Citation information: Applied Composite Materials, Vol. 12, No. 3-4, 2005, pp. 247-261.

Enhancement of Energy Absorption in Syntactic Foams by Nanoclay Incorporation for Sandwich Core Applications

Nikhil Gupta[1] and Rahul Maharsia[2]
[1]Mechanical Engineering Department, Polytechnic University, Brooklyn, NY 11201 Email: ngupta@poly.edu, Phone: 225-773 9555
[2]Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA 70803

ABSTRACT

Syntactic foams are closed pore foams fabricated by the mechanical mixing of hollow glass particles in a matrix resin. The present study deals with change in compressive properties of syntactic foams due to the incorporation of nano-sized clay (nanoclay) particles. A surface modified clay, Nanomer I.30E, has been used in the fabrication of specimens. Six different types of syntactic foams are fabricated and tested for compressive properties. Three types of hollow particles (microballoons) of glass having different densities are used for fabrication. Each type of microballoon is combined with 0.02 and 0.05 volume fraction of nanoclay, respectively. The combined volume fraction of microballoons and nanocparticles is 0.65 in all kinds of foams. Compressive properties of these samples are compared with those of syntactic foams without nanoclay particles. It is observed that partial intercalation of nanoclay has taken place in the specimens and remaining nanoclay particles are present in small clusters. Such microstructure leads to nearly the same strength with considerable enhancement in fracture strain. Hence, the toughness of the material, measured as the area under stress-strain curve, is found to increase by 80-200% for various kinds of foams tested in the study. Fracture features of syntactic foams with and without nanoclay are compared.

Key Words: Syntactic Foam, Nano-sized clay, Microballoon, Polymer matrix composite, compression testing.

Introduction

Sandwich structured materials are widely used in structural applications requiring low density, high strength and high damage tolerance. Several of their properties, including low density and high damage tolerance, are contributed by the core materials used in their construction. Several types of light weight polymer composites are being developed for use as sandwich cores for applications ranging from aerospace structures to automobile components. Light weight high strength composites can be obtained by reinforcing the matrix resin with different types of filler and reinforcing materials such as solid particles, hollow particles, and short fibers etc. Several studies have looked at using solid particles for reinforcement [1, 2]. However, high density of most solid particles increases interest in hollow particles as fillers. Hollow particle (microballoons) filled composites or syntactic foams have recently gained a lot of attention as they provide higher strength to weight ratio as compared to solid particle filled composites. The microballoons used in syntactic foams can be made of aluminum, steel, polymeric, ceramic and glass particles [3]. However, glass microballoons have emerged as the most suitable fillers for syntactic foams because of their high strength and low density resulting in high strength to weight ratios. Syntactic foams have porosity in the closed form and are particularly useful in applications where a combination of low weight, high compressive strength, low moisture absorption and low thermal and electrical conductivities are desired [4]. These properties have made them an attractive material for sandwich core applications. Many published studies on syntactic foam core sandwich composites examine their compression, bending and moisture absorption properties and affirm the suitability of such materials for aerospace and marine applications [5-8].

There are two methods of increasing the strength of syntactic foams. The first method is to reduce the microballoon volume fraction in the structure of syntactic foams [9]. The second method is to use higher strength microballoons [10]. Both these methods lead to increase in syntactic foam density also. However, the second method is found to be much more effective as it increases compressive strength and modulus with least increase in density [11]. The second method gives additional advantage of varying only one material parameter, microballoon wall thickness, giving better control over the properties of syntactic foams. Matrix related properties such as fracture strain and coefficient of thermal expansion can be optimized by selecting appropriate volume fractions of matrix resin and microballoons. Then, microballoons of appropriate strength can be selected to achieve desired level of strength in syntactic foams.

Syntactic foams having high compressive strength and modulus can be fabricated by using high density microballoons (350-460 kg/m^3). However, such foams suffer from disadvantages of high density and low fracture strain of about 8-10%. It is observed that syntactic foams using low density microballoons (200-350 kg/m^3) have lower strength but their fracture strain is about 15-20% [10]. Hence, there is a need to modify the phase structure of syntactic foams in order to achieve a combination of high strength and high fracture strain to improve the toughness and damage tolerance of high density foams.

