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## Effect of Varying Mixing Ratios and Pre-Heat Temperature on the Mechanical Properties of Polyurethane (PU) Foam

C. Oppon<sup>a,\*</sup>, P. M. Hackney<sup>a</sup>, I. Shyha<sup>a</sup>, M. Birkett<sup>a</sup>

<sup>a</sup>*Department of Mechanical and Construction Engineering, Faculty of Engineering and Environment, Northumbria University at Newcastle, Newcastle upon Tyne, NE1 8ST, UK.*

### Abstract

The continuous growth of the usage of Polyurethane foams requires that designers and manufacturers investigate the appropriate factors that affect their production and full usage in order to exploit their full potential. This research reports the effects of the mixing ratio of the main constituents (polyol and diisocyanate) which form the polyurethane foams and different pre-heat temperatures of the separate chemicals before mixing. The work has documented that there is a significant reduction of foaming time of 452 seconds at 20oC to 54 seconds at 100oC when the main constituents are pre-heated before mixing. Both tensile and compressive strengths are improved with increasing the ratio of diisocyanate to polyol. The density of the foam also increases when the concentration of polyol is increased.

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**Keywords:** Polyurethane Foam; Polyol; Diisocyanate; Mixing Ratios.

### 1. Introduction

Polyurethanes (PU's) are used in many applications, such as aeronautics (e.g. friction dampers), automobile (e.g. car dashboard), building construction (e.g. insulation purposes), marine (e.g. boat body), and many household applications (e.g. furniture) [1]. Their usage continues to grow as they can be used in areas where other materials do not work due to their lightweight stiff structure [2]. PU's are among the widely used construction materials that can be formulated for medical devices [2, 3]. Designers and manufacturers need to investigate the significant factors that

\* Corresponding author. Tel.: +44-191-243-7834

E-mail address: [charles.oppon@northumbria.ac.uk](mailto:charles.oppon@northumbria.ac.uk)

affect their production and full usage in order to leverage these versatile properties [3, 4, 5]. PU's are polymers containing soft segment (polyol) and hard segment (diisocyanate) that are altered to control their structures and properties. The reaction between the diisocyanate and the chain extender produces the rigid, hard segments, whereas soft segments are comprised of polyether, polyester or polycarbonate diol (polyol). The soft matrix is strengthened by the hard fields. The degree of phase separation which in turn affects the physical and mechanical properties [6], biocompatibility, and biodegradability [7] are influenced by the content of the hard segment [8]. The molecular weight of the main constituents of polyurethane (polyol and diisocyanate) and other segments can be varied to tune or modify these properties to serve in many areas such as in tissue engineering, either for reconstruction of soft tissue or for cartilage and bone generation [9]. One interesting application of PU is silicone implants containing a cohesive gel with the outside coated with polyurethane foam. When used as implants, PU's have the advantage of preventing capsular contracture and displacement or rotation of the implant thereby reducing re-operation in breast augmentation surgery [10]. Even though these implants coated with PU foams take about 3-6 months to soften, various articles have reported that they feel warmer and more like real breasts than other implants [11].

The processing of polyurethane foam requires certain chemicals and some aids such as blowing agents to ensure sufficient control to produce useful polyurethane foam required for commercial products. During the foaming process, a surfactant controls an interaction that takes place between the non-homogeneous components of the reacting system. In many cases, chain extenders or cross linkers, as well as fire retardants, fillers and pigments are used to modify the properties of the polymer structures [12]. Depending on the formulation, the catalysts and the application, the reaction is typically started within few seconds and completed in a few minutes. Within this time, it is essential to dispense the reacting liquid mixture into the mould and also to clean the combined 'mixing and dispensing' equipment ready for the operation. The exothermic chemical reaction is completed within the mould and the manufactured article can then be removed from the mould [13]. In addition to the effect of mixing ratio and the pre-heat temperature, manufacturing the polyurethanes requires various chemicals to control the polyurethane-foaming reactions and to create the right properties in the end-product. It has been researched and established that all practical polyurethane systems include some of the additives mentioned in Table 1. This study reports on the effects of varying mixing ratio and pre-heat temperatures of the main constituents (polyol and diisocyanate) on the mechanical properties of the polyurethane foam to make it suitable in applications such as for Additive Manufacturing also known as 3D Printing technology.

