Rubber Particles Coating Layer on Macroballoons and Its Physical and Compression Properties in Syntactic Foam

L Anusha1, Z Zakaria1 and KK Chew1
1School of Materials Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, Taman Muhibah, 02600 Jejawi, Arau, Perlis, Malaysia.
E-mail: zunaida@unimap.edu.my

Abstract. The effect of epoxy and acrylonitrile butadiene rubber (NBR) layers on physical and compression properties of macroballoons in syntactic foams was investigated. Epoxy mixture was used to coat on the surfaces of expended polystyrene (EPS) beads template, and the beads were cured to produced epoxy macrobaloons (EM). The cured EM coat with NBR powders in order to form epoxy rubber macrobaloons (ERM). Subsequently, the cured ERM was coated with epoxy mixture as the outermost layer on macrobaloons to form epoxy rubber epoxy macrobaloons (EREM). The EM, ERM, EREM were then filled into syntactic foam and post cured to ensure the shrinkage of EPS beads to produce hollow structures. Three syntactic foams with EM, ERM and EREM were characterized in terms of physical and compression properties, respectively. It was found that EREM exhibited the highest density and average wall thickness in syntactic foam. Overall, the inclusion of NBR powders as rubber coating of macrobaloons with epoxy as the outermost layer resulted in improved compressive strength and toughness by absorbing energy with enhanced interfacial adhesion.

1. Introduction

Syntactic foams have gained considerable attention due to their unique properties such as lightweight, good impact behaviour and high specific compressive properties [1]. Syntactic foams are composite materials consisting of macroballoons embedding in a polymeric matrix [2]. Macrobaloons acts as reinforcing particulate dispersed in the polymeric resin of syntactic foam. The addition of macroballoons enhances the properties of syntactic foam and reduces the material costs simultaneously. The common macroballoons used are glass macrobaloons, polymer macrobaloons and metal macrobaloons [3,4,5]. Syntactic foams are classified as closed-cell foam as the porosity in syntactic foams exists in the form of discrete hollow particles. The closed-cell configuration of syntactic foam provides the benefits of superior strength, low moisture absorption and low density [6].

On the other hand, epoxy is widely used as based syntactic foam due to its chemical and physical cross-linked rigid 3D network of polymer matrix [7,8]. Syntactic foams have been applied in various applications, such as marine structures, aircraft, construction and transportation [9,10]. Previous study reported that syntactic foam has been used in marine structural application because of its low density of buoyancy materials which are used to balance gravity and buoyancy of the oilfield drilling pipe. Alternatively, high pressure resistance materials are needed to withstand the high hydrostatic pressure in deep water [11]. In order to overcome this problem, the rubberized syntactic foam has been introduced for absorbing impact energy. Li and Jones found that syntactic foam filled with microballoons coated with rubber latex aid increased the toughness and impact tolerance [12].

In the present study, rubberized syntactic foam by coating a layer of recycled acrylonitrile butadiene rubber (NBR) gloves powder on macrobaloons was prepared. The effect of a layer of...
rubber particles content on macroballoon on physical (i.e density and morphology) and compression properties of syntactic foam were investigated.

2. Materials and Methods

2.1. Materials
Clear epoxy D.E.R 331 or diglycidyl ether of bisphenol A (DGEBA) and isophorone diamine (IPD) or hardener 8161 were supplied from Euro Chemo-Pharma Sdn. Bhd. (Malaysia). Epoxy resin D.E.R 331 was a clear liquid of epoxide equivalent weight of 182–192, and density and viscosity at 25 °C are 1.16 g/mol and 11000–14000 mPa·s, respectively. IPD has viscosity and amine value of 300–600 mPa·s and 260–284 mg KOH/mg, respectively at 25 °C. Potassium hydroxide (KOH) pellets with content more than 85% was supplied from Sigma-Aldrich (M) Sdn. Bhd. KOH acted as diluent to lower down the viscosity of resin mix. Calcium carbonate (CaCO₃) was obtained from the Sun Minerals Sdn. Bhd and used to prevent expended polystyrene (EPS) beads from sticking to each other. The EPS beads with particle size in the range of 3-6 mm was supplied from San Yong Enterprise Sdn. Bhd. Rejected acrylonitrile butadiene rubber (NBR) glove was supplied from Top Gloves Sdn. Bhd.

