>, Edison Omollo<sup>2</sup>, Edwin Khamala<sup>3</sup>, Josphat Igadwa Mwasiagi<sup>1</sup>, Lucy Ciera<sup>1</sup>, Yimin Wang<sup>4</sup>

<sup>1</sup>EiTEX, Bahir Dar University, Bahir Dar, Ethiopia,, (CHINA)

<sup>2</sup>Technical University of Kenya, Nairobi, Kenya, (CHINA)

<sup>3</sup>Busitema University, Kampala, Uganda, (CHINA)

<sup>4</sup>Donghua University, College of Material Science, 210620, Shanghai, (CHINA)

E-mail: nziokafredrick@yahoo.com

### ABSTRACT

Current foam materials do not meet the requirements for high performance. Minimal research has been done on thermoplastic polyurethane (TPU) foams fabricated by non-synthesis approach. In this study, Hollow Glass Microspheres (HGMS) reinforced TPU foam was fabricated by compression molding using TPU polymer. Interfacial adhesion between the filler and the matrix was enhanced by surface modification of the HGMS. The morphology of fabricated foam was studied using Scanning Electron Microscope (SEM). Density, hardness and mechanical tests were done to study the foam properties. Increasing the foaming agent content from 1% to 2% led to a decrease in tensile strength of the foam by about 50%. The tensile strength decreased by about 40% when the filler content was increased from 0% to 3%, while the compressive strength of the composite foam increased by about 47% when the filler content was increased from 0% to 7%. Increasing filler content led to a decrease in the density and increase in hardness of the foam. After a 75% compressive force, SEM observation of 7% HGMS reinforced TPU foam had a more stable structure than 5% HGMS reinforced foam which depicts enhancement in mechanical properties, a property desired for high impact absorption applications.

© 2015 Trade Science Inc. - INDIA

### KEYWORDS

Thermoplastic Polyurethane (TPU);  
Hollow Glass  
Microspheres (HGMS);  
Surface modification;  
High speed mixing;  
Compression molding;  
Extrusion molding.

### INTRODUCTION

Structures for aerospace, marine and sporting equipments require lightweight materials with high strength capable of withstanding destructive forces. Such materials can be fabricated by using reinforced polymeric foams as core materials for sandwich

composites. The presence of a blowing agent in a polymer has a plasticizing effect on the polymer, because blowing agents are small molecules that can be trapped between polymer molecules and reduce their interactions. Lowering of glass transition temperature ( $T_g$ ) is the direct impact of this effect,  $T_g$  depression normally has a linear relationship with

gas solubility<sup>[1, 2]</sup>. This is associated with the decrease of solid polymer modulus and the decrease of liquid polymer viscosity<sup>[3, 4]</sup>, which affect the bubble growth directly. The presence of sufficient blowing agent is essential to support efficient cell growth. This depends on the gas pressure generated inside the cells, which in turn is dictated by the solubility and diffusivity of the blowing agent in the polymer, as well as its physical properties. Thus, a certain level of solubility is necessary to achieve low foam density<sup>[5]</sup>.

According to Mark F.S. *et al.*<sup>[6]</sup> polyurethane foams exhibit a phenomenon called compression set whereby, the foams undergo non-recoverable deformation under a defined compression load caused by temperature and humidity. This is caused by stress induced deformation of polyurethane co-continuous hard phase decomposition of the urethane bond and hard phase slippage through co-continuous soft phase. Plasticization and disruption of the hard segment or soft segment hydrogen bonding causes compression set under humid conditions. This phenomenon is strongly temperature dependent with clear threshold behavior. As a result, two foams which may appear similar in most aspects may yield different compression set of results due to sensitivity of the samples to the test conditions.

Hollow Glass Microspheres (HGMS) are low weight reinforcing materials, also called micro balloons, hollow glass balls or glass bubbles and have diameters sized in micrometers<sup>[7]</sup>. They have a wide variety of uses which include light weight filler in composite materials, light weight concrete, paints, plastics, putties, fiberglass, sealants, varnishes and resins. HGMS consist of an outer stiff glass and an inner inert gas, which results in some unique properties, such as low weight and low thermal conductivity. Based on these properties, HGMS have been used in preparing composites with various polymers<sup>[8-10]</sup>. HGMS composites exhibit multifunctional properties, including high specific compressive strength<sup>[11, 12]</sup>, high thermal stability, low density, and low moisture absorption<sup>[13-14]</sup>. As explained by Patankar<sup>[15]</sup>, HGMS give syntactic foam its light weight, low thermal conductivity, and a resistance to compressive stress that far exceeds that of other

foams. These properties are exploited in the hulls of submersibles and deep-sea oil drilling equipment, where other types of foam would implode. HGMS have high crushing strength of 69 MPa and can withstand injection molding pressures as high as 207 MPa.

HGMS have a lower specific gravity than the pure resin. This makes it possible to use them for reducing the weight of resin dominant compounds<sup>[16]</sup>. They find wide applications in aerospace and automotive industries where weight reduction for energy conservation is one of the main considerations. However, their use in systems requiring high shear mixing or high-pressure molding is restricted as their crush resistance is low compared to that of solid spheres. Microspheres, whether solid or hollow, show properties that are directly related to their spherical shape they behave like minute ball bearing, and hence, they give better flow properties. They also distribute stress uniformly throughout resin matrices.

As explained by Narkis<sup>[17]</sup>, influence of outside environment and operation conditions (which include; temperature, strain rate, the form and time of applied force, etc.) on the mechanical properties are also important. These influence some important mechanical characteristics, such as tensile strength, stiffness, impact toughness and brittle-ductile transition in addition to the interfacial adhesion between the matrix and the filler particles<sup>[18-20]</sup>. Study of the mechanical properties of particulate reinforced polymer composites for different applications indicates that the Young's modulus can be readily improved by adding either micro or nano particles because rigid inorganic particles generally have a much higher stiffness than polymer matrices<sup>[21-23]</sup>. Strength strongly depends on the stress transfer between the particles and the matrix. For well-bonded particles, the applied stress can be well transferred to the particles from the matrix; which improves the strength<sup>[20, 24]</sup>. Research on rigid inorganic particulate-filled polymer composites has showed that, interfacial adhesion between the filler particles and the matrix is an important factor influencing impact toughness of materials. Macroscopic behavior of particulate composites is affected by the size, shape, and the

## Full Paper

distribution of the inclusions<sup>[25-29]</sup>.

Interfacial strength plays an important role in the mechanical behavior of the particulate filled composites. Packham<sup>[30]</sup> showed that the work of adhesion can be determined by contact angle measurement or by contact mechanics. It can also be done using direct determination of adhesion strength between a single particle and the surrounding matrix<sup>[24]</sup>. These tests provide the adhesion strength at the interface. Hyungu *et al.*<sup>[31]</sup> showed that, TPU/TPU-g-HGM composites exhibit increased tensile and low swelling behaviors. This is due to interfacial adhesion between the TPU matrix and the HGMS. Amine groups lead to hydrogen bonding with urethane linkages in the TPU matrix, thus TPU/HGM-NH<sub>2</sub> composites might have better interfacial adhesion than TPU/HGMS composites<sup>[32,33]</sup>. Further studies on surface modification of HGMS have been studied by Mutua *et al.*<sup>[34]</sup> using FTIR analysis and SEM observations.