### Nomenclature

AM	Additive Manufacturing
PU	Polyurethane
3D	Three Dimensional
EDX	Energy Dispersive X-ray analysis
SEM	Scanning Electron Microscope
ASTM	American Society for Testing and Materials

Table 1. Polyurethanes additives and their functions [13]

Additives	Reasons for use
Catalysts	To speed up the reaction between polyol and polyisocyanate
Cross-linking and chain-extending agents	To modify the structure of the polyurethane molecules and to provide mechanical reinforcement to improve physical properties (e.g. adding a polyisocyanate or polyol with more functional groups)
Blowing agents surfactants	To create polyurethane as a foam to control the bubble formation during the reaction and, hence, the cell structure of the foam
Pigments	To create coloured polyurethanes for identification and aesthetic reasons
Fillers	To improve properties such as stiffness and to reduce overall costs
Flame retardants	To reduce flammability of the end product
Smoke suppressants	To reduce the rate at which smoke is generated if the polyurethane is burnt
Plasticisers	To reduce the hardness of the product

## 2. Experimental Work/Methodology

Different densities and thicknesses of polyurethane skin are produced depending on the blowing agent and the concentration in the reacting mix, but in this research, only the main constituents (polyol referred to as part 'A' and diisocyanates referred to as part 'B' respectively) of polyurethane foam were considered for analysis (A:B). A mixing ratio of 1:1 (50:50) was used as a reference and varied in both directions for 9 screening tests which included 30:70, 35:65, 40:60, 45:55, 50:50, 55:45, 60:40, 65:35 and 70:30. Results obtained indicated that for mixing ratios of 60:40, 65:35 and 70:30 (Part A higher than 55), the foam formed was soft and dimensionally unstable and worsened with increasing part 'A'. In the other direction of the mixing ratio where part 'A' decreased whilst part 'B' increased (i.e. 45:55, 40:60, 35:65, and 30:70), a rise in the foam strength was obtained however, above 60% of part 'B', the obtained foam was brittle and could be crushed by hand force. This means that further increase of part 'B' (such as 20:80 and 10:90) will be far more brittle and weaker. It was therefore agreed to use only 45:55, 50:50 and 55:45 mixing ratios for further investigations and analysis. Furthermore, tests to evaluate the effect of pre-heating on the produced foam were conducted by using 50:50 mixing ratio. The constituents were pre-heated prior to mixing at several pre-heating temperature ranging from 20°C to 100°C at a step of 10°C. In each case the foam was cast and the outer skin removed to a depth of about 10mm to obtain a homogeneous part. Samples of the foams produced at 20°C with mixing ratios of 55:45; 50:50 and 45:55 were scanned using an FEI Quanta 200 Scanning Electron Microscope (SEM) in order to assess the micro-structure of these samples. This was repeated for the samples produced from 50:50 mixing ratio and pre-heat from 20°C to 100°C at intervals of 10°C.

Blocks of foam produced with different mixing ratios were cut to 150mm x 100mm x 100mm and weighed using a calibrated sensitive scale of readability and reproducibility of 0.001g and  $\pm 0.003$ g linearity, 3sec stabilization time and standard error of  $\pm 0.5\%$ . Whilst the 50:50 mixing ratio was maintained and the main constituents pre-heated and hand mixed uniformly, the time taken for each mixing ratio to complete foaming from the beginning of bubbling (nucleation) to the complete stoppage of foaming was recorded using a stop clock. This was carried out to evaluate the effect of pre-heat temperatures on the foaming time. Standard tensile specimen sizes were cut from the foam according to ASTM D3039 and then tested using an Instron E3000 with a 3kN load cell under a crosshead speed of 8 mm/min and  $\pm 0.005\%$  load cell accuracy as shown in Fig. 1. Similarly for compression testing, blocks were cut to 40mm x 40mm x 40mm according to ASTM 3410M and then tested using the Instron-3382 with a 100kN load cell under a crosshead speed of 8 mm/min  $\pm 0.2\%$ , maximum resolution of 0.1N and a load measurement of  $\pm 0.5\%$ , see Fig. 2. For both compressive and tensile tests as well as foam weight and size measurements, three readings were obtained and the average was computed and used for analysis.