2.2. Preparation for Micron-Sized NBR Powders
The rejected NBR gloves were milled into powders with ambient milling method using two rolls mill machine model X(S)K-160X320. The gloves were added into the mill between two nips, as a continuous sheet onto the front roll. The milling of NBR gloves was repeated until micron-sized of rubber powders was obtained. Dino-Lite Digital Microscope was then used to characterize the rubber powders. The rubber powders were sieved at the size of 250 μm after the characterization of the rubber particles.

2.3. Preparation of Epoxy Macrobaloons (EM)
The weight ratio of epoxy resin and IPD was 2E:1IPD. Total weight of epoxy resin and IPD was considered as one hundred part resin. Epoxy was mixed with IPD using overhead mechanical stirrer at 300 rpm for 2 min to produce epoxy system. EPS beads were added into the prepared epoxy system until half-filled the polypropylene (PP) cup to ensure that the EPS beads were fully-coated with the epoxy system. The epoxy-coated EPS beads were transferred to the PP tray that was covered with adequate amount of CaCO₃. A wooden chopstick was used to roll over the uncured epoxy-coated beads with CaCO₃ powder until their surfaces were fully-coated to hinder them from clumping one another. The CaCO₃-coated EPS beads were cured in the air-circulating oven at 80 °C for 15 min. Excess CaCO₃ powder on the surfaces of macroballoons was washed with distilled water and dried in the air-circulating oven at 100 °C for 1 h.

2.4. Preparation of Epoxy Rubber Macrobaloons (ERM)
EM was added into the prepared epoxy system until half-filled the PP cup to ensure that all the macroballoons were fully-coated with the epoxy system. They were then transferred to the PP tray with sufficient amount of NBR powders. The macroballoons were rolled on the NBR powders with wooden chopstick to produce rubber layer on macroballoons. The macroballoons were rolled until the surfaces were fully-coated with the rubber particles. ERM were cured in the air-circulating oven at 80 °C for 15 min.

2.5. Preparation of Epoxy Rubber Epoxy Macrobaloons (EREM)
ERM was used as template and was added into the prepared epoxy system until half-filled the PP cup. The macroballoons in the epoxy system were stirred gently until they were completely coated
with epoxy to produce epoxy rubber epoxy macroballoons. The epoxy-coated macroballoons were transferred to the PP tray that was covered with adequate amount of CaCO₃. A wooden chopstick was used to roll over the uncured EREM with CaCO₃ powder until their surfaces were fully-coated to prevent them from clumping to each other. The calcium carbonate-coated macroballoons were cured in the air-circulating oven at 80 °C for 15 min. The excess CaCO₃ powder on the macroballoon surfaces was washed with distilled water and dried in the air-circulating oven at 100 °C for 1 h.

2.6. Preparation of Syntactic Foam with Coated Macraboalloon

EM was poured and filled in the PP mold, and the stacking volume of 100% was ascertained. EM was then removed from the mold and left aside after measuring the amount of macroballoons for 100% of stacking volume. The mixture of epoxy resin and hardener was prepared by mixing the epoxy and hardener together with concentration of 3% KOH aqueous solution (10% by weight with respect to the resin mix) at 300 rpm for 5 min. EM was added into the epoxy mixture at regular interval subsequently within 15 min. Uncured matrix compound was then casted into the PP mold with the dimension of 113×113×25 mm. A constant load of 5 kg was placed on the top of the lid to maintain the well-dispersed state. The mixture was left to cure in room temperature for 24 h and post-cured at 120 °C for 90 min to shrink all the EPS beads inside the epoxy-coated macroballoons to produce hollow structure within the sphere. The cured syntactic foam was demoulded and cut into standard dimension of 50×50×25 mm for further testing and characterization. The steps for preparing syntactic foam were repeated for ERM and EREM.