HGMS can enhance selected mechanical properties of the matrix resin and provide high performance core materials for sandwich structures<sup>[35]</sup>. Consequently syntactic foams can have higher specific static and storage modulus than the matrix material. Some properties, such as modulus and strength, play an important role in defining the performance of syntactic foams as core material in sandwich composites<sup>[36, 37]</sup>. Such properties can be tailored by selecting appropriate matrix material and HGMS material, wall thickness, and volume fraction<sup>[38-40]</sup>. It has been proved that fracture in HGMS/epoxy syntactic foams normally starts in the tensile side of the specimens.

The maximum normal stress ( $\sigma$ ) and maximum normal strain ( $\varepsilon$ ) are calculated from the load–displacement data using the following equations

$$\sigma = \frac{3PL}{2bd^2} \quad (1)$$

$$\varepsilon = \frac{6Dd}{L^2} \quad (2)$$

Where P is the applied load, D is the mid-span deflection, b is the specimen width, d is the specimen thickness, and L is the span length<sup>[41]</sup>.

The flexural strength of syntactic foams is esti-

mated using the concept of effective load-bearing sections where the composite strength is estimated by assuming that the composite failure is primarily due to interface de-bonding and matrix fracture in the tensile region. This concept states that the inclusions are distributed in the resin material in a simple cubic array. Liang<sup>[42]</sup>, suggested that, a parameter angle  $\theta$  quantifies the portion of de-bonded interface region. As the value of  $\theta$  increase from 0° towards 90° the adhesion between the matrix and inclusions decrease leading to reduced load transfer from the matrix to the inclusion and consequent poor performance of the composite under mechanical loading. Thus the strength of the composite is directly proportional to the effective load-bearing cross-section area. The effective strength of composite containing spherical particles can be estimated by:

$$\sigma^u = \sigma_m^u \left( 1 - \pi \left( \frac{3}{4\pi} \right)^{\frac{2}{3}} \sin^2 \theta \phi^{\frac{2}{3}} \right). \quad (3)$$

Where  $\sigma^u$  and  $\sigma_m^u$  are the composite and matrix flexural strengths, respectively.

The strength of the composites is generally higher than the strength of the pure resin. Above the optimal inclusion content, the strength decreases as the inclusion volume fraction increases. This implies that the composite strength decreases as the resin volume content decreases. Interface de-bonding followed by matrix cracking is the primary mechanism of syntactic foam failure. The composite flexural modulus can be effectively tailored by varying the inclusion volume fraction and wall thickness. Microspheres are de-bonded from the matrix material during the deformation and fracture processes. This implies that during the loading process most of the stress in the composite is withstood by the matrix material whose tensile cracking determines the composite failure. The flexural strength is primarily influenced by the resin content of the composite thus the composite strength decreases as the inclusion volume fraction increases<sup>[43]</sup>.

Patankar *et al.*<sup>[15]</sup> showed that, in processing HGM/HDPE composites via mixing and compounding, it is possible to obtain composite with high vol-

ume fraction of HGMS in HDPE matrix. In absence of compatibilizer the HGMS/HDPE interface is very discrete with no sign of bonding between HGMS and the matrix. While use of 1wt.% PE-g-MAH as compatibilizer influences the mechanical properties of HGMS/HDPE composites, but it has little or no effect on the relaxation behavior, crystallinity and thermal conductivity of the composite. Studies by Hongyu *et al.*<sup>[44]</sup> established that, on increasing the filler concentration from 1 to 7%, the density of soybean oil-based polyurethane foams (SBO PUF) with microspheres decreased from 47 to 43 kg/m<sup>3</sup>. The compressive strength slightly reduced when raising this filler concentration from 0 to 3% and then gradually increased at 7% microsphere concentration. SBO PUF without fillers had a large number of cells in the shape of irregular polyhedra. When an increasing filler concentration was introduced, it was found that the cell number raised and foam cell size reduced.

Du Bois *et al.*<sup>[45]</sup> studied crashworthiness of polymeric foams and found out that under dynamic uniaxial compressive loading, larger samples result in higher stress values at the same compression than smaller samples. This could be due to the outflow of air from the low strength open cell foam, which takes longer, in larger samples. The dependency of the material characteristic on sample size and shape becomes negligible once the foam strength becomes significantly higher than the atmospheric pressure as is the case in bumper and padding foams.

Considerable amount of research has been done on polymeric foams accompanied by academic publications and patents. Reinforced foams fabricated

by synthesis techniques have also been registered. This method of foam fabrication is usually associated with byproducts especially toxic gases which lead to environmental pollution. With this plight in mind, we have fabricated composite foam using alternative method (compression molding) and tested its mechanical properties as well as other related properties for possible application in sporting activities like motorcycle racing.

## EXPERIMENTAL

### Materials

Hollow glass microspheres (HGMS) composed of sodium borosilicate (grade HGMS im30k, particle size=5-60 $\mu$ m, density=0.66g/cm<sup>3</sup>) was obtained from 3M corporation, China. 3-Aminopropyltriethoxysilane (APTES, Sinopharm Chemical Reagent co., Ltd, China) was used as the silane coupling agent to form an amine-terminated organic compound on the HGMS. To hydroxylate (attach hydroxyl groups) the hollow glass microspheres, sodium hydroxide was used. N-propylamine (Sinopharm Chemical Reagent co., Ltd, China) and ethanol were used as catalyst and solvent respectively. Commercial grade TPU and 1,1'-Azobisformamide (AC foaming agent) were obtained from Plastic materials Co., Ltd., Dongguan City, Guangdong. According to manufacturer's data sheet, the diameter of the HGMS was not uniformly distributed thus the need for initial preparation. This was done by size selection using a twin sieve to eliminate diameter above 45  $\mu$ m using the upper sieve

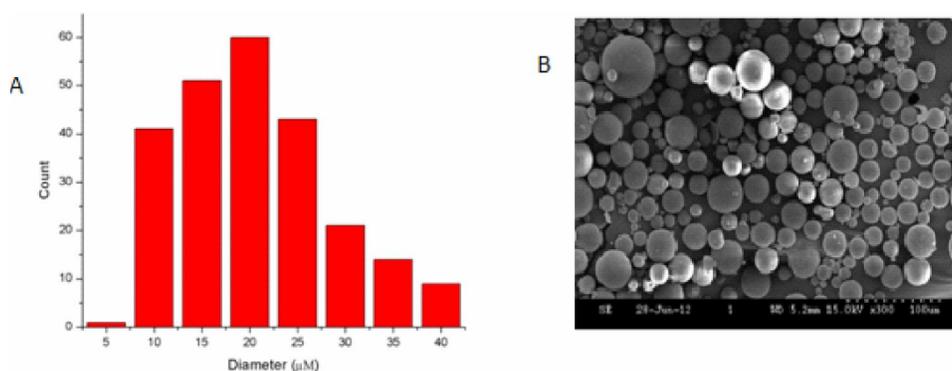


Figure 1 : Diameter distribution of hollow glass microspheres in (A) Bar graph, (B) SEM microphotograph, magnification 100 $\mu$ m

## Full Paper

and allow HGMS with diameter less than 10  $\mu\text{m}$  to pass through the bottom sieve. HGMS with the desired diameter were trapped between the two sieves and were collected for further processing. The HGMS collected were observed under SEM and the diameter distribution was analyzed using adobe acrobat. The distribution achieved was presented using the bar chart in Figure 1. The distribution in the bar chart shows that, the range of the diameter of HGMS used for this study was between 10 and 40 $\mu\text{m}$ .

