FLEXURAL BEHAVIOURS OF NANOPHASED RIGID POLYURETHANE FOAM CORE SANDWICH COMPOSITES

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ABSTRACT

Reinforcing foam cored sandwich composites with nanoparticles occupies an important place in expending the utility of sandwich structures with multifunctional properties. This study focuses on improving the flexural properties of foam cored sandwich structures by addition of carbon nanotubes (CNT) and nanosilica (nSi) particles to the polyurethane (PU) foam. The increased surface area in PU foams cores makes them promising candidates over honeycomb with enhanced bonding between core and skin. By effective dispersion and distribution of CNTs and nSi at various weight fractions, the compressive strength of nanophased PU foams increased up to 32.2% for CNTs and 10% for nSi followed by a rise in density, as well. Through morphological and micromechanical characterizations, it is also found that the geometry of nanomaterial has a significant effect on the reinforcing mechanism through formation of cellular characteristics of foams. Using CNTs as rod like nanostructures, the cell edge length is increased and high surface energy causing cells to stretch through the longest direction of nanoparticle during cell growth. Compared to CNTs, nSi showed tighter cell packings with decreased cell edge length, respectively. As a result, PU foam cored sandwich composites have shown an enhancement more than 5% in core shear yield strengths of both nSi/PU and MWCNT/PU cores under three-point bending tests.

1 Introduction

Overcoming the challenges of conventional honeycomb core material with a higher surface area, polymer foams cores can spread the impact, distribute the loads and stresses more effectively and increase the strength of sandwich structures with very low density eliminating moisture absorption and delamination of face sheets[1]. These cores also enable better mechanical performance, lower weight, less fabrication cost and maintenance cost as well as ease of manufacture[1]. The mechanical properties of core material and quality of bonding between core and face sheets lead the flexure characteristics of sandwich structures[2]. Developing polymer foam cores with higher strength and multifunctionality have also attracted the possibility of adding nanoparticles to the existing foams to tailor the properties within industrial needs. Several methods and materials have been implemented for the investigation of micromechanical characteristics and foam properties to understand the synergetic effects of adding nanomaterials on the overall properties of these lightweight, low density materials.

Nanomaterials create some variations in micromechanics of foam such as cell wall thickness, cell edge length and cell density. The working mechanism of nanoparticles in polymer foams can be simply explained as nucleation points that cells start to grow around. Smaller cell edge lengths and lower cell densities refer higher density which is proportionally related to mechanical properties. In this study, closed cell rigid polyurethane foams are preferred as core materials due to their low density and their properties are reinforced by spherical (nanosilica, nSi) and rod-shaped (multi-walled carbon nanotubes, MWCNT) nanoparticles.

Besides existing studies on improving mechanical properties of PU foams using different types of nanoparticles such as CNF[3-5], CNT[5-7], nanoclay[4], titanium dioxide[4, 8] and nanosilica[9], there is still

lack of enough studies on flexural properties of nanophased polymer foam sandwich structures. In a sandwich structure, bending loads are carried by face sheet and transported through core. Thus, the bonding quality between skin-core and the strength of core are essential features to carry the load. Proper transportation of load through nanophased foam core can be achieved with a homogenous dispersion of nanoparticles which have larger surface areas compared to other fillers resulting in a higher surface energy and tendency to agglomerate. In order to achieve the desired enhancements in nanophased foams, nanoparticles must be dispersed homogenously through the structure by special processing techniques[10]. Kabir *et al*, studied the effect of ultrasound sonication on dispersing nanofibers in PU foams and observed that nanophased foam prepared by sonication showed higher enhancement in compressive properties[3]. Besides the processing method, nanoparticle concentration in polymer also affects the dispersion quality and so the mechanical property. The higher concentration of nanoparticles indicates narrow growth of cells, smaller cell size and higher density[11]. Despite the superior properties of nanoparticles, higher concentrations may not result with better mechanical performance since nanoparticles are in close approximity to each other in polymer and ready to agglomerate[10].