2.7. Characterization of Samples

The density of syntactic foam was measured according to ASTM D3574. The syntactic foam specimens with the dimension of 50×50×25 mm [13] were measured by Mitutuyo digital vernier caliper. The mass of syntactic foam was measured within ±1%. Samples were weighed to an accuracy of 0.001 g. The densities of the syntactic foams were obtained by calculating based on Equation 1. The average value of 5 samples was recorded for syntactic foam.

$$\rho = \frac{m}{V}$$

where $\rho$, $m$, and $V$ are density, mass, and volume of syntactic foam, respectively.

The morphology of syntactic foams was captured using the Dino-Lite digital optical microscope (AM521ZT) DinoLite Capture 2.0 software. Image J software was used to analyze microscope images; the average wall thickness of the EM, ERM and EREM were measured by taken 50 readings to represent a better results as according the Equation 2.

$$\text{Wall thickness} = r_o - r_i$$

where $r_i$ and $r_o$ are inner radius and outer radius of macroballoon.

The compression load deflection of syntactic foams was determined using Shimadzu Universal Tensile Machine fitted with a compression jig based on ASTM D3575. The specimens dimension of 50×50×25 mm [13] were compressed with the crosshead speed of 2.5 mm/min up to 60 % of strain under load of 250 kN, and the compressive value was recorded.

3. Results and Discussion

3.1. Density of Syntactic Foams

The density of syntactic foams with different type of macroballoon is illustrated in Fig. 1. It can be seen that, the syntactic foams with EREM marked the highest density of 1.2269 g/cm³, followed
by syntactic foam with ERM (0.8686 g/cm$^3$). Meanwhile, syntactic foam with EM marked the lowest density of 0.5736 g/cm$^3$. This significantly proved that the density of syntactic foam increased when the number of coating layer on macroballoons increased. In other words, the density of ERM in syntactic foams has increased by 51.4% by adding a layer of rubber powder on EM and its density inclined by 41.3% when another layer of epoxy mixture was coated on ERM. Moreover, EREM had the three layers coated of macroballoon contribute to the increasing density due to attribute the thicker shell of macroballoon compared to EM and ERM. Thus, the number of coating layer on macroballoon could alter the final density of syntactic foam.

![Fig. 1: Density of different type of macroballoon in syntactic foams.](image)

### 3.2. Morphology Analysis

The microscopy images of syntactic foam comprising different types of macroballoon are displayed in Fig 2. It can be seen that EM possessed a layer coated on the surface of macroballoon as shown in Fig. 1(2). Besides, ERM showed two layers coated on the macroballoon surface (Fig. 2(b)), while EREM had three layers coated on the macroballoon surface (Fig. 2(c)). In addition, it shows that by increased the number of coating layer will increase the diameter of macroballoon. This observed morphology is stated that the number of coating layer on macroballoons attributed the bigger the diameter of macroballoon, the thicker the wall thickness of the macroballoon thus affected the final density of syntactic foam as discussed in Section 3.1. Similar finding were reported by Wu et al, by increase the layer of glass fiber on macrospheres will increase the wall thickness and diameter of macrospheres [14].

Fig. 3 shows the relationship between the number of coating layer on macroballoons and their average wall thickness. The average wall thicknesses of EM, ERM and EREM were 0.1673 mm, 0.4850 mm and 0.7775 mm, respectively. As the number of coating layer on macroballoon increased, the average macroballoon wall thickness increased [14]. It was found that wall of EREM was thicker than that of ERM and EM as seen the trend in Fig. 2. Furthermore, the average wall thickness of EM increased at 65.5% when a layer of rubber powder was added onto the surfaces of EM, but it increased by 37.62% when another layer of epoxy mixture was coated on the outermost surface of ERM. This proven that, by increase the number of coating layer will increase the volume fraction of rubber powder and thus increased the wall thickness of the macroballoon.
Fig. 2: Microscopic images of different types of macroballoon in syntactic foam at magnification of 20X: (a) EM (b) ERM and (c) EREM.

Fig. 3: The effect of number coating layer on macroballoons on its wall thickness.