Published studies have shown that the use of nanoclay particles increases the tensile strength, modulus, resistance to thermal failure, and impact resistance of polymers [12]. This improvement in performance has been attributed to the unique phase morphology and better interfacial properties in the nanocomposite [13-15]. In conventional composites, phase mixing occurs on a macroscopic scale, whereas nanocomposite materials are formed when phase mixing occurs on a nanometer length scale [12]. A large number of interfaces are created in a nanocomposite upon dispersion of nanoparticles, resulting in an increase in strength of the composite matrix [16].

The present study is an attempt to increase the toughness and fracture strain of high density syntactic foams by means of incorporation of nanoclay particles. Small volume fraction of nanoclay (2% and 5%) will not lead to significant increase in density of these composites; however, it can affect the mechanical properties significantly, which is characterized in the present study.

Experimental

Materials

Nanoclay syntactic foam samples with six different compositions have been fabricated and tested for compressive properties in this study. Three types of glass microballoons have been used as hollow particles. Density and mean particle diameter of these microballoons are presented in Table 1. The compressive properties of unreinforced syntactic foams fabricated using these microballoons are presented in Table 2. Each type of microballoons is mixed with two nanoclay volume fractions, 0.02 and 0.05, to fabricate six types of nanoclay foams. The total volume fraction of microballoons and nanoclay is maintained at 0.65 in all types of specimen. Nanoclay has been procured from Nanocor Inc., and has commercial name of Nanomer I.30E. Details of nanoclay syntactic foam compositions and measured density are given in Table 3. Nomenclature of all types of fabricated syntactic foams is also listed in Table 3. The first two letters in the nomenclature stand for "*Syntactic Foam*", next two numbers are related to the density of microballoons used to fabricate that foam. The next letter C refers to *"clay nanoparticles"* and the last number represents nanoclay volume fraction. For syntactic foams that do not contain nanoclay particles, only four digit alpha-numeric code is used, which is similar to the first four digits of nanoclay reinforced foams. For the ease of presentation, the nanoclay reinforced foams are referred as "*nanoclay foams*" to differentiate them from syntactic foams that do not contain nanoclay.

Epoxy resin D.E.R. 332 along with an amine based hardener D.E.H. 24, and C_{12}-C_{14} aliphaticglycidylether diluent (in 5% by weight quantity) has been used as matrix material. The diluent is used to reduce the viscosity of the resin, which makes it easier to mix high volume fraction of particles in the matrix resin.

Table 1 Properties of Microballoons.

Microballoon Type	True Particle Density (kg/m^3)	Mean Particle Size (μm)	Average Wall Thickness (μm)
S22	220	35	1.26
S32	320	40	1.86
K46	460	40	2.74

Table 2 Compressive properties of syntactic foam specimens.

Microballoon Type	Corresponding Syntactic Foam Type	Syntactic Foam Density (kg/m^3)	Peak Compressive Strength (MPa)
S22	SF22	493	30
S32	SF32	545	38
K46	SF46	650	72

Fabrication

In the first step nanoclay particles are mixed in the resin-diluent mixture at a mixing rate of 2540 rpm for 2 hrs followed by the addition of hardener and microballoons. Hand mixing is carried out at slow speed after microballoon addition to keep the microballoon damage minimum. The resin and particle paste obtained after mixing is poured into stainless steel molds and allowed to cure for 24 hours at room temperature. The mixture cures into a composite slab, which is then removed from the molds and post cured in an oven at a temperature of 100°C for three hours.

Table 3 Composition and density of nanoclay syntactic foams.

Nanoclay Volume %	Micro-balloon Type	Micro-balloon Density kg/m^3	Nanoclay Foam Nomenclature	Nanoclay Foam Density (kg/m^3)
2	S22	220	SF22C2	517
	S32	330	SF32C2	562
	K46	460	SF46C2	643
5	S22	220	SF22C5	567
	S32	330	SF32C5	605
	K46	460	SF46C5	674

Compression Testing

Compression tests are carried out in accordance with ASTM C365-94 standard. Specimens of 25×25×12.5 mm in length, width and thickness, respectively, are compressed at a rate of 1.3 mm/mm. The compression tests were carried out using a computer controlled MTS 810 mechanical test system. Five specimens of each type of material are tested. Load-displacement data obtained from the tests are used to plot stress-strain curves and calculate compressive strength.