Herein, CNT and nSi reinforced PU foams from 0.025 to 1 wt.% are studied to understand the effective reinforcing mechanisms of various geometry nanomaterials on the overall compressive characteristics of PU foams. To achieve desired performance for sandwich structures, higher strength is expected from nanoreinforced PU foam cores with the addition of CNTs and nSi which gain stiffness and toughness to foam, respectively. A three step fabrication process with homogenization, sonication and mechanical mixing of CNTs and nSi is applied to achieve a good dispersion and distribution of nanomaterials within the PU foam. The micromechanical characteristics of nanophased PU foams compared to the neat foam is also studied through morphological characterizations by SEM and optical microscopy that reveals the effects of geometry of nanomaterial on the overall cell characteristics. The flexural strength of sandwich structures is enhanced with the contribution of nanoparticle reinforced foam which promotes a better adhesion quality between skin-core and better stress transportation.

2 Experimental

2.1 Materials

PU foam, supplied in liquid form, has two parts consisting of polyol and polymeric diphenylmethadiisocyanate (PMDI) with a density in the range of 100±10 kg/m^3. Polyol consists of ingredients such as catalyst, stabilizer, blowing and curing agents. Mixing ratio between polyol and isocyanate is 1:1.16 by weight. CNTs are supplied from Sigma-Aldrich as multi-walled having an outer diameter of 10nm±1nm, inner diameter of 4.5nm±0.5nm and a length of 3-6μm. Nanosilica is also obtained commercially from Sigma-Aldrich in powder form and having a diameter of 12nm.

2.2 Fabrication of MWCNT and nSi reinforced PU Foam

Foam fabrication has three main steps as homogenization, ultrasound sonication and mechanical mixing. During fabrication, main parameters are mixing time in homogenization, amplitude and duration of sonication. Nanoparticles are diffused in polyol since its viscosity is higher than isocyanate which allows better nanoparticle dispersion during mechanical mixing and foaming. Homogenization is made to allow the nanoparticles disperse in polymer homogeneously and ultrasound sonication is applied to avoid agglomeration of the nanoparticles which can act as stress-concentration points[3]. Figure 1a and 1b present the important effect of ultrasound sonication on dispersion and it is evident that sonication prevents nanoparticles (*e.g.*, CNTs) to gather in some focus points and provides a better dispersion quality. During the whole process, an external cooling process is applied to prevent undesired temperature rising which may affect the foaming procedure.

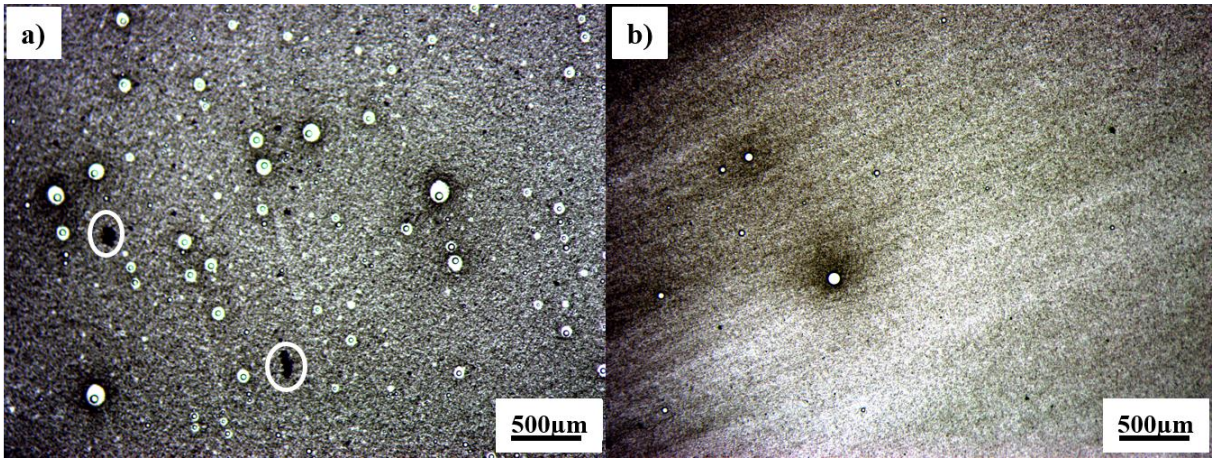

Figure 1: CNT reinforced PU foams **a)** before sonication **b)** after sonication is applied showing the clear effect of sonication on the quality of process

nSi/PU and CNT/PU fabrications are made with different protocols since each nanomaterial has its own dispersion characteristics within polymer. For nSi/PU, homogenization is made for 20 minutes at 10000rpm and sonication is made for 10 minutes at 50% amplitude. For CNT/PU fabrication, homogenization is performed for 30 minutes and sonication is run for 10 minutes at 50% amplitude. Finally, polyol/nanoparticle mixture and PMDI are mechanically mixed at 2200 rpm for 12s. Foam is poured into an aluminum mold at 40ºC and foaming is completed in room temperatures.