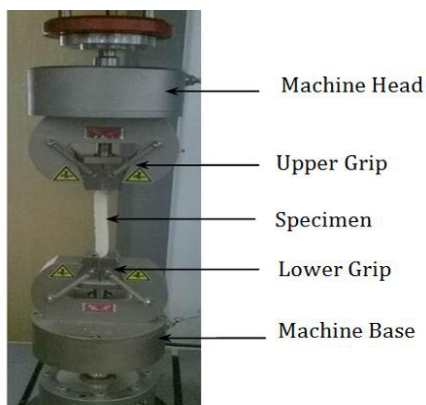


Fig. 1. Tensile testing using Instron E-3000

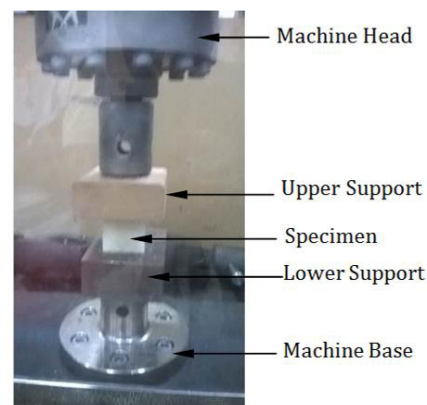


Fig. 2. Compressive testing using Instron 3382

The porosities of foam produced were determined using the liquid displacement method. In this method ethanol which penetrates into the pores of the foam was used as the displacement liquid. A specimen of each of the PU foam

scaffolds produced was dried at room temperature and placed in a graduated cylinder which is filled with ethanol to an initial volume ( $V_1$ ) and subjected under vacuum for 20 minutes for the ethanol to fill the pores of the scaffold. The volume ( $V_2$ ) of the ethanol with the scaffold was noted. The scaffold was then removed from the ethanol and the remaining volume ( $V_3$ ) was noted [12]. The percentage porosity 'P (%)' of the scaffold was then calculated as follows:

$$P (\%) = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100 \quad (1)$$

Where: ( $V_2 - V_3$ ) = total volume of the scaffold, and ( $V_1 - V_3$ ) = volume of ethanol retained in the scaffold sample.

### 3. Results and Discussions

#### 3.1. Effect of varying mixing ratio on Polyurethane foam

Fig. 3 shows that the density of the PU foam increases with increasing part B (diisocyanate) of the PU main constituents and vice versa. Densities for the produced foam using different mixing ratios are presented in Table 2. The average density for the 55:45 mixing ratio was 46.2 kg/m<sup>3</sup>, and that obtained from 50:50 mixing ratio was 48 kg/m<sup>3</sup>, whilst that obtained for 45:55 mixing ratio was 53.3 kg/m<sup>3</sup>. The average density obtained from the 55:45 mixing ratio indicates a 3.8% reduction when compared to the density of the 50:50 mixing ratio whilst that obtained for the 45:55 mixing ratio indicates an 11% increase when compared to the result for the 50:50 mixing ratio.

Porosities for the produced foam using different mixing ratios are presented in Table 3. From the results obtained using the liquid displacement method to measure the porosity level, it could be observed that the 55:45 mixing ratio had the highest porosity of 43%. This was followed by the 50:50 mixing ratio with a porosity of 33% and then the 45:55 ratio which had the least porosity of 29% as plotted in Fig. 4. This must therefore be precisely controlled by adding other chemicals to obtain the required standard of foam for the desired purposes. When the porosity of the 55:45 mixing ratio was compared to that of the 50:50 mixing ratio a 30% increase was obtained. The 45:55 mixing ratio indicates a 12.1% decrease in porosity when compared to the density of the 50:50 mixing ratio.