### Methods

The procedure for surface modification of HGMS was done according to the procedures given in our previous work, Mutua *et al.* [34]. The molecular weight distributions of the TPU pellets were tested using gel permeation chromatography (GPC). To conduct this test, 0.15mg of TPU were dissolved in 25 ml of tetrahydrofuran (THF). The test was done by monitoring the concentration of polymer molecules in each eluting fraction from the GPC column these were recorded by a differential refractometer which detected small differences in refractive index between pure solvent and polymer solution.

HGMS were evenly dispersed in the TPU matrix using a high speed mixing machine, which is simply a machine which disperses micro inclusions onto a surface of a polymer with which it would normally be immiscible; this is done by heating the polymer to make its surface rubbery by elevating the temperature of the mixing chamber using heated oil. A rotor or impeller, together with a stationary component known as a stator, is used either in a tank containing the polymer pellets and inclusions to be mixed. Rotating the rubbery polymer pellets and the inclusions at high speed allows the inclusions to stick on the surface of the polymer after which the mixture is ejected for further processing. Prior to processing, the TPU pellets were dried at 100°C for 3 hours to remove all moisture. The high speed mixer was set to a temperature of 165°C; the HGMS were dispersed on the surface of the TPU. The evenness of dispersion of HGMS on the TPU pellets was observed using an optical microscope.

Varying quantities of AC foaming agent was evenly mixed with the TPU/HGMS mixture to make

foam of different properties. The machine temperature was allowed to stabilize for foaming to take place at a constant temperature after which the right formulations of the raw materials were fed to the mold ready for processing. Using compression molding the polymer compound was molten in a heated mold and kept under pressure to fill the mold. This was done under varied conditions of time and pressure with varied ratios of the materials to fabricate composite foams of different properties. TPU showed high flow properties at elevated temperatures. Thus, the mold and its contents to be cooled under pressure before the foam could be ejected from the mold. Temperature and pressure were critical variables determining the cycle time and the quality of the foam. Complete filling of the mold during crosslinking was rather difficult and the degree of crosslinking had to remain much lower in order to preserve the desired elasticity of the fabricated foam.

The cross sectional structures of TPU/HGMS composite foam samples were studied using SEM (S-37004, Hitachi, Tokyo, Japan) observation. All TPU/HGMS composite foam samples were fractured under liquid nitrogen and their surface covered with gold nanoparticles for morphology study using SEM.

Thermo gravimetric analysis (TGA) was done using Discovery series TGA instrument to study the thermal effects of reinforcing TPU with HGMS. Further, using a universal mechanical testing machine, the mechanical behavior of the foam under conditions of tension and compression were tested to provide its property data which can be used for component design and performance assessment. The method used for compression and tensile strength values were as specified in ASTM D 3574 standard for TPU foams.

Compression test was done to determine the behavior of foam under a compressive load. It was conducted by loading the test specimen between two plates, and applying a force to the specimen by moving the crossheads of the universal testing machine together. During the test, the specimen was compressed, and deformation versus the applied load was recorded. The compression test was used to determine maximum compressive force, modulus of elasticity, and compressive strength of the fabricated

foam. Samples reinforced with different percentage of HGMS were prepared from the fabricated foam and subjected to this test.

The hardness of fabricated composite foam was tested to study the effects of fabrication parameters and composition on the overall hardness. The density of compression molded foam was calculated as described in ASTM 3574. Samples to be tested were cut from molded foam, weighed and volume calculated. Using the data obtained, the density was calculated. The data obtained was used to study the effects of filler content, pressure, and the foaming time on the density of the fabricated foam.

## RESULTS AND DISCUSSIONS

### Mixing of TPU and HGMS

Before mixing the foam and HGMS the molecular weight of the material was determined. The molecular weight data obtained for TPU was  $M_n=84,951$ ,  $M_w=130,780$  and  $PDI=1.54$ .

Mixing of TPU with HGMS was a rather complicated process as components differing in structure, viscosity and rheological behavior had to be homogenized. Physical processes, for example the adsorption of polymers or other additives onto filler surfaces needed to occur. The mixing equipment is not very flexible and a short-term adjustment of the mixing conditions was difficult. Different mixing processes took place in order to guarantee a homogeneous blend of all the compound ingredients on the required scale: laminar, distributive and dispersive mixing.

The effectiveness of a high speed mixer was

studied by observing TPU polymer pellets under an optical microscope as seen in Figure 2. Pure TPU gave a clear surface under optical microscope; while after dispersion of HGMS on its surface, a uniform distribution was observed.

Uniform dispersion was achieved by running TPU polymer in the mixer for 45 seconds to melt its surface before adding the HGMS. The filler material was fed, and the equipment was run for a further one minute. This method of dispersing micro fillers on the surface of polymer pellets was found to be effective in minimizing breakage of the filler material which would otherwise occur using other dispersing techniques. It was however found that, the polymer pellets surface could take up to a maximum quantity of HGMS above which the surface became saturated. This was supported by the presence of HGMS in the mixing chamber as the percentage of HGMS was increased at a constant quantity of TPU. Although this could be overcome by increasing the time for mixing, prolonged mixing time could lead to breakage of the HGMS thus loss of its reinforcing properties.

### Quenching of the Composite

To increase the productivity, cooling rate is increased by quenching after compression molding. In this study a big difference was realized between the samples quenched with water and normal cooling as shown in Figure 3. The tensile properties of quenched and unquenched foam were different. This resulted from the de-bonding during quenching as seen in the SEM photo alongside the graph due to the different thermal coefficients of the HGMS and

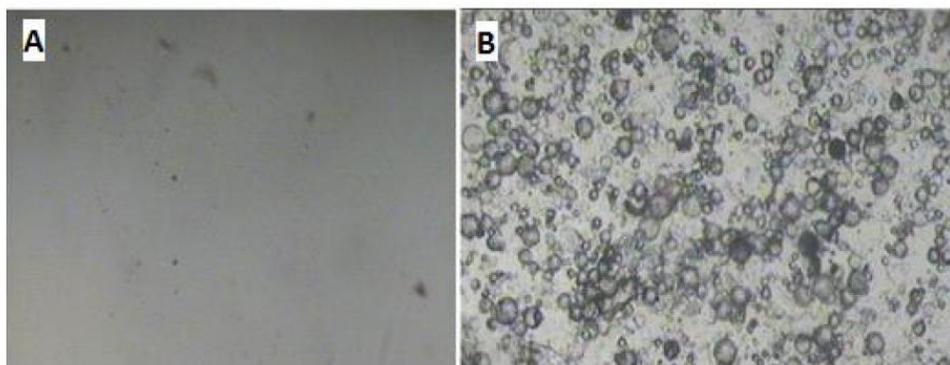


Figure 2 : Optical microscope images of TPU pellets (magnification x40) before dispersion (A) and (B) after dispersion of HGMS (circled in red)

