# Fabrication and Characterisation of Polyurethane/Sepiolite Polymer Nanocomposite Foams for Enhanced Energy Absorption

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**Abstract**
Polymer nanocomposite foams are unique materials that can be chemically, mechanically and structurally controlled in order to maximise the desired properties. Through size, shape and surface modification, the functionality of the foam can be enhanced or altered. This project looks at the incorporation of sepiolite clay nanorods into a polyurethane foam matrix in order to improve the sound vibration absorption properties of open cell flexible foams. Polyurethane foams are light weight, porous materials that can act as good thermal and sound barriers, while sepiolite nanorods have a high aspect ratio associated with the production of well dispersed composites as well as the possibility for the surface chemistry to be easily modified. The sepiolite rods were incorporated into the foam matrix through the mechanical dispersion of the rods into a foam precursor to allow the in-situ polymerisation of the foam matrix and sepiolite nanofiller. Three different grades of sepiolite clay were explored with varying surface chemistry. Cyclic and static compression testing were used to show how the change in surface treatment of the sepiolite lead to an increase in the energy dissipation of the system.

## 1. Introduction

Polyurethane (PU) foams are widely studied due to their extensive chemical and physical properties and the ease with which they can be tailored for a specific purpose [1-3]. Due to this adaptability of properties, PU foams have multiple applications from thermal insulation and packaging to filters and structural materials [4]. Due to their high damping capacity PUs have also been increasingly used for energy and sound absorption applications [5-8]. Open cell polymer foams can absorb and help insulate sound waves through the dissipation of the sound waves into heat as well as the air pumping through the structure causing a viscous loss to the sound wave [4].

The addition of a nanofiller to the foam matrix is believed to increase the energy dissipation [2] through the solid with many groups looking at different nanofillers. For example, Lee *et al.* added nano-silica to PU foams and found an increase in the sound absorption properties with added silica whilst the cell size of the foam decreased [5]. The exact cause of the effect nanofillers have on polymer matrices is not yet fully understood, though it is believed to be a combination of aspect ratio, filler dimensions being on the same order of magnitude as the polymer chains, therefore increasing interactions, and optimised surface chemistry increasing the dispersion within the matrix [3].

This investigation aims to look at improving the energy dissipation of a synthesised PU foam through the addition of a sepiolite clay rod nanofillers. This is a precursor to understanding the energy and sound absorption pathways through the cellular material in order to design open cell foams with specific absorption requirements. PU foam is formed through the addition reaction of polyol and isocyanate in the presence of a catalyst. A blowing agent is also present to form the cellular structure of the foam, in this case the blowing agent used was water. Using water as the blowing agent causes the release of

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carbon dioxide through the formation of urea linkages, therefore resulting in hard and soft phases of the resulting PU foam, giving it different properties depending on the ratio and distribution of these phases [9]. Sepiolite clay is a rod shaped nano clay with a high aspect ratio with a surface chemistry that can be easily modified for optimisation in different polar or non-polar environments [10]. Through altering the surface chemistry of the sepiolite clay and the weight loading into the PU matrix, it is investigated how much of an impact these two properties have on the mechanical properties of the nanocomposite.

## 2. Materials and methods

The polyurethane (PU) foam precursors, polymeric methylene diphenyl diisocyanate (MDI) and polyol blend, were obtained from Jacobsons Chemicals and are specifically formulated to synthesise open cell flexible PU foams The sepiolite clay rods were provided by Tolsa in the form of two different grades, the S9 clay was a bare sepiolite with no surface modification whilst the B40 had been pre-treated and stated to be optimised for alcohol type systems such as ethanol. (3-Aminopropyl) trimethoxysilane (APTMS) was purchased from Sigma Aldrich and used unmodified. All mechanical testing was performed on a Shimadzu compression test machine in the Department of Engineering at the University of Bristol using a 1kN load cell and all SEM micrographs were obtained using a Joel IT300lv SEM fitted with an Oxford Instruments Aztec X-Max 80 mm2 SDD at the Chemical Imaging Facility, University of Bristol.

### 2.1 Synthesis of Polyurethane (PU) Foam

The PU foam was prepared in accordance with the information provided with the precursors. The MDI and the polyol blend were mixed in a 2:1 ratio and stirred at 500 rpm for 9 seconds using an overhead stirrer. The foam was then left to rise and set overnight before being cut into the desired cube shapes, of known dimensions, for testing.