Table 2. Densities of different mixing ratios

Mixing Ratio	55:45	50:50	55:45
Density (kg/m <sup>3</sup> )	46.2	48.0	53.3

Table 3. Porosities for different mixing ratios

Mixing Ratio	55:45	50:50	55:45
Density (kg/m <sup>3</sup> )	43	33	29

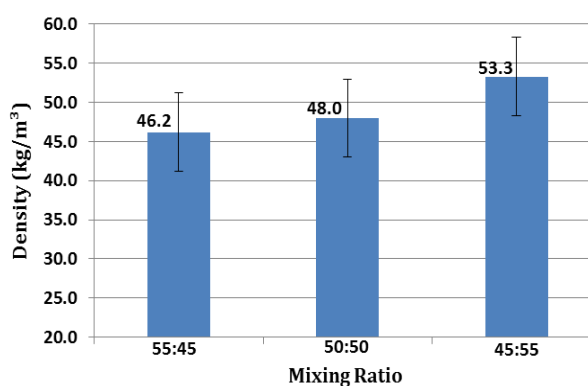


Fig. 3. Density results versus mixing ratios

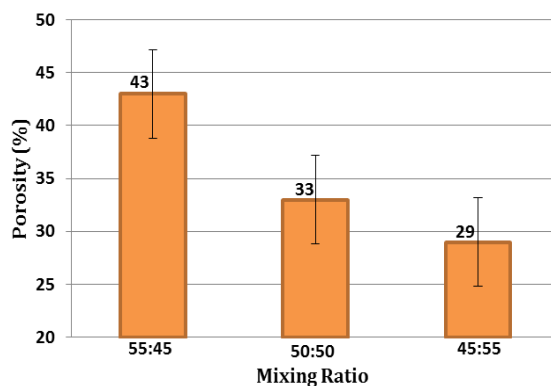


Fig. 4. Porosity results versus mixing ratios

The tensile stress-strain curves for the produced foams with varying mixing ratio are presented in Fig. 5. The results show that at the standard 50:50 mixing ratio, the tensile strength was 430.0kPa. This significantly increased to 516.6kPa when the mixing ratio was changed to 45:55 and reduced to 322.5kPa at mixing ratio of 55:45. This means the tensile strength of the PU foam was improved by 20.1% when the diisocyanate (part 'B') was increased from 50% to 55% mixing ratio and decreased by 33.3% when the polyol (part 'A') was increased from 50% to 55% of the mixing ratio. Unlike the tensile strengths which were quoted at just before failure, the compressive strengths were quoted at yield points. Fig. 6 shows that the maximum compressive stress is 240kPa for the 45:55 mixing ratio; followed by 185kPa for 50:50 mixing ratio and 148kPa for the 55:45 mixing ratio. This follows a similar trend to the tensile test results. When the 50:50 mixing ratio was used as reference, the compressive strength was increased by 30% when the diisocyanate was increased from 50% to 55% of the mixing ratio. This means that with careful control, the compressive strength of the PU foam can be improved to suit a particular application by increasing the diisocyanate and vice versa if higher strain of the material is required.

Images obtained from SEM analysis (shown in Fig. 7) for mixing performed at 20°C showed that the 45:55 mixing ratio (Fig. 7c) has closer and better structured pores which makes it stronger than the 50:50 (Fig. 7b) and the 55:45 (Fig. 7a) mixing ratio foams. Even though the 55:45 mixing ratio also had closed pores, its dimensional stability is poor. Specimens cut out from the foam produced from 55:45 mixing ratio disfigured after 24 hours whilst that of 45:55 and 50:50 ratio foams of the same dimensions maintained their dimensional accuracy after the same period of time. This result suggests that beyond 50:50 mixing ratio which is the suppliers' recommendation, increasing the polyol decreases the dimensional stability as well as affecting the porosity and density of the polyurethane foam.

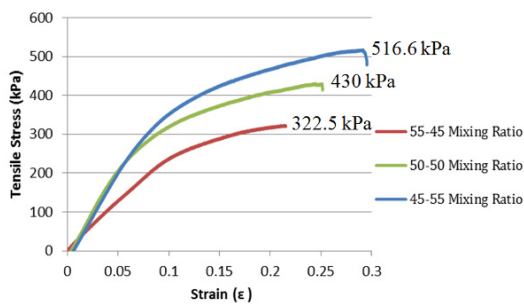


Fig. 5. Tensile stress strain curves for different mixing ratios

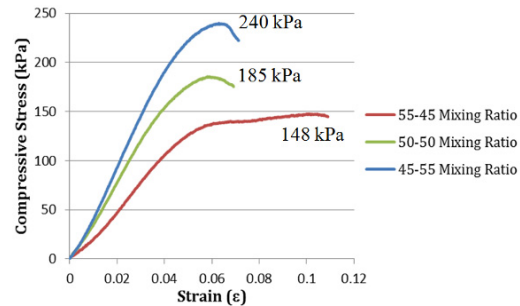
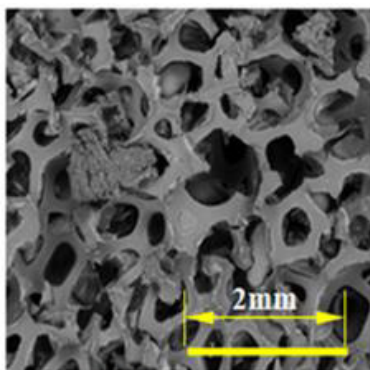
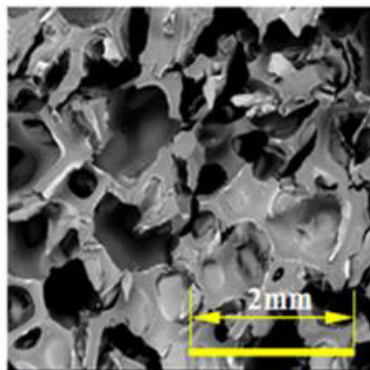


