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Nanofiller Reinforcement Versus Surface Treatment Effect on the Mechanical Properties of Syntactic Foams

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ABSTRACT

Syntactic foams are one of the special kinds of composite materials which can be prepared in a mechanical way by mixing hollow particles (the filler) with a resin system (the binder). To improve the mechanical properties of syntactic foams, in our work, carbon nanofibers (CNFs) were added to reinforce the syntactic foam. Results showed that although the presence of carbon nanofiber improved the mechanical properties of the syntactic foam, it dramatically increased the density, i.e., destroyed the main advantage of syntactic foams. In addition, the introduction of CNFs could cause difficulty in fabrication and increase the production cost. In order to overcome these problems, two approaches of the surface treatment of hollow microspheres, namely coupling agent and polydopamine (PDA) coating, were applied. Results showed that better interfacial adhesion between hollow microspheres and matrix could be induced from both coupling agent and PDA treated hollow microspheres, which led to the enhancement in mechanical properties of the syntactic foam while maintaining their low density. Compared with the coupling agent approach, the facile one-step PDA coating was much more effective. The failure mechanisms of the CNFs reinforced syntactic foam (CNFRSF) and the syntactic foam containing treated hollow microspheres were discussed in detail.

Keyword: carbon nanofiber, coupling agent, polydopamine, interface, syntactic foams, mechanical properties

1. INTRODUCTION

Syntactic foams were developed in the early 60's and are widely applied to aerospace and submarine industry now¹⁻². It is a special kind of composite materials which can be prepared in a mechanical way by mixing hollow particles (the filler) with a resin system (the binder). Using hollow microspheres, having a lower density compared to the binder material, allows for the manufacturing of light-weight syntactic foams with the increase of filler content. The mechanical properties are important parameters for the performance of syntactic foams and have been reported by many researchers. Tagliavia et al.³ studied the flexural properties of vinyl ester based syntactic foams containing hollow glass particles. Results showed that the flexural modulus was higher as compared to that of the neat resin though the flexural strength decreased with increasing filler content. Wouterson et al.⁴ reported that the specific mechanical properties of epoxy based syntactic foams containing various types of hollow microspheres. The specific properties depended on the volume fractions and types of hollow microspheres. The flexural and compressive strengths decreased with increasing filler content.

To enable wider applications for syntactic foams, it is essential to further increase their mechanical properties. In this work, nanofiller reinforcement and surface treatment effect of hollow microspheres on the mechanical properties of syntactic foams were studied and compared. Carbon nanofibers (CNFs) were used as the reinforcement filler. A systemic mechanical study was carried out. It is worth noting that the specific mechanical properties were discussed in this paper as well because the density of syntactic foams changed with the amount of reinforcement filler introduced. Specific mechanical properties allow for the comparison of the performance of various syntactic foams to other foams, such as polyurethane and aluminum foam. Furthermore, specific mechanical properties aid the comparison between nanofiller reinforcement and surface treatment effect in this study. It is believed that the results would be fruitful for guiding future design for syntactic foams based on specific mechanical properties.

2. EXPERIMENTAL SECTION

2.1 Raw materials

Hollow carbon microspheres (HCMs) were used as the filler in this work. They were produced by heat-treating the raw hollow phenolic microspheres (BJO-093, Asia pacific/Eastech)⁵. Phenolic resin (International laboratory, USA) and Epoxy epicote 1006 resin were used as the binder matrix material. The CNFs used for reinforcement of syntactic foams were Pyrograf®-III supplied by Applied Sciences, Inc, OH, USA. The fiber diameters vary from 60 nm to 150 nm, and the density is 1.95 g/cm³. Nitric acid (65%) and glutaric dialdehyde were purchased from Sigma-Aldrich. Dopamine hydrochloride (99%) and tris(hydroxymethyl)aminomethane hydrochlorid were purchased from Regent Chemicals Pte Ltd. All the chemicals were used as received.