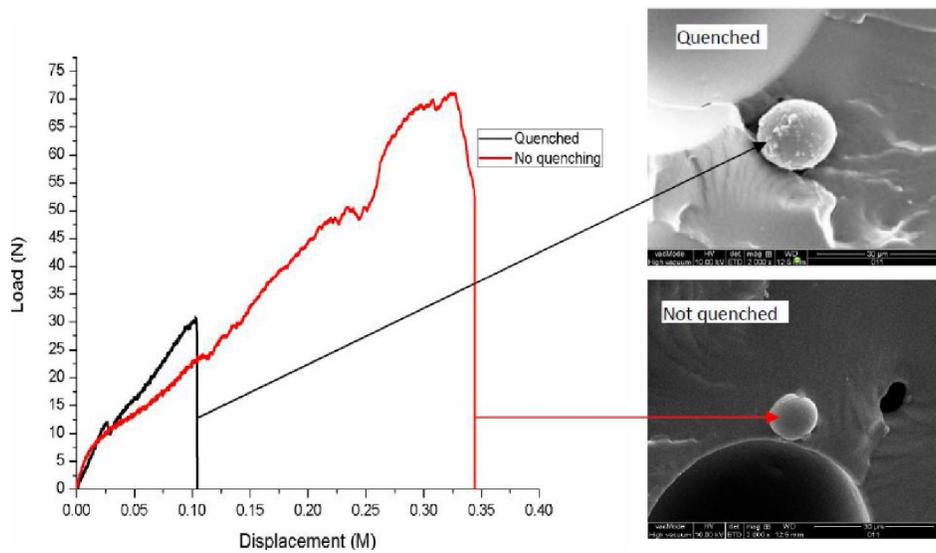


Figure 3 : Tensile behaviors of quenched and unquenched samples of HGMS/TPU composite foam fabricated under same, temperature, HGMS (3%) and AC (1.5%) contents

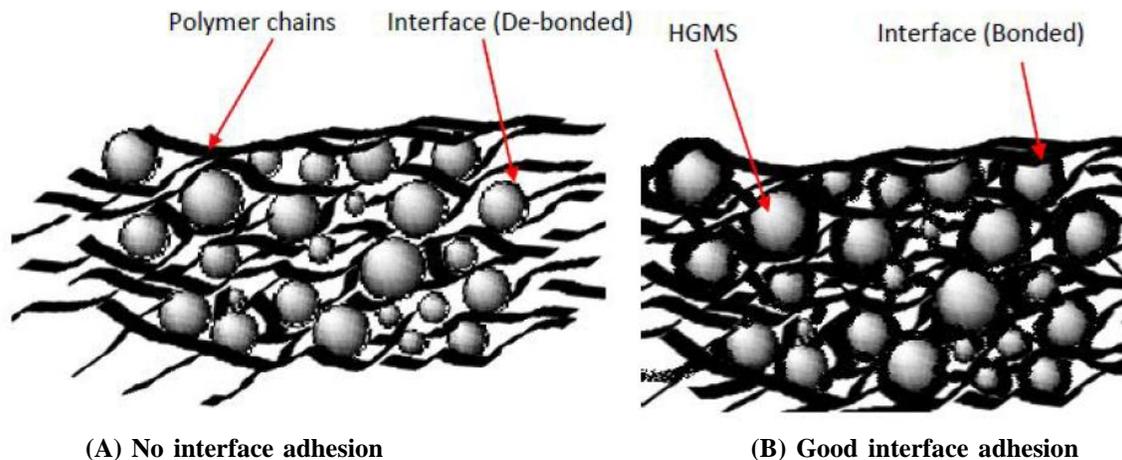


Figure 4 : Model showing the effects of quenching reinforced foam

TPU.

The results obtained in Figure 3 were further explained using a simple model suggested in Figure 4.

A simple model was suggested and shown in Figure 4 to explain the effects of quenching HGMS reinforced TPU composite foam. Quenching is not desirable in reinforced foam because, the HGMS and the TPU matrix have different thermal expansion coefficients. Instant cooling resulting from quenching would lead to sudden different rates of contraction; this would likely result in de-bonding of the HGMS from the TPU matrix thus a structure similar to the one shown in Figure 4(A). Allowing the foam to cool slowly would make the HGMS and TPU have a relatively same rate of cooling the overall

effect would be formation of a good interface between the HGMS and the TPU resulting in a structure as shown in Figure 4(B). Comparing these two structures it is logical to conclude that the quenched foam would have inferior mechanical properties to the unquenched composite foam.

### The Morphology of HGMS reinforced Foam

The morphological structures of HGMS reinforced TPU foam fabricated by compression molding was studied using SEM observations. The SEM microphotographs of foam fabricated by compression molding with an increasing percentage of AC foaming agents are shown in Figure 5. At 0.5% AC content, it was observed that, the cells were varying in size while the distribution was uneven. This was

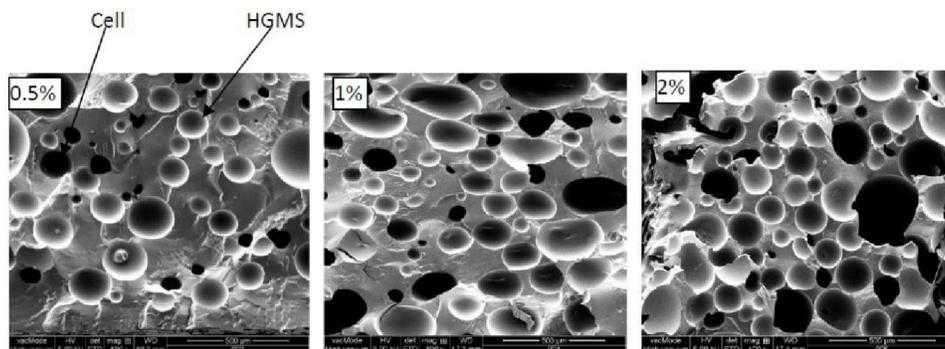


Figure 5 : SEM microphotograph of foam fabricated using compression molding at 185°C, 5 MPa, 5Min 3% HGMS and varying AC content

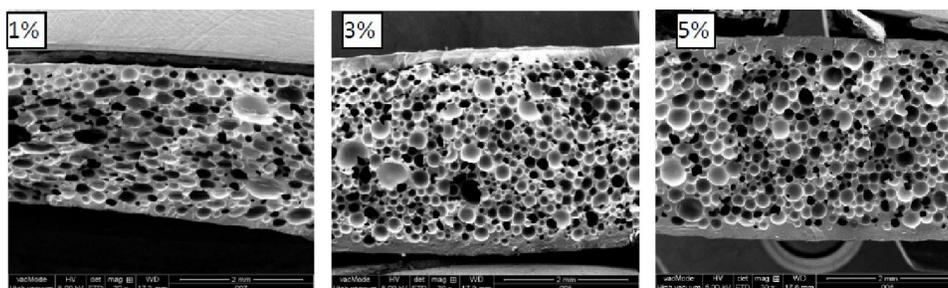


Figure 6 : SEM microphotograph of foam fabricated using compression molding at 185°C, 5 MPa, 5Min and 1.5% AC