3.3. Compression stress of Syntactic Foams

Fig. 4 shows the compressive strength of different wall thickness of macroballoon in syntactic foam. The compressive strength of EM, ERM, and EREM in syntactic foam were 7.9139, 13.2105, and 24.7986 MPa, respectively. ERM showed higher compressive strength compared to EM as depicted in Fig. 4. It can be claimed that the presence of rubber layer could absorb deformation energy and delays the crack propagation in syntactic foam during compression process [15]. Interestingly, the results indicated that EREM had the highest compressive strength compared to others. This could be due to outstanding interfacial area between the rubber layer and outermost layer of epoxy resin [16]. Therefore, EREM exhibited resistant to compression when load was applied which resulted in enhanced compressive strength of syntactic foam.
Fig. 4: Compression strength of syntactic foams with different type of macroballoon.

Compressive toughness is defined as the ability of material to absorb energy and deform plastically before failure by its density [17]. Material with high toughness tends to have high ductility and strength. Fig. 5 depicts the compressive toughness syntactic foam with EM, ERM and EREM. It can be observed that the compressive toughness was increased as the increase of number of coating layer on macroballoon surface. The compressive toughness of syntactic foam of ERM was improved by 34.74% through addition of a layer of rubber powder on the macroballoon surfaces. The crack deflection at the rubber particles and plasticizing effect of rubber reduced the brittleness, as well as increased the ductility of syntactic foam. Besides, rubber layer on the macroballoons surfaces delays crack initiation by absorbing higher amount of energy during compression test which results in higher compressive toughness [18]. Thus, syntactic foam with ERM has higher specific compressive toughness compared to syntactic foam with EM. Surprisingly, the compressive toughness of syntactic foam with EREM was dramatically improved by 69.19%. It can be explained that when another layer of epoxy coated on the outermost surfaces of EREM in syntactic foam (clearly seen in Fig. 1) that the compressive toughness of syntactic foam indicated substantial increment.

Fig. 5: Compression toughness of syntactic foams with different type of macroballoon.
4. Conclusion

The addition of NBR powders as coating layer on macroballoons in syntactic foam was developed to improve the compression properties of syntactic foam. Besides, another layer of epoxy mixture coated on the outermost surfaces of macroballoons was also developed to improve the surface adhesions between the matrix and macroballoons. The macroballoon wall thickness increased by increasing the number of coating layer on the macroballoon. Thicker macroballoon wall thickness of EREM resulted in higher density (1.2269 g/cm³) of syntactic foams. The compressive strength and compressive toughness of syntactic foam with EREM were the highest compared to the other foams. Syntactic foam with EREM had achieved excellent compressive properties due to the ability of NBR powders as coating material in absorbing high energy before failure as well as epoxy outermost layer on macroballoon surface which improved the interfacial adhesion to syntactic foam matrix.

References

[1] Wang L, Zhang, J, Yang, X, Zhang C, Gong W, and Yu J 2014 Fiber Mater. Design 559 29–936
[2] Dando K R et al 2018 J. Cell. Plast. 54(3) 499–514
[3] Altenaiji M et al 2014 Mater. Design 59 296–302
[4] Vogiatzis C A et al 2015 Mater. Design 85 444–454
[5] Wu X et al 2018 Fibers and Polym. 19(1) 170–187
[6] Salleh Z, Islam M M and Ku H 2014 J. Multifunct. Composite. 2(1) 21-27
[7] Li Y and Kessler M R 2014 Polym. 55(8) 2021–2027
[8] Wang L et al 2014 Composites Part B Engineering 56 724–732
[9] Yazici M et al 2014 Acta Physica Polonica A 125 526–528
[10] Salleh Z, Islam M M and Ku H 2014 J. Multifunct. Composite. 3 71–77
[11] Wu X et al 2014 Polym. Composite. 37 497-502
[12] Li G and Jones N 2007 Compos Part A Appl Sci Manuf. 38(6) 1483–1492
[13] Samsudin S S et al 2011 Express Polym Lett 5(7) 653–660
[14] Wu X F et al 2015 RSC Adv 5 61204–61217
[15] Basuli U et al 2012 Elastomers Compos. 47(4) 297–309
[16] Sanjay O S 2012 Effect of Crumb-Rubber Particle Size on Mechanical Response of Polyurethane Foam Composites Oklahoma State University
[17] Lakshminarayan A K, Balasubramanian V and Salahuddin M 2010 J. Iron Steel Res. Int. 17(10) 68–74
[18] Zhang L and Ma J 2010 Compos. Sci. Technol. 70(8) 1265–1271