2.3 Compression Tests of CNT and nSi Reinforced PU Foams and Micromechanical Characterization

All compression tests were conducted under ambient laboratory conditions on specimens with CNT and nSi reinforced PU foams. Flatwise compression tests were performed according to ASTM C365/C365M-16. Specimen dimension for compression test is used as $27x27x13$ mm^3. A typical stress strain plot of PU foams shows a linear portion followed by an abrupt yielding and a plateau region where cells start to collapse followed by an increase until the failure. Macroscopic failure did not occur under quasi-static compressive loading for all specimens and within these conditions the tests were run in strains up to 0.6%. CNT reinforced PU foams were studied initially up to 0.3 wt.% however due to increased agglomeration identified through morphological characterization and compressive tests, the highest addition amount of CNT is identified as 0.1wt.%, respectively. CNT addition to PU foams were performed as 0.025, 0.05 and 0.1 wt.%. The highest increase achieved at 0.1% CNT/PU as 32.2%. The gain in compressive strength of 0.1% CNT/PU is related to the cross-linking influence of nanotube in polymer. It is also observed that foam density increases proportionally with more embedded MWCNTs since these rod-shaped nanoparticles attract polymer cells with a high surface energy, behave as a nucleation starting point and promote narrow packing of cells. Compressive stress-strain diagram of nSi/PU foam refers that in all concentrations of nSi compressive strength is enhanced as expected since nSi adds toughness to foam. 0.5 wt.% nSi showed the best compressive stress and followed with a decrease in 1 wt.%. The reason can be simply explained as the impossibility to homogeneous dispersion with increased concentration of nanoparticles. The results of both CNT and nSi reinforced PU foams is presented in Table 1.

Table 1: Compression test results of neat and MWCNT and nSi reinforced PU foams

Specimen	Density (kg/m^3)	Compressive Stress (MPa)	Enhancement (%)
Neat PU[1]	104.5	0.90	0
0.025% CNT/PU	101.4	0.90	0
0.05% CNT/PU	103.6	1.03	14.4
0.1% CNT/PU	119.9	1.19	32.2
Neat PU[2]	106.0	0.94	4.4
0.5% nSi/PU	107.9	0.99	10
1% nSi/PU	98.4	0.64	-28.8
[1] CNT/PU processed		[2] nSi/PU processed	

To understand the mechanical behavior of nanophased foams, investigating their cellular characteristics geometric shape, cell edge length and cell wall thickness is also essential. In Table-2, cell edge length, cell wall thickness and density variation is shown in details for CNT and nSi reinforced PU foams. When nanoparticles are embedded to foam, cell properties have an adverse effect on the geometry and energy of nanoparticles which affects cell seeding process. Optical microscopy and SEM images showed in Figure 2 and 3 shows the intrinsic effects of different geometry nanoreinforcements on the PU foam cellular structure.