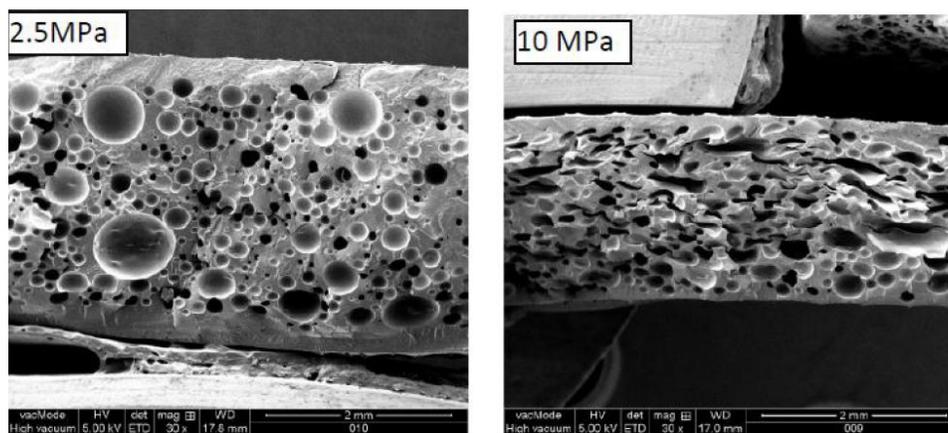


Figure 7 : SEM microphotograph of foam fabricated using compression molding method at 185°C, 1.5% AC, 5Min and varying pressure

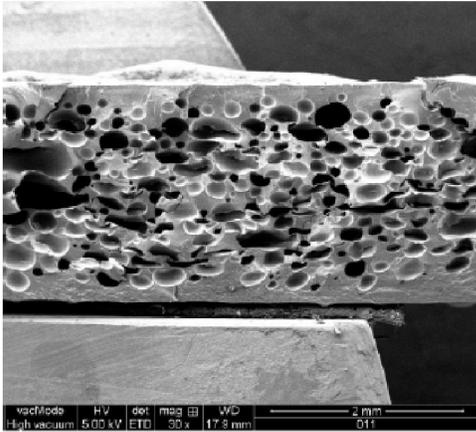
because; the foaming agent was not enough to give the desired number of cells, having a uniform distribution. The number of cells was observed to increase with an increasing percentage of AC content. At and above 2% of AC, the cells size was found to be very large. This resulted from the high concentration of foaming agent per unit area which on decomposition at foaming temperature led to the large cell sizes.

When the AC foaming agent was held at 1.5% and the HGMS content was increased from 1-5%, SEM observation gave images as seen in Figure 6.

Increasing the percentage of HGMS was found to have a cell size reducing and cell number increasing effect. This was as result of nucleation sites for bubble formation provided by the surface of the fillers during foaming process. The HGMS were also seen to be well arranged around the cell as the HGMS content was increased in the TPU matrix. It was also reported by Tagliavia *et al.*<sup>[43]</sup> that micro balloons showed a tendency to be distributed around the voids in the matrix.

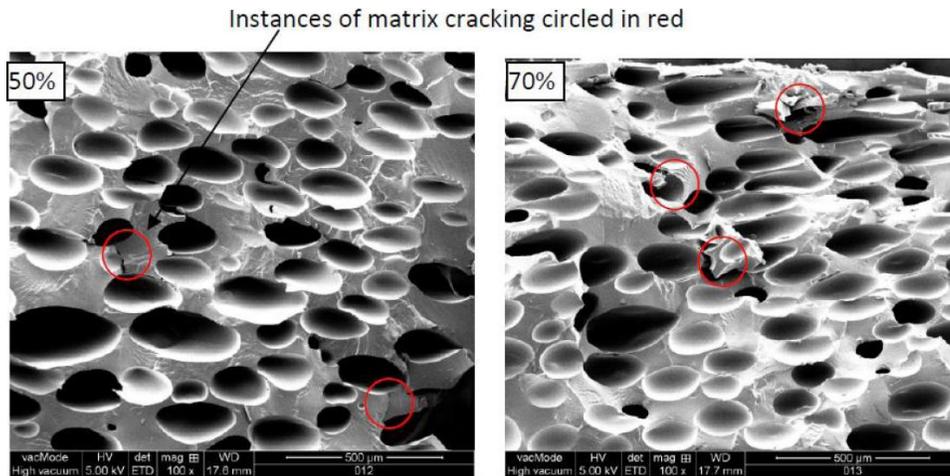
Studies on the effects of pressure on the result-

## Full Paper



**Figure 8 :** SEM microphotograph of foam fabricated by compression molding at 195°C, 1.5% AC, 5Min and 5MPa

original circular cell structure of the foam was changing to oval shape. When subjected to compressive force to reduce its thickness by 70%, the cells near the foam edges were almost completely flattened, while the ones in the middle adopted an oval shape. Further, matrix cracking was seen at 70% compressive force on 3% HGMS reinforced TPU foam. 7% HGMS reinforced TPU foam (Figure 10) showed a more stable structure under SEM observation. At 50% compressive force, some of the cells circular shape changed to oval, increasing the compressive force to 70% didn't give any further noticeable change on the cells shape. There was however some filler cracking observed. This shows that at high



**Figure 9 :** SEM microphotograph of 3% HGMS reinforced TPU foam after 50% and 70% compression

ant foam showed that, although a pressure of 5MPa gave foam with uniform characteristics, a low pressure of 2.5MPa didn't have much effect on the cell structure. At higher pressure of about 10MPa, the cells were seen to collapse as shown in Figure 7. This was as a result of high pressure exerted on the foam by the machine during processing high temperature also gave a similar effect as high pressure as shown in Figure 8. This was as a result of low viscosity of the polymer that was caused by increase in temperature leading to high flow of the TPU melt making it difficult to control the shape of the foam.

The effects of compressive force on the reinforced foam are shown in Figure 9 and 10. When 3% HGMS reinforced TPU foam (Figure 9) was subjected to compressive force till its thickness was reduced by 50%, SEM observation showed that, the

percentage of HGMS, the foam structure became more stable and could withstand high compressive force. The stable structure was as a result of cell size reduction with increasing filler percentage and the reinforcing effects of the HGMS.