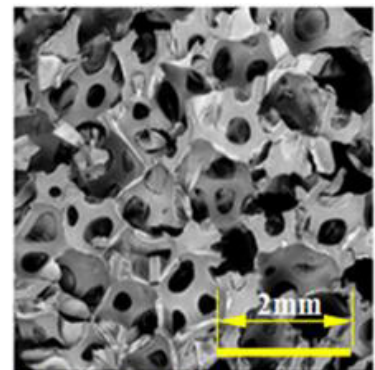
Fig. 6. Compressive stress strain curves for different mixing ratios



(a) 55:45 Mixing ratio at 20°C



(b) 50:50 Mixing ratio at 20°C



(c) 45:55 Mixing ratio at 20°C

Fig. 7. SEM Images of PU Foam

### 3.2. Effect of pre-heat temperature on the produced foam

Results of foaming time versus pre-heat temperature are shown in Fig. 8. The results indicate that the foaming time at the standard temperature of 20°C was 452 seconds. This was reduced to 54 seconds at 100°C pre-heat temperature, indicating 88% reduction in foaming time. From the graph, there is a trend that the foaming time reduces as the pre-heat temperature increases, but the decrease in foaming time above 80°C pre-heat temperature is relatively insignificant.

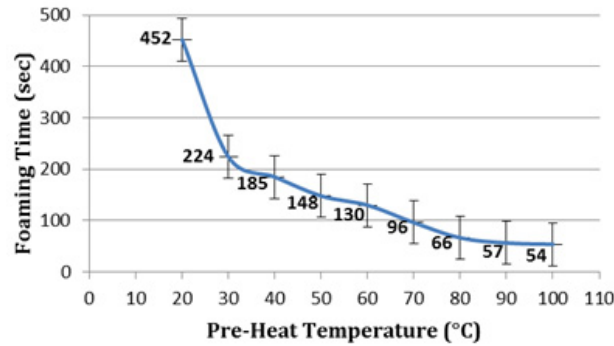


Fig. 8. Foaming time for different pre-heat temperature

The tensile stresses obtained for 50:50 mixing ratio foams, pre-heated from 20°C to 100°C are presented in Fig. 9. The 20°C pre-heat temperature had the highest tensile strength of 430kPa. This follows a reduction trend with increasing pre-heat temperature except the stresses at 70°C and 100°C pre-heat temperatures which were out of the trend. The least tensile stress recorded was 245kPa at 70°C pre-heat temperature. It could therefore be concluded that the tensile strength of the PU foam reduces with increasing foaming pre-heat temperature. Therefore, where the applications do not require much tensile strength and fall within the stated range of strength, the pre-heat would be of great advantage to significantly reduce foaming time which would make the PU material suitable for high speed process applications.

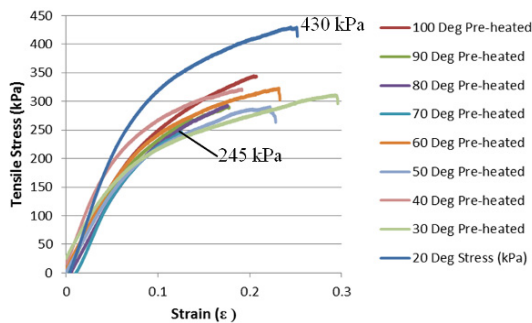


Fig. 9. Tensile stress results for foams produced at different pre-heat temperature

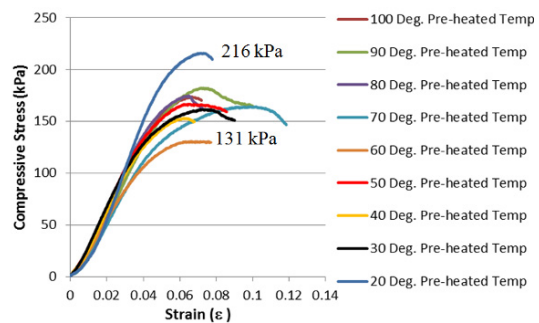


Fig. 10. Compressive stress results for foams produced at different pre-heat temperature

