Effect of crumb rubber type on macroballoons towards physical and mechanical properties in syntactic foams

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Abstract. The effect of crumb rubber types on physical and compression properties of macroballoons in syntactic foams was investigated. Expanded polystyrene (EPS) beads were used as initiation material for starting up the macroballoons. The epoxy and hardener system were prepared to be coated with EPS beads and these coated EPS beads were later cured and post-cured to shrink the EPS beads thus producing epoxy macroballoons (EM). The prepared epoxy macroballoons then were coated with different crumb rubber type which is rejected NBR glove crumb (CG-EM) and waste tire rubber crumb (CT-EM). The EM, CG-EM, and CT-EM were then filled in the epoxy mixture to produce syntactic foam. The fabricated syntactic foam was characterized through physical and compression properties, respectively. Results indicated that the syntactic foam embedded with CT-EM shows high density, reduced radius ratio, and high compressive properties. The syntactic foam embedded with CT-EM shows the highest compressive strength and compressive modulus as compared to syntactic foam embedded with CG-EM and EM. The inclusion of the crumb rubber as the coating layer results in high energy absorption and stress transfer in syntactic foam.

1 Introduction

The microballoons or hollow spheres are normally can be made up of glass, carbon, epoxy [1] and ceramic and widely used in thermal insulation, energy absorption and structural uses due to their unique properties, such light weight, high specific strength and thermal insulation. The hollow sphere in syntactic foam which is currently available is brittle in nature, expensive and involving complicating processing procedure. Waste tires discarded every year are rapidly reducing the available sites for disposal, which is turning out to be a serious environmental issue. Reuse of the waste tire by grounding into crumb rubber helps to reduce the unwanted waste. A few examinations have been completed trying to utilize crumb rubber as filler in development [2-3]. Gloves are commonly recycled such as natural rubber gloves and nitrile gloves. However, nitrile gloves are more preferable compared to the natural rubber gloves due to its excellent properties. The nitrile gloves are having a good solvent resistance and protection over a wide range of chemicals. Besides, it could acts as reinforcing

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filler in the rigid composites by modifying the compressive properties. These investigations show that, despite the fact that the compressive and flexural quality of solid material is brought down by expansion crumb rubber because of the absence of holding, by addition of crumb rubber particles due to the lack of bonding, the crumb rubber particles are found to increase the toughness, crack resistance, shock wave absorption, noise level reduction and also the flexibility of the material. Therefore, in this research by incorporating a layer of rubber waste on macroballoons can produce excellent properties, reduce disposal issues, as well as reduce the production cost of macroballoons.

Syntactic foams are composite materials in which hollow microspheres are embedded in a matrix. Syntactic foams are also known as foam composites since the hollow microspheres can be viewed as reinforcements in a [4-5]. Matrix utilized in syntactic foam incorporates polymers, metals or earthenware production. Polymer matrices are generally classified into thermoplastics and thermosets. Syntactic foams are principally arranged by utilizing thermosetting frameworks on account of the good handling conditions avoiding breakage by gently mixing the hollow microspheres with the thermoset precursor of low density. Thermosetting syntactic foams can be handled at much lower temperatures compared with thermoplastic syntactic foam, accordingly lessening the material and costs for preparing. The blend of diglycidyl ether of bisphenol A (DGEBA), the most broadly utilized epoxy resin used as the matrix in the syntactic foam. Crumb rubber used as the coating layer on macroballoons to expand the strength and stiffness; the epoxy macroballoon serves to decrease the weight; and the rubber coating serves to absorb impact energy and capture microcracks.

2 Materials and methods

2.1 Materials

D.E.R. 331 or diglycidyl ether of bisphenol A (DGEBA), a clear liquid epoxy resin manufactured by Euro Chemo- Pharma Sdn Bhd was selected for the study. Clear epoxy hardener 8161 or isophorone diamine (IPD) was chosen as the curing agent for this study and this chemical was supplied by Euro Chemo-Pharma Sdn Bhd (Malaysia). When used with D.E.R 331 resin, the curing agent would provide a reasonably good curing process within 2 to 7 days at ambient temperature. The Potassium hydroxide (KOH) used for this study was obtained from Sigma – Aldrich Sdn.Bhd. KOH aqueous used as diluent with a concentration 3% (w/w) was added to reduce the viscosity of the resin mixture. Calcium carbonate (CaCO₃) was supplied from Sun Minerals Sdn.Bhd is used to ensure that the stickiness problem of the uncured epoxy-coated beads was addressed thus preventing the beads from clumping to each other. The EPS beads were supplied from San Yong Enterprise Sdn. Bhd and in the range of sizes between 3– 6 mm. The waste tire rubber crumb (0.4 mm) were supplied by Gcycle Tyre Recycling Sdn.Bhd and rejected NBR gloves (1.4 mm) were supplied by Top Glove Sdn. Bhd.

2.2 Methods

2.2.1 Preparation of EM

A resin blend containing clear epoxy resin (D.E.R 331) and polyamine hardener (clear epoxy hardener 8161) with 2:1 proportion was formulated and mixed by chopstick for 3 minutes to
create the epoxy system. The EPS bead were later included into the epoxy system and filled the container at the half and were completely covered by the epoxy system. The epoxy covered EPS beads were then moved into a polypropylene tray which was readily filled with calcium carbonate powder. The epoxy covered EPS beads were then moved over the calcium carbonate by using wooden chopstick until the point when they completely covered with calcium carbonate to ensure that the stickiness of the uncured epoxy covered globules was tended to accordingly keep the beads from clustering to one another. These coated EPS beads were then cured in an oven for 15 minutes at 80 °C and post-cured at 120 °C for 1 hour 30 minutes to shrink all the EPS beads inside the epoxy-coated spheres to deliver empty structures inside the epoxy-coated spheres. The resultant cured EM was then splashed with compressed air to evacuate abundance CaCO₃ powder on their surface.