### Instances of matrix cracking circled in red

### Thermal Properties

After TGA analysis, tests for pure TPU, TPU with 1%, 3%, and 5% HGMS, gave the comparative curves shown in Figure 11. From the Figure it can be deduced that, 1% HGMS had no thermal effects on the reinforced TPU foam. As the percentage of filler was increased to 3% and 5%, there was a slight positive shift in the thermal behavior in the TPU composite. The onset of degradation was found to slightly increase with increasing percentage of

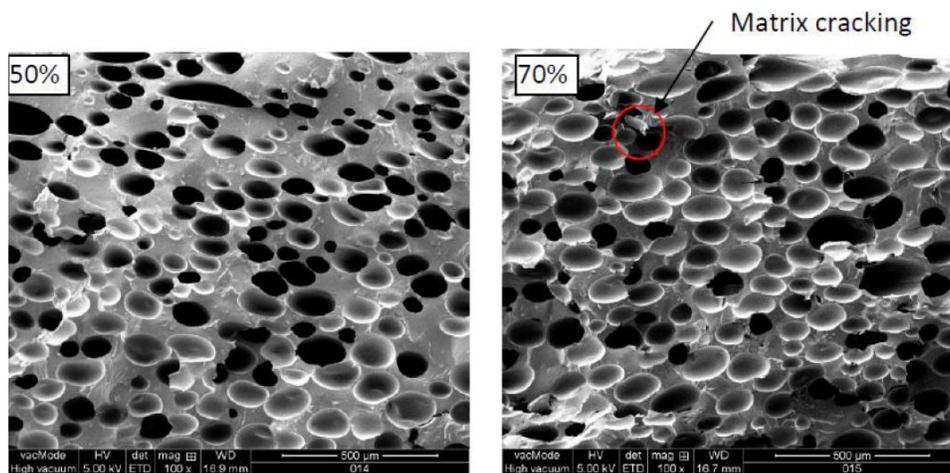


Figure 10 : SEM microphotograph of 7% HGMS reinforced TPU foam after 50% and 70% compression

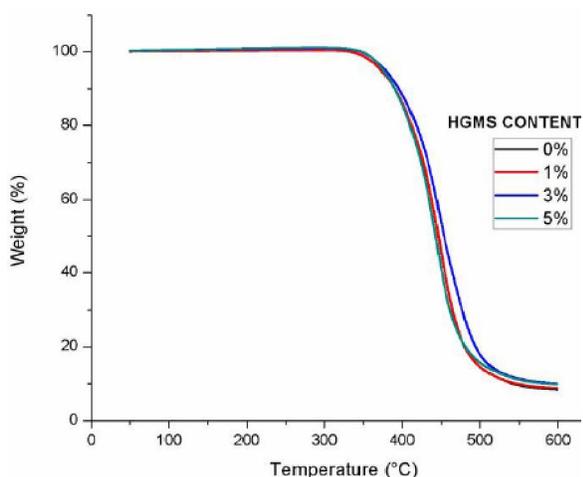


Figure 11 : Comparative TG curves for TPU reinforced with varying percentages of HGMS

HGMS in the foam. The residue percentage weight was found to be higher at 3% and 5% HGMS content, this resulted from the presence of thermally stable HGMS in the matrix. These can be summarized as in TABLE 1.

From TABLE 1, it can be deduced that, as the percentage of HGMS was increased in the foam, there was a significant improvement in the foam thermal as depicted by the standard deviation.

TABLE 1 : Onset of decomposition and residue mass after decomposition of pure TPU foam and foam reinforced with different amounts of HGMS

Composition of HGMS (%)	Onset of decomposition (°C)	Residue after decomposition (% mass)
0	332.5	8.2
1	332.8	8.7
3	346.7	9.9
5	347.8	9.8
Standard deviation	8.44	0.85

### Tensile Properties

The effects of increasing the content of foaming agent on the tensile properties of compression molded foam are presented in Figure 12(A). Increasing the percentage of foaming agent led to a decrease in the tensile properties of the foam. The tensile properties of the foam were best at 0.5% AC content and the tensile load bearing capability of the foam reduced as the foaming agent was increased up to 2%. Increasing the foaming agent increased the number of cells in the foam which consequently lowers molecular orientation of the polymer chains. Further, introduction of cells in the polymer structure increase the possibility of developing lines of weakness in the polymer thus the reduction in tensile properties with increasing content of foaming agent. The actual results are as tabulated in TABLE 2.

The effects of increasing HGMS content on the tensile properties of the foam were analyzed and presented in Figure 12(B). The breaking force reduced as the HGMS content was increased from 0-3%. The best strength of the foam was achieved at a HGMS concentration of 1%. The tensile properties

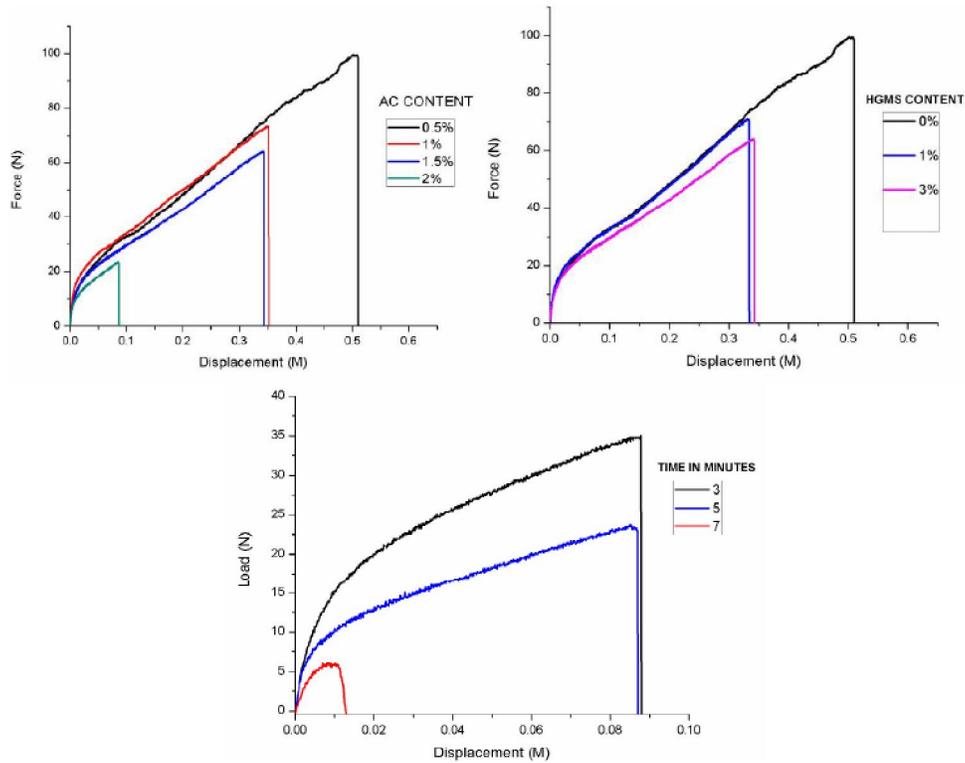


Figure 12 : Change in tensile strength with (A) increasing content of AC (B) increasing content of HGMS and (C) Increasing foaming time

TABLE 2 : Change in tensile strength with increasing content of AC

AC Content (%)	Force(N)	Strength (MPa)	Elongation (%)
0.5	99.67	553.70	17070.08
1.0	73.50	408.33	1906.42
1.5	64.17	356.48	1154.16
2.0	23.67	131.48	3057.28
Standard deviation		175.18	7556.04

were poorest at 3% HGMS concentration. Reinforcing TPU foam with HGMS interferes with the orientation of molecules in the polymer chains. The effect is reflected through reduction in the tensile properties of the foam. The decrease can be very high especially in the case where there is no interfacial adhesion. The actual results with corresponding standard deviations are presented in TABLE 3.