Results and Discussion

All types of microballoons selected in the present study have mean particle diameter around 40 μm. The difference in their wall thickness causes a difference in their density and strength. This scheme allows changing the density of syntactic foams while keeping the particle volume fraction constant in the structure. This scheme also leads to the same interfacial area between microballoons and matrix resin. Hence, only one parameter, the microballoon strength, changes among various types of foams fabricated in the present work.

Published studies have indicated that upon exfoliation of nanoclay particles in epoxy-clay nanocomposites, an increase in the compressive strength and modulus of the epoxy polymer is obtained [12]. It was reported that the compressive strength increased from 76 MPa to 84-88 MPa and compressive modulus increased from 1.4 GPa to 1.7-1.8 GPa for various kinds of clays. However, there are some identified problems in syntactic foams with increase in modulus and strength. In the compression testing of syntactic foams, it is observed that increase in strength and modulus increase the stiffness of the sample and lead to cracking under secondary tensile stresses [10]. These secondary tensile stresses are generated due to the Poisson's Ratio effect. One such high density syntactic foam specimen tested under compressive loading is shown in Figure 1. Prominent cracks can be observed in the direction of compression in this specimen, which led to its failure at a strain of only about 10%. This effect is so strong that high density (650 kg/m^3) foams fracture at strains of only 8-10% compared to a fracture strain of over 20% for lower density (450 kg/m^3) foams. The aspect ratio of the specimen shown in Figure 1 is 0.5. If the aspect ratio of specimens is increased to 2, then the effect of secondary tensile stresses is observed clearly as seen in Figure 2 [17]. The specimen shown in Figure 2 is also of high density (650 kg/m^3) and has fractured predominantly under secondary tensile stresses at a strain of about 8%. The lower fracture strain leads to poor energy absorption characteristics in high density foams. Therefore, it was decided to incorporate high volume fractions of nanoclay in matrix resin to achieve the aim of increasing the toughness by means of increasing the fracture strain with little change in strength. In the fabricated nanocomposites, 2 and 5% by volume nanoclay content actually gives nanoclay to resin ratio of about 5.7 and 10% by volume. The corresponding weight fractions of nanoclay in matrix material were about 9.5 and 20%, respectively. It is known that intercalation or exfoliation of such large amounts of nanoclay in matrix resin is not possible. Generally it is observed that for better exfoliation of clay particles in the epoxy matrix, the nanoclay loading should be restricted to around 5 weight percent and below [18]. Beyond this limit poor exfoliation results are obtained. Hence, partial intercalation/exfoliation will lead to increase in strength of epoxy resin, whereas remaining nanoclay in the form of micron size clusters may act as plasticizer/lubricant for deforming matrix material. The overall strength of the composite will depend on these two competing parameters. The expected microstructure of the material is presented in Figure 3.

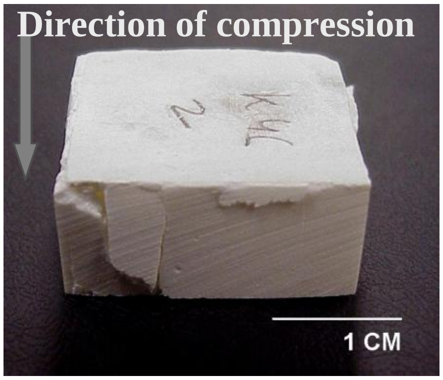


Figure 1 Low aspect ratio syntactic foam samples showing three vertical cracks in the side wall.

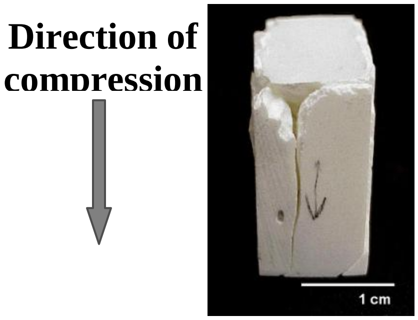


Figure 2 High aspect ratio syntactic foam specimen failed under secondary tensile stresses.