2.2 Preparation of syntactic foams

Three types of syntactic foams were prepared in this work. The first one is CNFs reinforced syntactic foam (CNFRSF). Various amounts of CNFs, namely, 0.5, 1.0, 1.5 and 2.0 vol %, were added to the phenolic resin. The resin was heated to 50 °C to reduce its viscosity before adding the CNFs. The mixture was then stirred by high-shear homogenizer (Sliverson L4R) at 4500 rpm for 30 minutes to obtain uniform dispersion of CNFs. To avoid a temperature rise during the stirring process, external cooling was employed by submerging the beaker containing the mixture in an ice-bath. A stoichiometric quantity of hardener was then added and stirred in the mixture. After well dispersed CNFs were attained, a weighed quantity of HCMs was added in multiple steps to the mixture. The amount of HCMs was fixed at ~28.0 vol % as this ratio has been shown to have the highest fracture toughness of the syntactic foam⁴. The fibers-first-microspheres-second processing route was applied in order to avoid a situation where a greater number of regions display accumulated voids⁶. After the addition of HCMs, the mixture was molded using an aluminum mold coated with a silicone release agent and then left under a constant pressure of 2.0 MPa for 24 hours to cure at room temperature.

The second one is coupling agent treated HCMs (CA-HCMs)/phenolic resin syntactic foam. The surface of HCMs was ultrasonically cleaned in acetone for 30 minutes. After cleaning, the microspheres were subjected to oxidation in 65% nitric acid (Sigma-Aldrich) for 5 h at 25 °C, followed by filtering and washing with distilled water and then dry in a vacuum oven at 50 °C. A coupling agent, glutaric dialdehyde, was used to generate interfacial chemical bonds. 10 g of oxidized HCMs was immersed in 90 g of coupling agent solution for 24 h. The surface treated HCMs were then filtered and washed with distilled water and dried in a vacuum oven at 50 °C. After that, 28.0 vol% of pristine HCMs and CA-HCMs were slowly added to the phenolic resin, respectively with stirring of the mixture to minimize gas bubbles in the resin. In order to avoid agglomeration, the microspheres were added in multiple steps to the phenolic resin. The syntactic foam was then molded using an aluminum mold coated with a silicone release agent and left under a constant pressure of 2.0 MPa for 24 h to cure at room temperature.

The third one is polydopamine coated HCMs (PDA-HCMs)/epoxy resin syntactic foam. The surface of HCMs was ultrasonically cleaned in acetone for 30 minutes prior treatment. 1 g of cleaned HCMs was added into 500 ml 10 mM Tris buffer solution (pH 8.5), followed by adding 2.5 g of dopamine hydrochloride. The suspension was mechanically stirred for 6 h at room ambient. The PDA-HCMs were then filtered and washed with deionized (DI) water, followed by freeze-drying. After that, same volume fractions of pristine HCMs and PDA-HCMs were added to the epoxy resin, respectively with slow stirring to minimize gas bubbles in the resin. The well mixed mixture was poured into an aluminum mold pre-coated with a silicone release agent. The syntactic foam was then left to cure at room temperature under a constant pressure for 24 h, followed by post-curing at 80 °C for 16 h.

2.3 Mechanical tests

Two tests were performed on the mechanical properties of the foams. For the compression tests, the specimens were machined to blocks of 25.0×25.0×12.0 mm³ according to ASTM Standard C365/C 365M – 05. The tests were carried out at room temperature using an Instron Tester (Model 8516), which has a maximum capacity of 100 KN. The cross-head speed applied was 0.5 mm/min.

For the flexural tests, syntactic foams were machined to specimens in dimensions of 127.0×12.70×3.0 mm³ according to ASTM Standard D790-07. The tests were performed using an Instron Tester (Model 5567), which has a maximum capacity of 30 KN. The strain rate was maintained at 0.01/min.