As shown in Figure 12(C), Studies on the effects of foaming time on the tensile properties of fabricated composite foam showed that; a foaming cycle of 5 minutes yielded the best tensile properties. Holding the composite foam under high temperature for a long time leads to degradation of the polymer chains, it also reduces the adhesion between the HGMS and the TPU thus good tensile properties

were realized at shorter foaming time. The discussed representative curves are as tabulated in TABLE 4.

### Compression Properties

Analysis of the data obtained after compression gave the following curves as shown in Figure 13. The data used to plot the curves was an average of 3 tests per sample type.

Reinforcing TPU foam with HGMS led to an increase in compressive strength of each of the reinforced foams, 3% HGMS showed the least compressive strength although it was higher than the compressive strength of pure TPU foam. 7% HGMS reinforced foam had the highest compressive strength. The same trend was observed with modulus of elasticity whereby, 7% HGMS reinforced foam gave the

TABLE 3 : Change in tensile strength with increasing content of HGMS

HGMS Content (%)	Force(N)	Strength (MPa)	Elongation (%)
0	110.17	612.04	16473.80
1	71.00	3944.44	11251.30
3	64.17	356.48	11545.16
Standard deviation		2001.82	2934.06

TABLE 4 : Change in tensile strength with change of foaming time

Time (Min)	Force(N)	Strength (MPa)	Elongation (%)
3	61.12	340.19	11041.67
5	64.17	356.48	11545.16
7	36.00	133.33	632.59
Standard deviation		124.40	6160.18

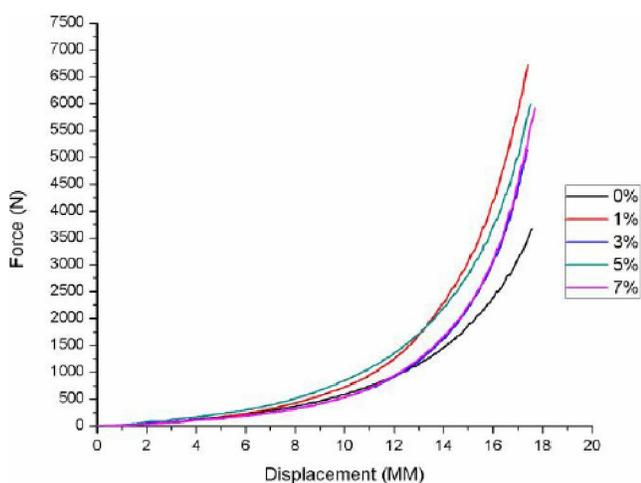


Figure 13 : Graphical representation of compression test data for HGMS/TPU composite foam containing different amounts of HGMS

highest modulus and 3 % gave the lowest modulus which was much higher than the modulus of unreinforced foam. The improvement in the compressive properties of reinforced foam were as a result of the HGMS capability to withstand high compressive force coupled with a good interfacial adhesion between the TPU and the HGMS which led to a good load transfer from the matrix to the reinforcing HGMS.

The graphical representation of the hardness test for HGMS/TPU composite foam is shown in Figure 14. Note that the figures presented are averages of four tests per sample type to give representative information about the foam hardness based on shore hardness A scale.

When the HGMS percentage in the composite was gradually increased, the foam hardness in-

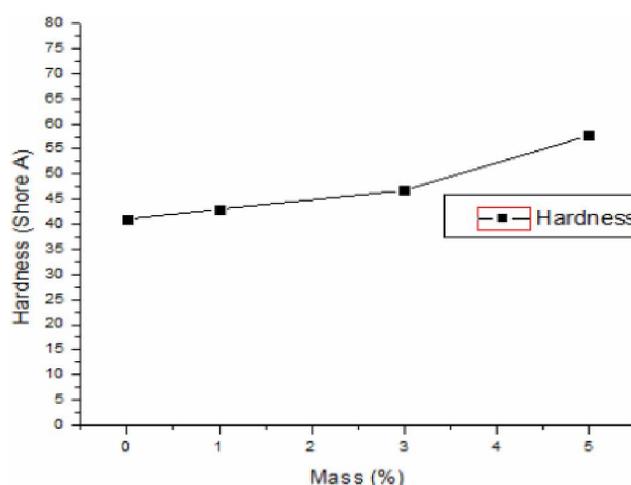


Figure 14 : Effects of increasing HGMS content on the hardness of reinforced foam.

creased. This means that, the hardness of foam increase with increasing filler content. The hardness was as a result of the reinforcing effects of the HGMS. For applications requiring different levels of hardness, the filler content can be varied to achieve desired results.

### Density of the HGMS reinforced foam material

The results after testing the density of HGMS/TPU reinforced foam are presented graphically as shown in Figure 15. Six samples of each composition were tested and the curves given are averages of the samples tested. Sample sizes measuring 1cm by 1cm by 0.5cm were used during the foam density test.

The above graphs show that; pressure, time, HGMS content have density reduction effect on the resultant foam. Foaming time and pressure had the

## Full Paper

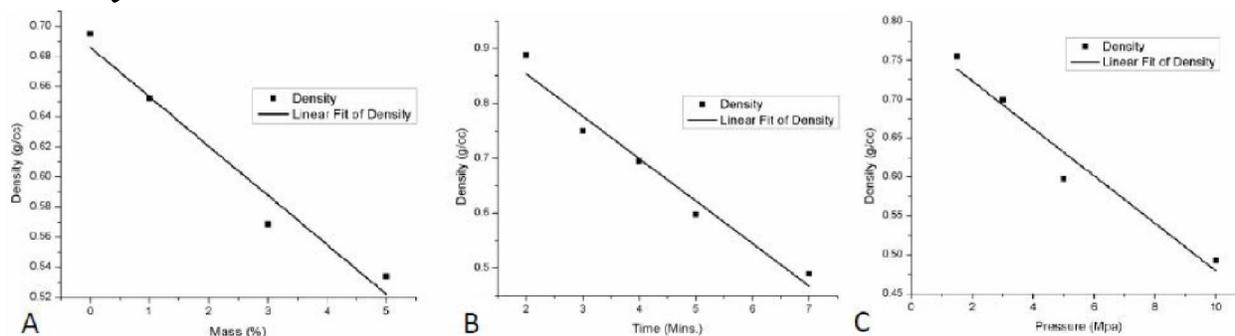


Figure 15 : Graphical representation (A) Increasing HGMS content (B) Increasing foaming time and (C) Increasing foaming pressure on the foams' density.

highest density reducing effect. This effect is not desirable because high pressure and foaming time result in non-uniform foam, because loss of material resulting from low viscosity of the polymer on prolonged melting was noticed and this led to difficulty in material control during molding. Increasing the amount of foaming agent was also found to cause reduction in density of the resultant foam but as earlier seen in SEM morphology study the cell size and distribution becomes uneven with increasing amount of foaming agent.

## CONCLUSION

The objective of this research work was to fabricate HGMS reinforced foam (TPU) material for high performance applications, which include high compression loading, high tensile loads, pressure and elevated temperatures. This need, combined with desire to reveal the full potential of a novel material, HGMS reinforced TPU foam, motivated this study. The initial task was selection of required raw materials. This was followed by surface modification of the HGMS to enhance adhesion with the polymer matrix. The HGMS were then dispersed in the TPU by means of a high speed mixer, and finally different combinations of filler, matrix and foaming agent were used to fabricate reinforced TPU foam of different morphology and mechanical properties.