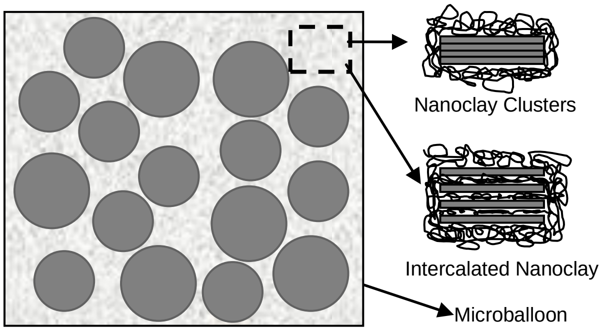


Figure 3 Schematic representation of the microstructure of nanoclay filled syntactic foam.

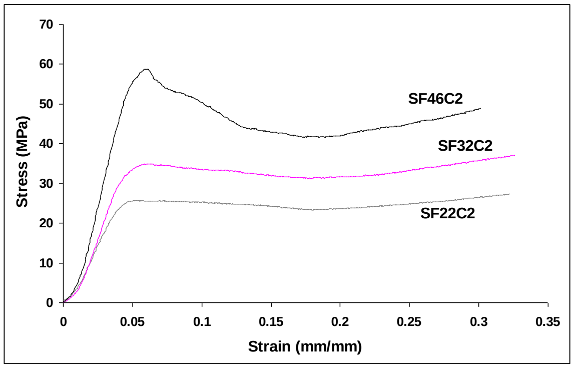


Figure 4 Representative stress-strain curves for Nanoclay Syntactic Foams with different microballoon types having 2% Nanoclay by volume.

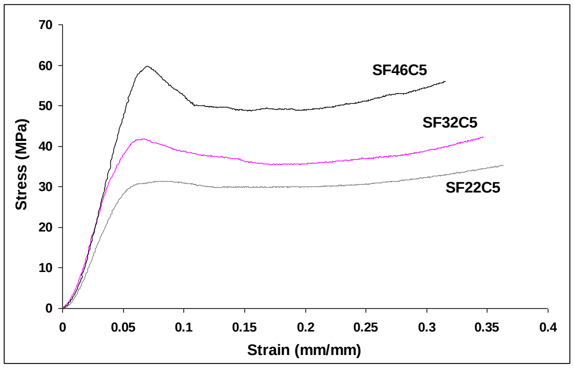


Figure 5 Representative stress-strain curves for Nanoclay Syntactic Foams with different microballoon types and 5% Nanoclay by volume.

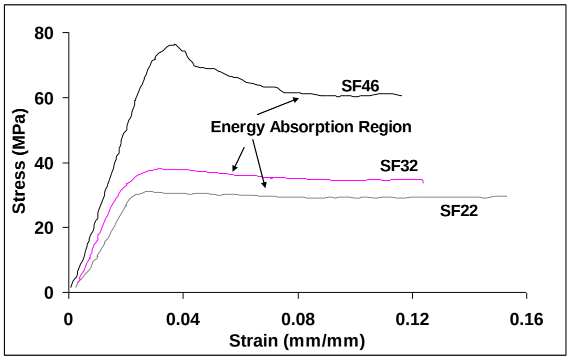


Figure 6 Stress-strain curves for various syntactic foams for comparison with those of Nanoclay Syntactic Foams.

Representative stress-strain curves for compression tests of 2% and 5% nanoclay foams are presented in Figure 4 and 5, respectively. Features of these curves are compared with the stress-strain curves of syntactic foams without any nanoclay content shown in Figure 6. It can be observed from these graphs that the fracture strain has improved considerably for high density foams due to the nanoclay incorporation. Extended stress plateau can be observed for all kinds of nanoclay foams, which is a typical feature in compressive stress-strain curves of syntactic foams [19]. Higher strength of higher density foams coupled with large fracture strain, over 30%, makes them more damage tolerant for applications requiring high strength.