2.4 Characterization

After the mechanical tests, the fracture surface of specimens was sputtered with a layer of gold, and examined in Jeol JSM 6360 scanning electron microscope (SEM) and Joel 6340F field emission scanning electron microscope (FESEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the flexural test stress-strain curves for the CNFRSF containing various amounts of CNFs. It is observed that the stress increased whereas the strain reduced with increasing CNFs content. The increase in stress was attributed to the increase in load bearing of the fibrous reinforcements. The decrease in strain meant that the specimen became more brittle with the addition of CNFs. It can also be seen that the stress of the CNFRSF containing 2.0 vol% CNFs slightly decreased compared to that of the CNFRSF containing 1.5 vol% CNFs. This was ascribed to the stress concentration which resulted from the agglomeration of CNFs. At higher concentration, CNFs might tangle and produce agglomeration because of their high aspect ratio and vander-waals attractive interactions, but the flexural property of CNFRSF containing 2.0 vol% CNFs was still much better than that of the CNFs-free syntactic foam. It is also noted that the modulus (the slope of individual curve) of CNFRSF increased with increasing CNFs content. There was an increase of $\sim 400\%$ in modulus by adding 2.0 vol% CNFs. Pawlak and Galeski⁷ studied that the relationship between the matrix and the inclusion. They found that the higher the modulus of the inclusion compared to the matrix used, the higher the stresses developed in the composites. In this study, the bending modulus of CNFs was 63 GPa which was reported by Zussman et al⁸ whereas the matrix had a modulus of 6.8 GPa⁴. The higher modulus of CNFs was believed to be an important factor to the enhancement in both stress and modulus.

Luxmoore and Owen⁹ suggested that the failure of the foam was attributed to the failure of the resin matrix. Figure 2(a) shows the SEM micrograph of the fracture surface of CNFRSF containing 0.5 vol% CNFs after flexure test. It is observed that the process under flexural loading involved small amount of debonded and fractured microsphere. This was ascribed to the fact that the failure was dominated by the matrix fracture and the microspheres in CNFRSF were not the primary load bearing phase under flexural loading. It can also be seen the matrix around CNFs showed increased deformation compared to areas without CNFs. The pulled-out and debonding of CNFs led to the formation of non-linear and non-planar micro-cracks. These micro-cracks were considered as new step structures that consumed more bending energy. With low volume fraction of CNFs, the phenolic resin sufficed to wet CNFs, leading to effective load transfer from matrix to CNFs. However, agglomeration of CNFs were observed at 2.0 vol%. From Figure 2(b), it can be seen that the CNFs were not completely wet by the resin matrix. Hence, the CNFs were less effective in bearing the load that was transferred from the matrix. In addition, the interfaces between incomplete wetting CNFs and matrix could be filled with some air gaps which behaved as some open porosities and thus reducing the overall flexural strength.

Figure 3 shows the comparison of flexural and compressive yield strengths of CNFRSF as a function of CNFs content. The error bar is the standard deviation for five measured values. It is obvious that the flexural strength increased and the compressive yield strength remained nearly constant with increasing CNFs content. The unchanged compressive properties was resulted from the presence of hollow microspheres which acted as the primary load bearing phase in the CNFRSF when the specimen was subjected to compressive loading. The details were discussed in somewhere else¹⁰. The similar observation was also reported by Dimchev M et al¹¹. The flexural strength increased $\sim 196\%$ from 0 to 1.5 vol%. The increase in strength was attributed to the increase in load bearing of the fibrous reinforcements. On the other hand, the decrease in strength of the CNFRSF containing 2.0 vol% CNFs compared to that of the CNFRSF containing 1.5 vol% CNFs was ascribed to the stress concentration resulting from the agglomeration of CNFs. Although the decreasing trend from 1.5 vol% to 2.0 vol% was about 10%, the stress increased ~ 1.8 times compared to the CNFs-free syntactic foam.

Figure 1. Flexure stress-strain curves of CNFRSF containing various amounts of CNFs

Figure 2. SEM images of fracture surface of CNFRSF containing 0.5 vol% (left) and 2 vol% CNFs (right)

Figure 3. Comparison of the compressive and flexural strengths of CNFRSF containing various amounts of CNFs