Fig. 10 shows compressive stress results for foams produced using 50:50 mixing ratio and at different pre-heat temperatures. The results indicate that foam produced with 20°C pre-heat temperature had the highest compressive stress (216kPa) compared with other pre-heat temperatures. When the pre-heat temperature is altered from 20°C, the compressive strengths do not have a consistent trend with the pre-heat temperature. The least compressive stress recorded was 131kPa for 60°C pre-heat temperature foam. Where compressive yield strength required for a



particular application is not high, pre-heat temperature would be of great advantage. This can further be improved with the addition of other chemicals for higher compressive strength applications. The results obtained by maintaining the mixing ratio at 50:50 and varying the pre-heat from 20°C to 100°C at intervals of 10°C, show that the density decreases with increasing pre-heat temperature up to 60°C and increases with increasing pre-heat temperature beyond 60°C up to 100°C, as shown in Fig. 11.

Porosity results for PU foams produced using various pre-heat temperatures are shown in Fig. 12. From the results, it can be observed that the porosity increases from 33.3% at 20°C up to 45.2% at 60°C and decreases up to 37.3% at the earmarked 100°C. Even though this is not directly proportional to the density plot shown in Fig. 11, there is a trend which shows that the porosity increases with decreasing density and vice versa in relation to the pre-heat temperature as in figure 11. The increase of porosity from 20°C pre-heat temperature indicates a loss of strength when the temperatures of the PU chemicals were pre-heated before mixing.

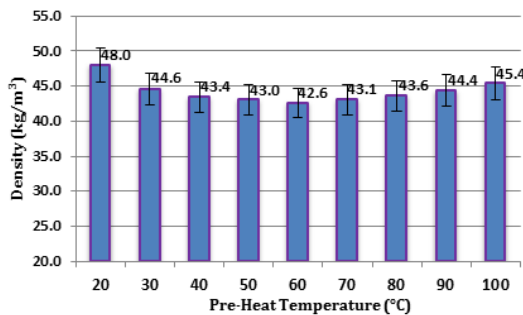


Fig. 11. Density of Different Pre-Heat Temperatures.

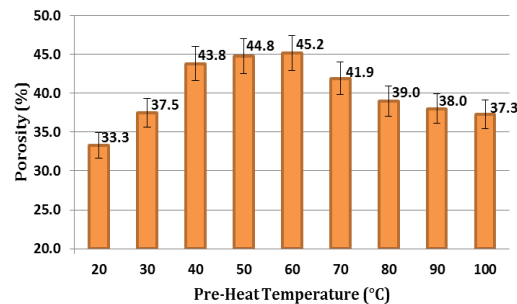


Fig. 12. Porosity of Different Pre-Heat Temperatures

The SEM images shown in Fig. 13 show that the scaffold structure of the 50:50 PU foam varies considerably with increasing pre-heat temperature. The results show that from 20°C to 40°C, the size of the pores of the foam increases which most likely corresponds to the increase of porosity and decrease of density. The pores of the 50°C specimen were marginally greater in size than the 40°C specimen but also slightly smaller in size than the 60°C specimen, also indicating an increase in porosity and a corresponding decrease in density. The pore size reduction continues until 100°C which indicates a decreasing trend of porosity and an increasing trend of density of the PU foam from 60°C pre-heat temperature to 100°C.