### 2.2 Synthesis of Nanocomposite PU Foam

The sepiolite clay was mixed with the polyol precursor, at varying weight percentages, at 7000 rpm using a Silverson high shear mixer for 1 minute. The foam was then synthesised in the same way as the pure foam, stated above. The same procedure was used for each of the three types of clay at all weight percentages tested.

### 2.3 Procedure for Silane Treatment of S9 sepiolite.

The treatment of the sepiolite clay with silane was based on work previously performed by Chen *et al.* [11]. S9 grade sepiolite (0.5 g) was dispersed (20000 rpm for 1 minute) in a water ethanol mixture (10 ml: 5 ml) using a high shear mixer. The dispersion was added to ethanol (85 ml) and stirred continuously at 500 rpm whilst APTMS (0.25 ml) was added. After 2 hours the mixture was Buchner filtered and washed with deionised water, air dried and then vacuum dried at 60 °C overnight. The dried clay was crushed with a pestle and mortar before being ready to disperse in the polyol as previously stated.

### 2.4 Mechanical Testing of Foam Samples

All three nanocomposite foam systems and the pure PU foam, were cut into 5 cuboid shapes of known dimensions. Each sample was compressed in a triangular cyclic pattern at a displacement rate of 5 mm/min. Each test consisted of 5 cycles within the linear region of the stress-strain curve and the 5th cycle only was looked at in order to avoid effects of rib failure from early cycles. The data was used to determine the energy dissipation per unit weight and the loss factor using a Matlab code [12]. The Young's modulus was calculated from a static compression curve (compressed at 5 mm/min), as the modulus between 2-4% strain.

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## 3. Results and Discussion

The aim of this study was to investigate any changes in energy pathways through PU foam systems through the addition of sepiolite clay rods with different surface chemistries. Three different surface chemistries were investigated and compared with the pure PU foam; the first was the bare S9 sepiolite with no surface modification, the second was the B40 clay that was pre-modified to optimally disperse in alcohol systems, and the third was the S9 clay modified with APTMS in order to aid dispersion in the polyol precursor. Each of the three clays were dispersed in the polyol at 2 different weight percentages, 0.5 wt% and 1 wt% using high shear mixing before the foams were visualised using SEM and mechanically investigated through static and cyclic compression testing.

Figure 1 shows the SEM micrographs of each nanocomposite PU foam as well as the pure PU foam with no nanofiller. When comparing the pure foam with the nanocomposite foams it can be qualitatively seen that the foams with S9 clay and the APTMS modified clay have, on average, smaller cell sizes than the pure foam. It has been previously observed that there is an inverse correlation between the cell size of a foam and the sound absorption properties [5]. The nanocomposite foam with the B40 grade clay, however, shows no significant difference in cell size to the pure foam and therefore would be expected to have no significant change in the energy dissipation of the system.

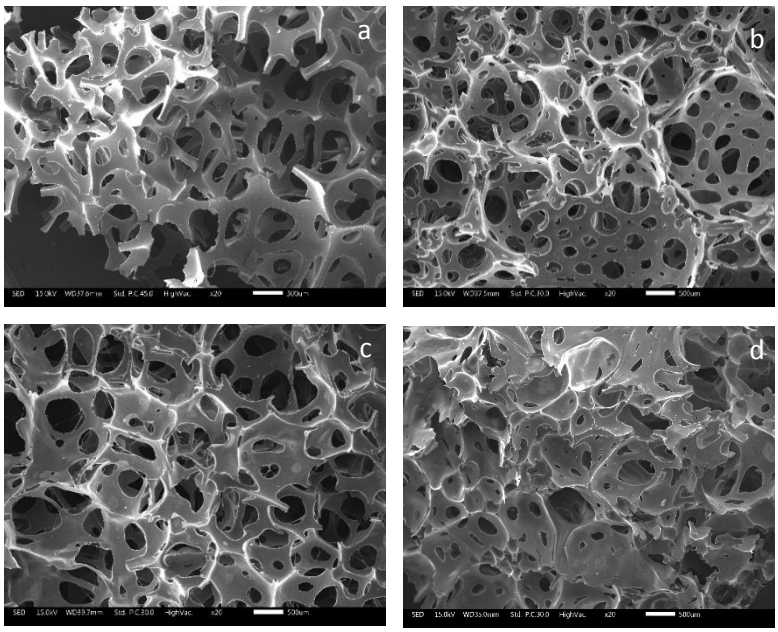


**Figure 1**: SEM micrographs of polyurethane foam with: a) 0 wt% clay, b) 1 wt% S9 sepiolite, c) 1 wt% B40 sepiolite and d) 1 wt% silane modified S9. Each sample has been magnified 20 times in the above micrographs.