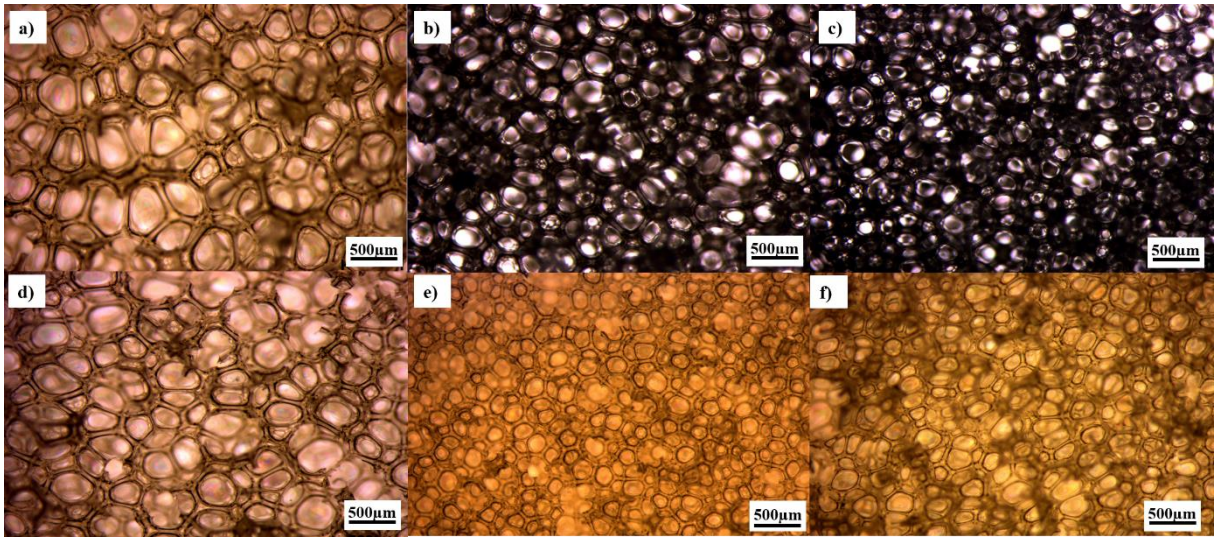

Figure 2: Optic microscope images of **a)** Neat PU **b)** 0.05% CNT/PU **c)** 0.1% CNT/PU **d)** nSi/PU Processed Neat PU **e)** 0.5% nSi/PU **f)** 1% nSi/PU

In Figure 2, it is evident that cells continue to protect uniformity with nSi addition but becomes less uniform in size and more complex shaped with CNTs. In nSi/PU foams, tighter cell packings are observed due to the decreased cell edge length and average cell size, as stated also in literature[11]. In CNT/PU foams, CNTs increased the cell edge length due to its rod-shaped geometry and high surface energy causing cells to stretch through the longest direction of nanoparticle during cell growth, as expected[4].

Table 2: Cell properties of neat and nanophased foams

Specimen	Cell Edge Length l (μm)	Cell Wall Thickness t (μm)	t/l	Density (kg/m^3)
Neat PU[1]	239.8	39.1	0.16	104.5
0.025% CNT/PU	219.0	36.9	0.17	101.4
0.05% CNT/PU	194.6	51.2	0.26	103.6
0.1% CNT/PU	172.6	43.7	0.25	119.9
Neat PU[2]	218.6	39.5	0.18	106.0
0.5% nSi/PU	137.6	32.8	0.24	107.9
1% nSi/PU	148.8	32.6	0.22	98.4

[1] CNT/PU processed [2] nSi/PU processed

The morphological characterization of all specimens was characterized in details within SEM as can be seen in Figure 3, which were taken at high vacuum and 2~5 kV to estimate the average cell dimensions of neat and nanophased foams. As a result, CNT increases average cell sizes even with 0.025% concentration while cell dimension decreases with nSi addition on the overall PU foam cellular characteristics. Average cell dimensions can be given as 404.9μm, 554.2 μm, and 346.2 μm for neat PU, and 0.025% CNT/PU and 0.5% nSi/PU, respectively.