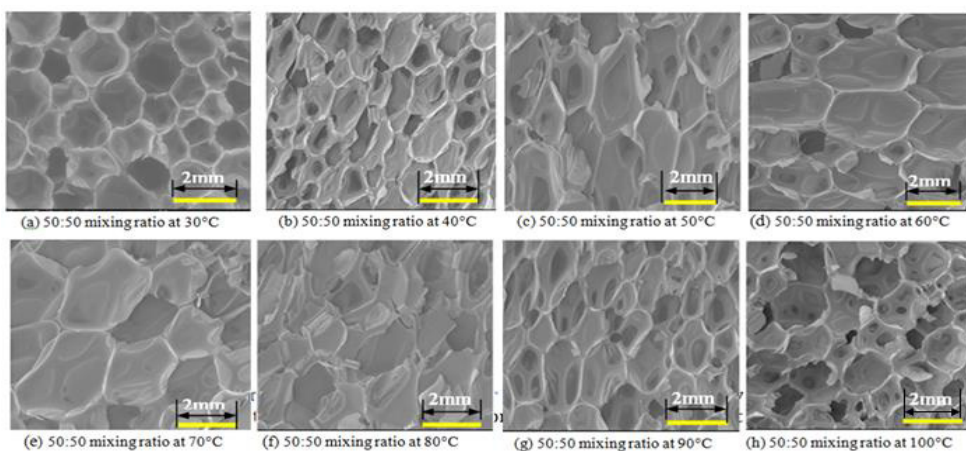


Fig. 13. SEM images of the PU foam produced at pre-heat temperatures from 30°C - 100°C

#### 4. Conclusions

The results showed that varying the mixing ratio significantly affects the mechanical properties of the polyurethane foam. The measured tensile strength was improved with increased diisocyanate which is referred to as 45:50 mixing ratio and can further be improved with the addition of other chemicals depending on the intended application. The produced PU foams were found to have lower compressive strengths compared to the tensile strengths. These were only measured up to the yield point and also exhibited a similar trend as the tensile strengths. The variation of density was found to be very small. Increasing the pre-heat temperature resulted in a dramatic reduction of foaming time from 452 seconds at 20°C to 54 seconds at 100°C. It can be also concluded that there is significant effect on the mechanical and other properties such as foaming rate of polyurethane foam when the mixing ratio and pre-heat temperature of the main constituents are altered. The soft matrix is strengthened thereby improving the mechanical properties when the diisocyanate increases and the foaming rate improved with increasing pre-heat temperature. These variations make the PU foam suitable for fast build time technologies such as 3D Printing for soft matrix scaffold, provided the properties due to the effects of the pre-heat temperature and mixing ratio variations are within the acceptable range for its intended purpose. There is also potential to further enhance the properties of these PU foams by adding one or more of the additives detailed in Table 1.

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#### References

- [1] D.C. Allport, D.S. Gilbert, S.M. Outterside. MDI, TDI and the Polyurethane Industry, MDI and TDI: Safety, Health and the Environment. A Source Book and Practical Guide, (2000).
- [2] A. Bezazi, F. Scarpa. Tensile fatigue of conventional and negative Poisson's ratio open cell PU Foams, *International Journal of Fatigue*, Bristol, UK (2008).
- [3] mmdiaadmin. Using Polyurethane in medical applications, MDDI, medical plastics, (2006). (Retrieved–November, 2014).
- [4] Bil, Monika, J. Ryszkowska, K.J. Kurzydłowski. "Effect of polyurethane composition and the fabrication process on scaffold properties". *Journal of Materials Science* 44.6 (2009).
- [5] H.W. Engels, et al., Polyurethanes: Versatile materials and sustainable problem solvers for today's challenges. *Angewandte Chemie International Edition* (2013).
- [6] K.S. Chen, Kun-San, et al. "Soft-and hard-segment phase segregation of polyester-based polyurethane". *Journal of Polymer Research* 8.2 (2001): 99-109.
- [7] J. Zhang, B.A. Doll, E.J. Beckman, J.O. Hollinger. A biodegradable polyurethane – a scorbic acid scaffold for bone tissue engineering. *Journal of Biomedical Materials Research, Part A* Vol. 67 (2003), pp. 389-400.
- [8] Y.W. Tang, R.S. Labow, J.P. Santerre. "Enzyme- induced biodegradation of polycarbonate polyurethanes: Dependence on hard- segment concentration." *Journal of Biomedical Materials Research* 56.4 (2001), pp. 516-528.
- [9] J. Guan, et al. Preparation and characterization of highly porous, biodegradable polyurethane scaffolds for soft tissue applications. *Biomaterials*, 26(18): (2005), pp. 3961–3971.
- [10] G. Vázquez, A. Pellon, Polyurethane-coated silicone gel breast implants used for 18 years. *Aesthetic plastic surgery*, 31(4): (2007), pp. 330–336.
- [11] <http://www.spirehealthcare.com> (Retrieved–January, 2015).
- [12] A. Asefnejad, et al. Manufacturing of biodegradable polyurethane scaffolds based on polycaprolactone using a phase separation method: physical properties and in vitro assay. *The International journal of nanomedicine*, 6 (2011), pp. 2375.
- [13] <http://www.essentialchemicalindustry.org/polymers/polyurethane.html> (Retrieved – May, 2015).