Using carbon nanofiber, having a higher density compared to the hollow microspheres and the binder material, could reinforce the syntactic foam. However, the density of the resulting foam increased; eventually destroy the main advantage of syntactic foams. In addition, the introduction of CNFs could cause difficulty in fabrication and increase the production cost. To solve these problems, it is essential to develop a novel method which is able to improve the mechanical properties of syntactic foams while maintain the low density. It is well accepted that the interface between filler and binder plays an important role in determining the mechanical properties of composite materials. Similarly, it is expected that an enhancement in the interaction at the hollow microsphere-matrix interface would improve the mechanical properties of syntactic foams without sacrificing their main advantage. Therefore, the coupling agent approach was applied in this work. Scheme 1 illustrated the process of chemical reaction between the oxidized HCMs and the coupling agent. The hydroxyl functional group was generated on the surface of HCMs by oxidation in a strong nitric acid. One aldehyde group of the coupling agent reacted with hydroxyl group to form acetal linkage and other aldehyde group reacted with phenolic resin monomers and form hemiacetal linkage with resin matrix. The formation of the linkages between HCMs and resin matrix resulted in strong adhesion. The FTIR results, which were discussed in somewhere else¹², indicated that the coupling agent reacted with -OH groups on the surface of HCMs to form acetal linkages. Figure 4 shows the comparison of the flexural and the compressive yield strength of the syntactic foams containing the same volume fraction of pristine HCMs and CA-HCMs. The error bar is the standard deviation for five measured values. It is clearly shown that when the pristine HCMs were replaced by the CA-HCMs, the strength of the syntactic foam improved dramatically as compared to its counterparts. The compressive yield strength and the flexural strength increased ~ 33.6% and ~ 44.1%, respectively. The enhancement was attributed to the introduction of the coupling agent, which generated and promoted stronger interfacial adhesion between the HCMs and the matrix. Figure 5 shows the SEM micrographs of the fracture surface of the syntactic foams containing same volume fraction of the pristine HCMs and the CA-HCMs, respectively. In Figure 5 (a), the partially or fully debonded microspheres could be seen clearly. There were gaps around the debonded microspheres, which resulted from the plastic dilatation of the matrix when debonding occurs¹³. The crack would be initiated and then propagate through the matrix as the specimen was subjected to loading. As the crack reached the interface between microspheres and matrix, it had to overcome the interfacial adhesion and create a new interface. When the interfacial adhesion was poor, the microspheres would be easily debonded. Therefore, in Figure 5 (a), the amount of fractured microspheres was much smaller than that of debonded microspheres. On the other hand, when the interfacial adhesion was strong, the microspheres might fracture before the interfacial adhesion was broken. As a result, compared to Figure 5 (a), Figure 5 (b) reflected opposites. It can be seen that the more fractured microspheres were present, which were ascribed to the strong interfacial adhesion.

Scheme 1. Schematic process of the formation of linkages between the HCMs and the phenolic resin due to the presence of coupling agent

Figure 4. Comparison of the compressive and flexural strengths of syntactic foams containing 28 vol% of the pristine HCMs and the CA-HCMs

Figure 5. SEM images of fracture surface of the syntactic foams containing 28 vol% of the pristine HCMs (left) and the CA-HCMs (right)

Figure 6 compares the specific mechanical properties of CNFRSFs containing various amounts of CNFs with those of the pristine HCMs and the CA-HCMs filled syntactic foams. For the CNFRSF, the specific compressive strength decreased with increase in the content of CNFs. The decreasing trend was caused by the relative constant value of compressive strength compared to the increased density of the specimen. The specific flexural strength increased up to 1.5 vol% of the CNFs addition and decreased beyond 1.5 vol% of CNFs content. The increasing trend was attributed to the relative increase in strength was larger than the relative increase in density whereas the decreasing trend was ascribed to the reduction in strength compared to the trend of increased density. For the pristine HCMs and the CA-HCMs filled syntactic foams, the specific compressive and flexural strengths increased ~29.5% and ~44.9%, respectively. It is also worth noting that the specific compressive strength of syntactic foam containing CA-HCMs was ~40.5% higher than that of the CNFRSF with 1.5 vol% of CNFs, whereas the specific flexural was ~23.9% lower. As a result, it was concluded that the introduction of the coupling agent was more beneficial for the compressive properties and the effect of CNFs reinforcement was better than that of the coupling

agent effect on the flexural properties in the syntactic foam. The specific properties listed here allowed for the comparison of the performance of CNFRSF and syntactic foam containing CA-HCMs to other potential composites and foam materials. Therefore, it is believed that the results would be fruitful for guiding future design for composite materials and beneficial for special application where weight is critical.