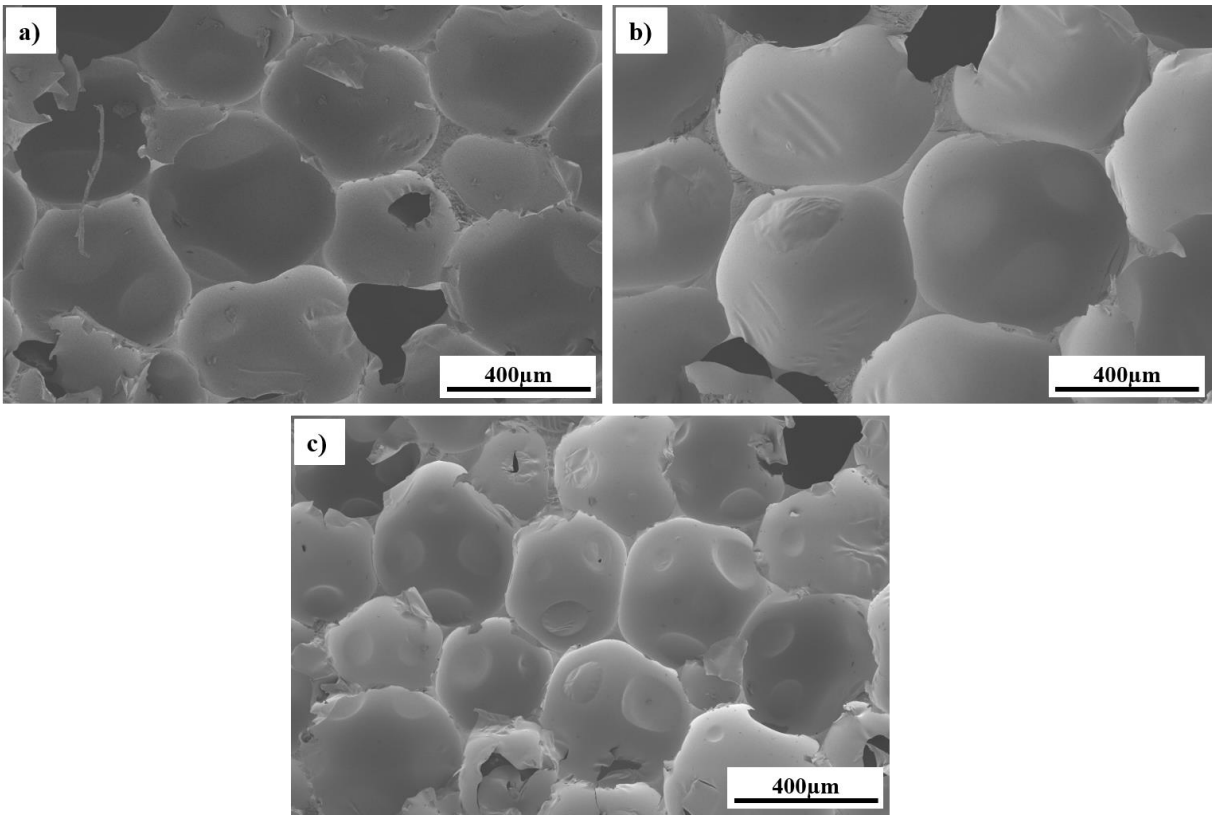

Figure 2: SEM images of **a)** Neat PU **b)** 0.025 wt. % CNT/PU **c)** 0.5 wt.% nSi/PU

2.4 Laminated Composite Manufacturing

Sandwich composite manufacturing was performed within the neat and nanophased PU foams cores consisting of materials listed in Table 3, by using hot press at 120ºC and 3 bar pressure for 2 hours.

Table 3: Materials used in sandwich structure manufacturing

Face Sheet Material	Core Materials
Twill 2/2 Carbon epoxy prepreg 2 plies each side (SPM Composite Advanced Materials Technologies Company, VTP H310 resin system)	Neat PU CNT/PU nSi/PU

2.5 Flexural Test

Three-point bending tests are performed according to ASTM C393/C393M-16 for foam cored sandwich composites. The dimensions for sandwich composites are as follows, 30*x*110*x*10 mm^3. At least 3 specimens are tested for each set. The flexural strength of nanophased foam sandwich composites is expected higher than neat composites since nanoparticles with a high strength to weight ratio are added to polyurethane foam which makes it stiffer. 0.5% nSi has increased the core shear ultimate and yield stresses over 5% because it provides toughness to core. More tests within the CNT reinforced PU foam cored sandwich structures are still ongoing and will be presented.

3 Conclusion

In summary, CNTs and nSi reinforced polyurethane foams are produced to enhance flexural strength of foam cored sandwich composites. Compressive strength of CNT/PU and nSi/PU foams were investigated and successful results were found compared to neat PU foams when very low loading of CNTs such as 0.1 wt.% was used, up to 32% of enhancement in compressive stress is observed. Homogeneous dispersion and decreased agglomeration rates of nanoparticles in polymer played a crucial role on cell structure and thus in compressive properties. Foam cored sandwich composites are easy to manufacture and cost-favorable in addition to their flexural strengths. More than 5% gain has been achieved in core shear yield strengths of sandwiches which displays the influence of nanoreinforcements in polymer and more mechanical testing is being performed for the CNT reinforced polymer foam core sandwich composites.

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