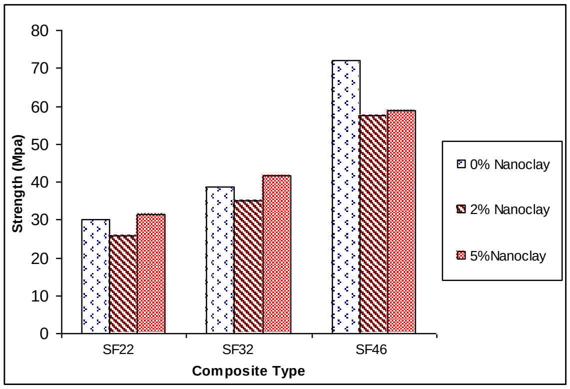


Figure 7 Comparison of compressive strength of foams with different types of microballoons and nanoclay volume fractions.

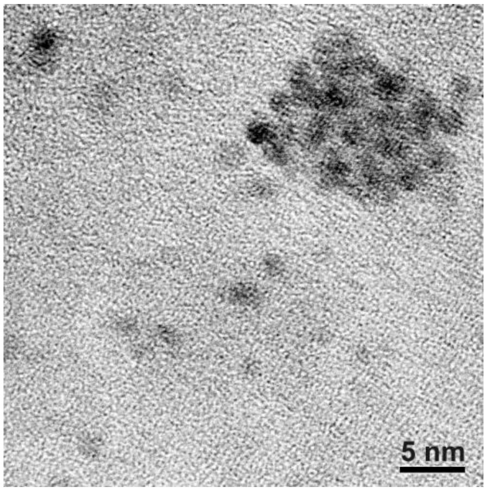


Figure 8 High-resolution TEM image of the synthesized nanoclay/epoxy composite with a 2% volume fraction of nanoclay.

Compressive strength values corresponding to foams with 0%, 2%, and 5% nanoclay particles have been calculated from stress-strain data and are presented in Figure 7 for comparison. The compressive strength values of nanoclay foams depend on the fraction of intercalated nanoclay particles. Comparison of the compressive strengths of nanoclay foams reveal that the increase in the nanoclay content from 2-5% has resulted in an increase in the strength. This increase is found to be 18, 16 and 3% for foams containing 220, 320 and 460 kg/m^3 density microballoons. Comparison of compressive strength of nanoclay foams with corresponding 0% nanoclay syntactic foams reveal that foams containing 2% nanoclay particles have 10-20% lower strength compared to the corresponding syntactic foams.

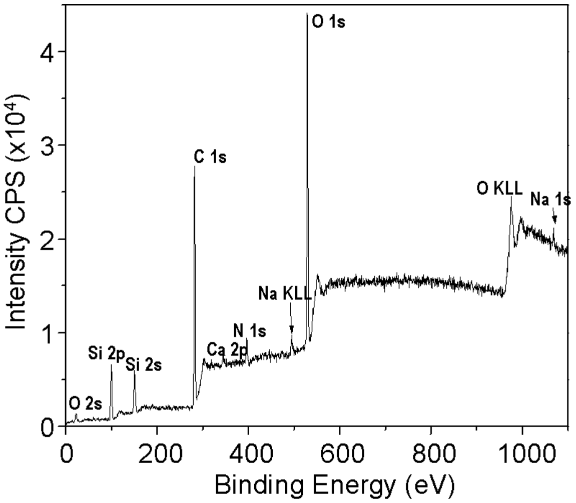
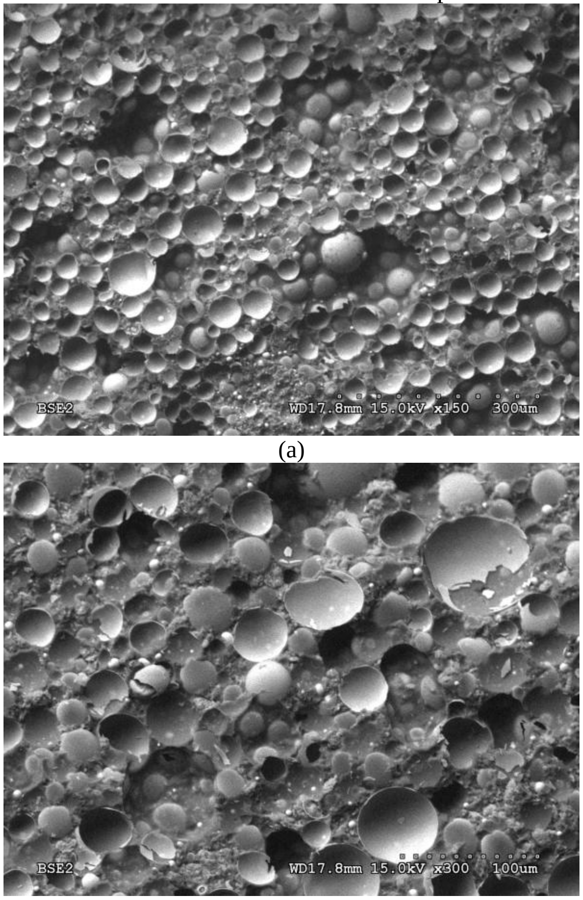