From the analysis of test results, several observations were determined. Unreinforced polyurethane foam has a low resistance to compressive force but has high elongation under tensile load. Polyurethane foam reinforced with hollow glass microspheres showed increased resistance to compressive force

and decreased resistance to tensile force as percentage of reinforcing filler was increased. The density of the reinforced foam was lower than that for pure TPU foam while hardness increased with increasing filler content.

Increasing the foaming agent content from 1% to 2% decreased the tensile strength of the foam by about 50%. Increasing the HGMS content from 0% to 3% decreased the tensile strength of the foam by about 40% due to decreased orientation of the polymer chains with increasing HGMS content. Increasing the HGMS content from 0% to 7% led to an increase in the compressive strength of the composite foam by about 47%. After a 75% compressive force, SEM observation of 7% HGMS reinforced TPU foam showed a more stable structure than 5% HGMS reinforced foam which indicates that a high content of HGMS in the composite foam gave a structure that was more stable to compressive force and less stable to tensile loading.

## REFERENCES

- [1] Z.Zhang, Y.P.Handa; *Journal of Polymer Science Part B: Polymer Physics*, **36**, 977 (1998).
- [2] Y.P.Handa, Z.Zhang; *Journal of Polymer Science Part B: Polymer Physics*, **38**, 716 (2000).
- [3] P.D.Condo, K.P.Johnston; *Macromolecules*, **25**, 6730 (1992).
- [4] D.Louis, G.Richard; in *Foam Extrusion*, CRC Press, (2000).
- [5] R.Gendron; *Thermoplastic foam processing : principles and development*, CRC Press, Boca Raton, Fla., 2005.
- [6] M.F.Sonnenschein, R.Prange, A.K.Schrock, *Polymer*, **48**, 616 (2007).

- [7] [http://www.cenotechnologies.com/glass\\_microspheres.php](http://www.cenotechnologies.com/glass_microspheres.php).
- [8] E.M.Wouterson, F.Y.C.Boey, X.Hu, S.C.Wong; *Composites Science and Technology*, **65**, 1840 (2005).
- [9] G.Tagliavia, M.Porfiri, N.Gupta; *Journal of Composite Materials*, **43**, 561 (2009).
- [10] J.S.Huang, L.J.Gibson; *Journal of the Mechanics and Physics of Solids*, **41**, 55 (1993).
- [11] H.S.Kim, P.Plubrai; *Composites Part A: Applied Science and Manufacturing*, **35**, 1009 (2004).
- [12] N.Gupta, R.Nagorny; *Journal of Applied Polymer Science*, **102**, 1254 (2006).
- [13] A.Calahorra, O.Gara, S.Kenig; *Journal of Cellular Plastics*, **23**, 383 (1987).
- [14] N.Bilow, P.M.Sawko; *Journal of Cellular Plastics*, **11**, 207 (1975).
- [15] S.N.Patankar, Y.A.Kranov; *Materials Science and Engineering: A*, **527**, 1361 (2010).
- [16] Z.G.An, J.j.Zhang, S.l.Pan; *Applied Surface Science*, **255**, 2219 (2008).
- [17] M.Narkis, L.Nicolais; *Journal of Applied Polymer Science*, **15**, 469 (1971).
- [18] J.Janèå, J.Kuèera; *Polymer Engineering & Science*, **30**, 714 (1990).
- [19] S.Mitsui, H.Kihara, S.Yoshimi, Y.Okamoto; *Polymer Engineering & Science*, **36**, 2241 (1996).
- [20] T.C.Tszeng; *Composites Part B: Engineering*, **29**, 299 (1998).
- [21] N.V.T.A.V.Sirotinkin, V.V.Bestouzheva, Y.V.Omelchouk; *Universal Decimal Classification*, 678.664, 678.02.
- [22] S.Y.Fu, X.Q.Feng, B.Lauke., Y.W.Mai; *Composites Part B: Engineering*, **39**, 933 (2008).
- [23] M.E.J.Dekkers, D.Heikens; *Journal of Applied Polymer Science*, **28**, 3809 (1983).
- [24] B.Pukanszky, G.VÖRÖS; *Composite Interfaces*, **1**, 411 (1993).
- [25] J.Z.Liang, R.K.Y.Li, S.C.Tjong; *Polymer Composites*, **20**, 413 (1999).
- [26] B.Pukanszky; *Composites*, **21**, 255 (1990).
- [27] S.N.Maiti, P.K.Mahapatro; *Journal of Applied Polymer Science*, **42**, 3101 (1991).
- [28] J.Jancar, A.T.Dibenedetto, A.Dianselmo; *Polymer Engineering & Science*, **33**, 559 (1993).
- [29] S.Ahmed, F.R.Jones; *Journal of Materials Science*, **25**, 4933 (1990).
- [30] D.E.Packham; *International Journal of Adhesion and Adhesives*, **16**, 121 (1996).
- [31] I.S.C.R.Hyungu, K.K.Chang; *Industrial & Engineering Chemistry Research*, **50**, 7305 (2011).
- [32] P.H.Harding, J.C.Berg; *Journal of Adhesion Science and Technology*, **11**, 1063 (1997).
- [33] T.M.Mower, A.S.Argon; *Journal of Materials Science*, **31**, 1585 (1996).
- [34] P.L.Fredrick N.Mutua, Jacob K.Koech, Yimin Wang; *Materials Sciences and Applications*, **3**, 856 (2012).
- [35] N.Y.R.Gupta, M.Porfiri; in *22nd Annual Technical Conference of American Society for Composites*, Seattle, USA, 072 (2008).
- [36] G.Gladysz, B.Perry, G.McEachen., J.Lula; *journal of materials science*, **41**, 4085 (2006).
- [37] J.Z.Liang; *Journal of Elastomers, Plastics*, **37**, 361 (2005).
- [38] N.Gupta, S.K.Gupta., B.J.Mueller; *Materials Science and Engineering: A*, **485**, 439 (2008).
- [39] Y.J.Huang, L.Vaikhanski, S.R.Nutt; *Composites Part A: Applied Science and Manufacturing*, **37**, 488 (2006).
- [40] E.Rizzi, E.Papa, A.Corigliano; *International Journal of Solids and Structures*, **37**, 5773 (2000).
- [41] F.J.E.Beer, J.DeWolf, D.Mazurek; *Mechanics of materials*, McGraw-Hill, New York (USA), (2008).
- [42] J.Z.Liang, R.K.Y.Li; *Polymer Composites*, **19**, 698 (1998).
- [43] G.Tagliavia, M.Porfiri., N.Gupta; *Composites Part B: Engineering*, **41**, 86 (2010).
- [44] F.A.T.Hongyu, J.Galen, H.FuHung; *International Journal of Polymer Science*, 2012 (2012).
- [45] P.A.D.Bois, S.Kolling, M.Koesters, T. Frank; *International Journal of Impact Engineering*, **32**, 725 (2006).