Figure 2 shows the Young's modulus calculated between 2 and 4 % strain from the static compression test of each foam system. A Welch's T test was performed on the data and showed that the null hypothesis, that the distributions are the same, was true for all systems [13]. This indicates that the addition of the sepiolite in the ranges investigated had no significant effect on the elastic properties of the system.

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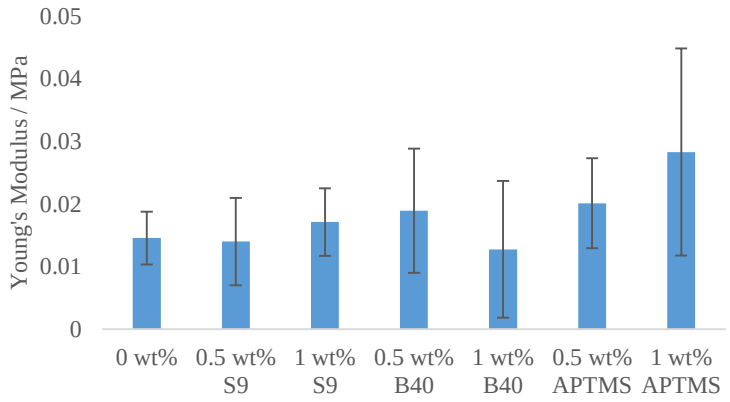


**Figure 2**: Young's modulus of each composite system, measured between 2 and 4% strain from the static compression testing. The error was calculated as the standard deviation over 5 samples.

This lack of change in the Young's modulus is likely due to the lack of induced alignment of the clay rods within the matrix [14]. Previous work with rod shaped nanofillers have shown that unaligned filler particles can cause local tearing in the matrix due to a stiffness mismatch and therefore balance any positive effect the addition of the nanofiller has on the system [15]. In order for the Young's modulus to be altered within this particular system the preparation method of the composite foam will need to be investigated further in order to find a way of implementing alignment of the rods as the PU foams and sets.

A lack of increase in the Young's modulus does not mean that the sound and energy absorption of the system will not be altered by the addition of the sepiolite, however, and therefore cyclic compression tests were performed (Figure 3) in order to obtain the value of the energy dissipation (Figure 4) and loss factor (Figure 5) for each system.

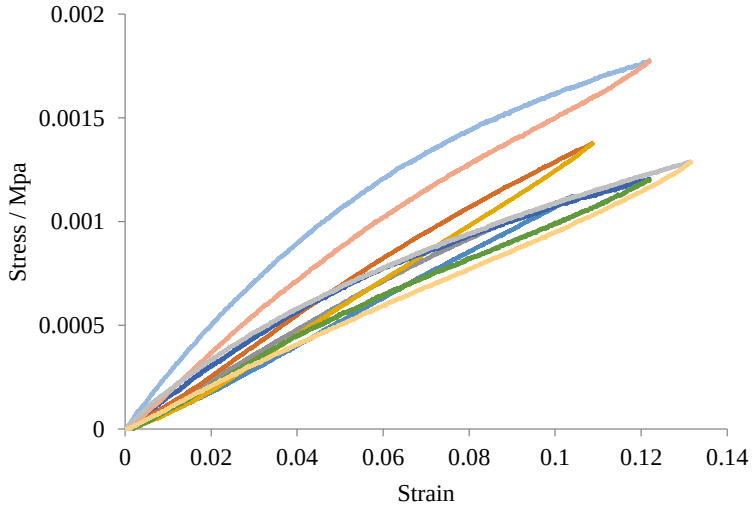


**Figure 3**: An example of the fifth cycle recorded in the cyclic compression tests performed on 5 different samples of each foam system. The energy dissipation was calculated as the area between the compression and returning curve and the standard deviation was taken over the 5 samples.