Figure 6. Comparison of the specific mechanical properties of the CNFRSF and the syntactic foam containing CA-HCMs

Although the mechanical properties of syntactic foams improved due to the introduction of the coupling agent, the coupling agent approach involved multiple-steps reactions which declined the efficiency and increased the costs of the approach. Moreover, the acid treatment might induce the defects on the surface of the HCMs and hence in turn affected the mechanical properties of syntactic foams. Recently, 3,4-dihydroxy-phenylalanine (precursor of dopamine) was found at high concentrations at the adhesive interfaces between the mussels and substrates, and thus responsible for the strong adhesion. The amazing adhesion ability to various kinds of surfaces have been attracting much attention in the research community¹⁴. It was found that polydopamine (PDA) layer could be formed on a wide range of materials including polymers, ceramics, noble metals and semiconductors by self-polymerization of dopamine in an aqueous solution¹⁵⁻¹⁶. The study on the composites incorporated with PDA-coated filler revealed that the interfacial PDA layers did not only facilitate the dispersion of the filler, but also strengthen the stress transfer from the polymer matrix to the filler, leading to greatly improved mechanical properties¹⁷⁻¹⁸. Inspired by these works, it is expected that the presence of PDA could promote strong interfacial bonding between HCMs and the resin matrix. PDA-HCMs could be prepared via a facile one-step surface functionalization with simple ingredients and mild reaction condition.

The schematic representation for the preparation of PDA-HCMs is illustrated in Scheme 2. Figure 7 confirms that dopamine was polymerized into PDA on the surface of the HCMs. It can be observed that the surface of the pristine HCMs was spherical and smooth, while the surface of the PDA-HCMs was much rougher than that of the pristine HCMs, as a result of the many regular grains composed of PDA nanoparticles deposited on the surface of pristine HCMs. Figure 8 compares the specific mechanical properties of the syntactic foams containing the same volume fraction of the pristine HCMs and the PDA-HCMs. It is clearly shown that when the pristine HCMs were replaced by the PA-HCMs, the specific strength of syntactic foams improved dramatically as compared to their counterparts. The specific compressive yield strength and the specific flexural strength increased by ~ 28.6% and ~ 48.2%, respectively. The enhancement was attributed to the presence of PDA, which generated and promoted stronger interfacial adhesion between the HCMs and the matrix. Compared with the coupling agent approach, PDA coating which was a facile one-step instead of multiple-steps surface treatment approach was much more efficient. The specific compressive strength of the syntactic foam containing the PDA-HCMs increased by ~ 48.2%, which was slight higher than that of its counterparts (~ 44.9%). The ~ 28.6% enhancement in the specific flexural strength for the syntactic foam containing the PDA-HCMs was comparable to that of its counterparts (~ 29.5%). The more increase in the specific compressive strength might be due to the more efficient of PDA coating. The slightly lower

increase in the specific flexural strength could be ascribed to the higher density of the HCMs after PDA coating. A systemic comparison of the effect of coupling agent and PDA coating on the mechanical properties of syntactic foams has not been finished and will be discussed in our future work. Here, we concluded that PDA coating is the facile one-steps surface treatment, which is an effective approach for the promotion of adhesion strength between fillers and matrix of syntactic foams.

Scheme 2. Schematic process for the preparation of PDA-HCMs

Figure 7. SEM images of pristine HCMs (a) and PDA-HCMs (b)

Figure 8. Comparison of the specific compressive and flexural strengths of the syntactic foams containing the same volume fraction of the pristine HCMs and the PDA-HCMs

4. CONCLUSIONS

In this work, the effect of the introduction of CNFs was studied to compare with the coupling agent and the PDA coating effect on the mechanical properties of syntactic foams. Results showed that the compressive strength remained almost constant and the flexural strength increased with the addition of CNFs. Load could transfer from the matrix to CNFs, resulting in the increase in mechanical properties of the syntactic foam. The approach of CNFs reinforcement improved the mechanical properties, but simultaneously increased the density of the syntactic foams. Both PDA coating and coupling agent approaches promoted the interfacial bonding between the HCMs and the matrix and hence improved the mechanical properties of the syntactic foam. The PDA coating was found to be more effective than the coupling agent approach. The specific mechanical properties showed in this work would be fruitful for guiding future design for syntactic foams and beneficial for special applications.

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