Figure 9 XPS spectrum of nanoclay reinforced foam.

However, as a general trend it is seen that the strength of 5% nanoclay containing foams is higher than corresponding 0% nanoclay syntactic foams. The only exception appears to be the high density (460 kg/m^3 microballoons) nanoclay foams that show a decrease in strength of about 20% as compared to the corresponding 0% nanoclay syntactic foams. Such difference may occur due to the lower extent of intercalation in these composites.



(a)

(b)

Figure 10 Scanning electron micrograph of nanoclay foam containing 5% nanoclay by volume (a) lower magnification micrograph and (b) higher magnification micrograph showing some small clusters of nanoclay among large number of glass microballoons.

A high resolution Transmission Electron Micrograph (TEM) of the matrix resin is shown in Figure 8. An intercalated clay region in matrix material can be observed on the upper right side of this micrograph. Several such regions were observed in the matrix material in the detailed TEM study. X-ray photoelectron spectroscopy (XPS) confirmed the presence of nanoclay particles in these regions (Figure 9). Scanning electron micrographs shown in Figure 10 present the microscopic structure of the material. Micron size clusters of nanoclay are observed in SEM observations. The TEM and SEM observations confirm that the expected microstructure presented in Figure 3 is obtained in the material. Presence of large number of small clusters is attributed to a decrease in strength. In such clusters only the outer layer is bonded with the matrix resin. Large number of nano-sized particles within the cluster, which are not bonded with matrix directly can slide and move when the localized stress becomes sufficiently high. Such a structure causes decrease in strength of 2% nanoclay containing foams, although the intercalated nanoclay particles are present in the matrix structure. An increase in intercalated and exfoliated nanoclay particles in the matrix material will lead to increase in strength, which is observed for 5% nanoclay foams.

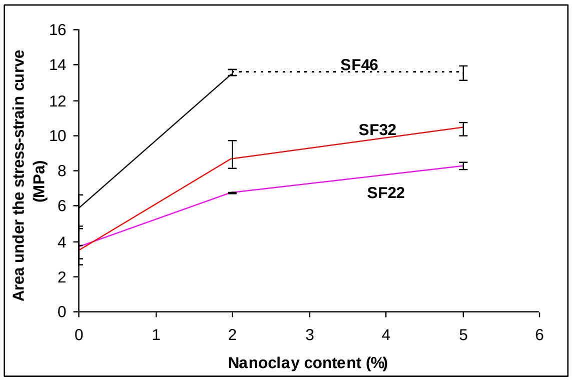
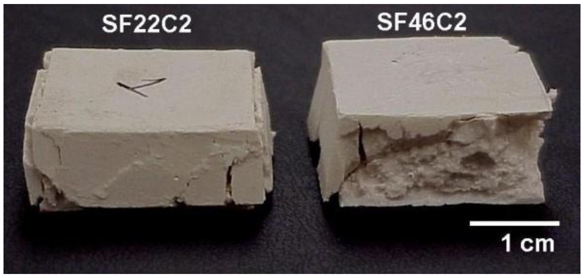
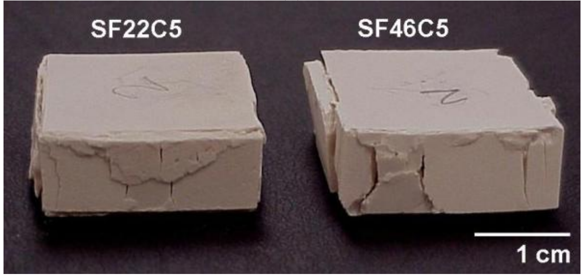


Figure 11 Effect of nanoclay content on the toughness of syntactic foams.