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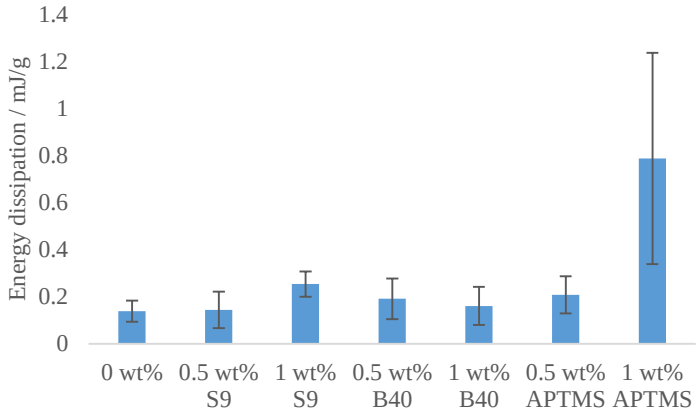


**Figure 4**: Energy Dissipation per gram values for each composite system. This is calculated as the area under the curve of the fifth cycle of each sample, divided by the sample density. The error was calculated as the standard deviation over 5 samples.

The energy dissipation was defined as the area under the curve of the fifth cycle in the cyclic compression divided by the density of the sample and was calculated using a Matlab code (Figure 4) [12]. The same Welch's T test, as performed above, was used to determine the significance of the distributions and resulted in all samples supporting the null hypothesis with exception of two systems. These two systems were the 1 wt% S9 clay and the 1 wt% APTMS modified clay. Both systems with the B40 clay as the nanofiller showed no statistically significant difference in the distribution. This shows that the surface chemistry and the weight loading of the nanofiller both contribute to any changes in properties observed.

To further investigate this the loss factor was calculated as the ratio of the energy dissipation over work applied (Figure 5). Once again the Welch's T test was performed and in the case of the loss factor, all systems agreed with the null hypothesis with the exception of the 1 wt% APTMS nanocomposite. This system rejected the null hypothesis and showed a statistically significant increase in the average loss factor.

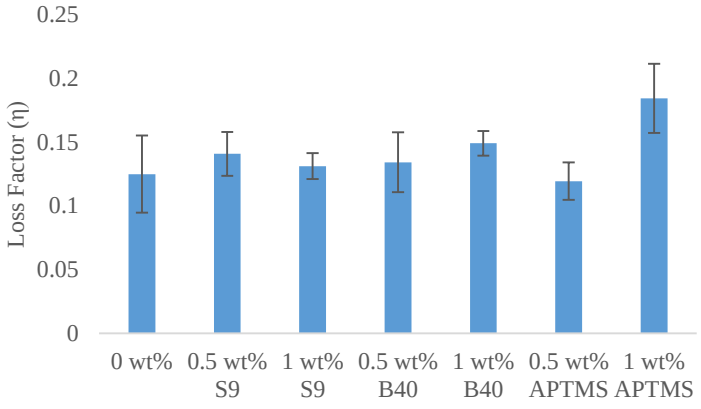


**Figure 5**: Loss Factor (η) for each composite system. Measured as the ratio of the energy dissipation over the work applied to the system. The error was calculated as the standard deviation over 5 samples.

This difference in the distribution for the APTMS sepiolite/PU composite supports the data from the energy dissipation that the APTMS surface coverage of the clay is causing favourable interactions with the PU matrix and therefore increasing the energy absorbed by the system, however loading is still an

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important factor when designing a material. This loading dependence indicates that the energy dissipation is, at least in part, reliant on the filler-filler interactions as well as the filler-matrix interaction. If this were not the case the loading would have independent of any significant changes in the energy dissipation or loss factor. Further investigation into these affects, including further variation of filler loading and dynamic mechanical analysis, is required before a fully optimised system can be achieved.

## 4. Conclusions

Polyurethane/sepiolite composites were prepared using three different surface chemistries at two different weight loadings. The composites were investigated using scanning electron microscopy and compression testing in order to try and understand the changes in energy dissipation with different clay loadings. The calculation of the energy dissipation and loss factor indicates that the loading as well as the surface chemistry of the clay is important in optimising the mechanical properties of the system. Whilst none of the clays showed any alterations in any of the measured properties at 0.5 wt% loading, both the bare clay and the silane modified clay showed a statistically significant increase in the energy dissipation at 1 wt%. The silane modified clay also showed a significant increase in the loss factor at 1 wt% loading however no samples showed any change in Young's modulus over the measured strain range. No induced alignment of the particles was present which could explain the lack of change in the Young's modulus, however, the friction between the sepiolite particles could be the reason for the increased energy dissipation at higher loadings of the 2 systems [15].

Further testing, such as dynamic mechanical analysis (DMA) is required to investigate this observation further as well as further variation in the loading of the clay to determine the optimal loading of filler to matrix. Along with further structural characterisation, such as micro CT and differential scanning calorimetry this will aid in the optimisation of the system to give increased sound and energy absorption with the most cost effective composite.

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