(a)



(b)

Figure 12 Specimen of nanoclay syntactic foam tested under compressive loading conditions (a) 2% nanoclay content (b) 5% nanoclay content.

The most attractive characteristic of syntactic foams is the prolonged energy absorption region of constant stress in the stress strain curves. Such region is observed in stress-strain curves of nanoclay filled syntactic foams also. It is highly desirable to extend this region to increase the toughness and the damage tolerance of syntactic foams. Matrix plasticization may be one method to achieve such properties, where brittleness of epoxy resins is reduced and plastic strain is increased. As observed in Figure 4 and 5, the plateau region is much longer in foams with nanoclay as compared to that of foams without nanoclay (Figure 6). A longer plateau region shows a higher amount of energy absorption in nanoclay foam specimens. In nanoclay foam specimens the stress starts increasing without occurrence of failure at the end of the stress plateau region. This corresponds to the complete crushing of microballoons and densification of the specimen. SF46 syntactic foams showed failure at a strain of 8-12% compared to 12-15% for SF32 and over 20% for SF22 foams. As a result of nanoclay incorporation, a considerable increase in failure strain is observed for all kinds of foams. Strain values as high as 35% were achieved, even for high density foams, without failure before the compression was stopped. These specimens did not show a definite compressive failure point and appear to be much more damage tolerant than the corresponding syntactic foams that do not contain nanoclay. Toughness of the specimens is measured in the form of area under the stress-strain curves. Nanoclay foams do not show a specific fracture point, hence, for these foams area under the stress-strain curve is measured for 30% strain. Syntactic foams have specific fracture points, hence, for these materials area under the curve till fracture is measured. It can be observed in Figure 11 that the toughness of materials has increased considerably due to the incorporation of nanoclay particles. It can be observed that for low density foams, having 220 kg/m^3 microballoons, the area under the curve has increased by about 125% for 5% nanoclay content. In medium density foams containing 320 kg/m^3 microballoons the increase is found to be about 150 and 200% for 2 and 5% nanoclay contents, respectively. The increase in toughness is found to be about 125% for both, 2 and 5% nanoclay containing syntactic foams of high density. As the strength values are close for nanoclay foams and syntactic foams, the increase in toughness is observed due to the increase in fracture strain of the material.

Nanoclay foam specimens having 2 and 5% nanoclay content, compressed to about 30% strain are shown in Figure 12a and 12b, respectively. Several cracks are observed in the sidewalls of these specimens. However, these cracks are not deep and do not have significant effect to cause fragmentation of the specimen. Material from the sidewall of SF46C2 specimen in Figure 12a. has been removed to show that the crack has not penetrated deep into the specimen. Several cracks can be observed in the sidewalls of 5% nanoclay specimens also. However, compared to syntactic foam specimen shown in Figure 1, which was compressed to only about 10% strain, these specimens show cracks at three times higher strain level. Increase in the plasticity of the specimens has occurred due to the modification of matrix resin system with nanoclay particles. Hence, the modified microstructure provides advantage of enhancement of toughness of the material.

Conclusions

Desired result of increase in fracture strain of high density and high strength syntactic foams was achieved in the study through microstructural modification. Nanoclay particles are incorporated in the matrix resin system of syntactic foams for this purpose. Partial intercalation of nanoclay particles is obtained in the matrix material, which is observed through TEM. The compressive strength has shown a decrease in the range of 10-20% due to the incorporation of 2% nanoclay by volume, whereas 5% nanoclay has given nearly the same level of strength. Increase in fracture strain with little change in strength caused considerable increase in toughness of the material. Toughness, measured as area under the stress strain curves, shows about 80 and 125% increase due to incorporation of 2 and 5% nanoclay in syntactic foams containing 220 kg/m^3 microballoons. In medium density foams containing 320 kg/m^3 microballoons the increase is found to be about 150 and 200% for the same nanoclay contents. In high density foams having 460 kg/m^3 microballoons the toughness has increased by about 125% due to the incorporation of nanoclay. Specimens do not show a definite fracture point even at strains as high as 35%.

Acknowledgments

The authors wish to acknowledge the Dow Chemical Company and 3M Corporation for providing the epoxy resin and microballoons, respectively and technical information on these materials. Help of Dr. Jiechao Jiang in TEM and XPS is gratefully acknowledged.

References

1. Katz, H. and Milewski, J.V., Handbook of reinforcements for plastics, Van Nostrand Reinhold Co., New York, 1987.
2. Leidner, J. and Woodhams, T., ‘The strength of polymeric composites containing spherical fillers’, J Appl. Polym. Sci. **18**, 1974, 1639-1654.
3. Ashida, K. in Handbook of Plastic Foams: Types, properties, Manufacture and Applications, A. H. Landrock (ed.), Noyes Publications, 1995, 147-163.
4. Gupta, N., Karthikeyan, C.S., Sankaran, S. and Kishore, ‘Correlation of Processing Methodology to the Physical and Mechanical Properties of Syntactic Foams With and Without Fibers’, Materials Characterization **43,** 4, 1999, 271-277.
5. Hiel, C., Dittman, D. and Ishai, O., ‘Composite sandwich construction with syntactic foam core: A practical assessment of post-impact damage and residual strength’, Composites **24**, 5, 1993, 447-450.
20.
6. Ishai, O., Hiel, C. and Luft, M., ‘Long-term hygrothermal effects on damage tolerance of hybrid composite sandwich panels’, Composites **26**, 1, 1995, 47-55.
7. Bardella, L and Genna, F., ‘Elastic design of syntactic foamed sandwiches obtained by filling of three-dimensional sandwich-fabric panel’, International Journal of Solids and Structures **38**, 2001, 307-333.
8. Gupta, N., Woldesenbet, E., Kishore and Sankaran, S., ‘Response of syntactic foam core sandwich structured composites to three-point bending’, Journal of Sandwich Structures and Materials **4**, 2002, 249-272.
9. D’Almeida, J.R.M., ‘An analysis of the effect of the diameter of glass microspheres on the mechanical behavior of glass microsphere/epoxy-resin composites’, Compos Sci Technol **59**, 1999, 2087-2091.
10. Gupta, N. and Woldesenbet, E., ‘Compression properties of syntactic foams: effect of cenosphere radius ratio and specimen aspect ratio’, Composites Part A: Applied Science and Manufacturing **35,** 1, 2004, 103-111.
11. Gupta, N. and Woldesenbet, E., ‘Microballoon wall thickness effects on properties of syntactic foams’, Journal of Cellular Plastics, 2004, in press.
12. Pinnavia, T.J. and Beall, G.W., Polymer-Clay Nanocomposites, Wiley Series in Polymer Science, 2000.
13. Messersmith, P.B. and Stupp, S.I., ‘Synthesis of Nanocomposites – Organoceramics’, Journal of Materials Research 7, 1992, 2599-2611.
14. Giannelis, E.P., ‘Polymer layered silicate nanocomposites’, Adv. Mater. **8,** 1, 1996, 29-35.
15. Novak, B.M., ‘Hybrid Nanocomposite Materials – Between Inorganic Glasses and Organic Polymers’, Adv. Mater. **5**, 1993, 422-433.
16. Yasmin, A., Luo, J.J., Abot, J.L. and Daniel, I.M., ‘Mechanical and Thermal Behavior of Clay/Epoxy Nanocomposites at Room and Elevated Temperatures’, Proceedings of ASC, 18th Annual Technical Conference, Oct 2003.
17. Gupta, N., Kishore, Woldesenbet, E., and Sankaran S., ‘Studies on compressive failure features in syntactic foam material’, Journal of Materials Science **36**, 18, 2001, 4485-4491.
18. Subramaniyan, A.K., Bing, O. Nakaima, D. and Sun C.T., ‘Effect of Nanoclay on Compressive Strength of Glass Fiber Composites’, Proceedings of ASC, 18th Annual Technical Conference, Oct 2003.
19. Bunn, P. and Mottram, J.T., ‘Manufacture and Compression Properties of Syntactic Foams’, Composites **24,** 7, 1993, 565-571.