2.2.2 Preparation of crumb rubber coated EM

A clear epoxy resin (D.E.R 331) and polyamine hardener (clear epoxy hardener 8161) were mixed with 2:1 ratio were formulated and mixed by using chopstick about 3 minutes. The EM was later added into the prepared epoxy system and filled the polypropylene cup at the half. Then the EM was stirred gently in the cup of the mixed epoxy system and ensures they were fully coated with epoxy. Then EM coated with epoxy resin was transferred into polypropylene tray filled with sufficient waste NBR glove crumb. The EM was then rolled on the crumb rubber with a wooden chopstick and ensure they were fully coated to produce NBR glove crumb coated EM (CG-EM). The EM coated with waste NBR glove crumb was then cured in the oven for 15 minutes at 80°C. Similar techniques were used in the preparation of tire rubber crumb coated EM (CT-EM).

2.2.3 Fabrication of epoxy syntactic foam

The pre-determined amount of EM needed in the mould was done by completely filling a polypropylene mould. The EM was then removed from the mould and properly put aside. Next, the resin mixture was prepared by mixing the epoxy resin and the hardener continuously (2:1) together with the 3% KOH solution for about 15 minutes. The amount of KOH solution was fixed at 15% by weight concerning for to the resin mixture. The prepared cured EM was then added at regular intervals into the mixture. Using such a procedure, the uncured matrix compound consisting of EM dispersed in the epoxy matrix was achieved. The mixture was then poured evenly into the mould and a constant load with standard weight (2 kg) was placed on top of the mould lid to maintain the EM in their well-dispersed state. The mixture was left at room temperature to complete the curing process for 24 hours [1]. The cured syntactic foam was then demoulded and cut according to standard dimensions for respective testing after seven days. Cutting process was done after seven days of the composites were produced due to the typical cure schedule (given by supplier) for epoxy resin with polyamine curing agent is around 2 to 7 days at room temperature. Similar techniques were repeated to prepare syntactic foam embedded with CG-EM and CT-EM.

2.3 Testing and Characterization

The morphology of these macroballoons was captured by using Dino-Lite Digital Microscope. The outer and inner radii of the macroballoons were then analysed using the
Image J software to measure the wall thickness of macroballoons. The parameter of radius ratio, $\eta$ was then calculated using equation below;

$$\text{Radius ratio, } \eta = \frac{\text{Inner radius, } r_i}{\text{Outer radius, } r_o}$$  \hspace{1cm} (1)

The density of the syntactic foams was obtained by the mass divided to the volume of syntactic foam in accordance to the ASTM D3574. The mass of the syntactic foams was measured within $\pm$1%. The density of the syntactic foams is calculated by using the following equation;

$$\text{Density} = \frac{\text{Mass, (g)}}{\text{Volume (mm}^3\text{)}}$$  \hspace{1cm} (2)

The compression load deflection of the specimens was performed by using Shimadzu Universal Tensile Machine fitted with a compression jig and in accordance to the ASTM D3575 [1]. The specimens with dimension of $40 \times 40 \times 25$ mm were tested with crosshead speed of 2.5 mm/min. The compressive properties of the samples were recorded and analyzed.

3 Results and Discussion

3.1 Wall thickness

The wall thickness of the epoxy macroballoons (EM) are varying with different layers of NBR glove crumb coated EM (CG-EM) and tire rubber crumb coated EM (CT-EM) are shown in Fig. 1. Based on the graph, the mean wall thickness of EM, CG-EM, and CT-EM are 0.67 mm, 1.35 mm and 2.07 mm. There are significant changes in the range of the wall thickness of the EM for a different layer of coating. The sample coated with rejected NBR glove crumb (CG-EM) is 0.68 mm thicker than the sample of control EM. While the wall thickness coated with waste tire rubber crumb (CT-EM) is 2.07 mm which is 1.4 mm thicker than control EM.

![Fig. 1. Wall thickness of macroballoons against different type of coating layer.](image-url)
The wall thickness of CT-EM is thicker compared to CG-EM and EM. This is because of the size of the coating particle playing a major role in the formation of a layer on the EM surface. The average size of the waste tire rubber crumb is 0.4 mm (40 mesh), whereby the average size of the rejected NBR glove crumb is 1.4 mm (14 mesh) therefore the macroballoons coated with tire crumb rubber forms thicker layer as compared to rejected NBR glove crumb. For the radius, the average radius ratio of control EM, CG-EM and CT-EM are 0.89, 0.81 and 0.68 respectively. It has shown the radius ratio of EM shows the highest and the CT-EM shows the lowest. This is because the wall thickness of macroballoons contributes to the radius ratio and it is inversely proportional to wall thickness [6]. The decrement of the radius ratio as the thickness increases is due to the increment of the outer radius of the macroballoon which can be explained by the formula of the radius ratio in methodology. The microscopic images of control EM, CG-EM and CT-EM are as shown in Fig 2.

![Microscopic image of macroballoons](image)

Fig. 2. Microscopic image of macroballoons (a) EM (b) CG-EM and (c) CT-EM at 20X magnification.

### 3.2 Density

Fig. 3 shows the effect of crumb rubber on the density of syntactic foams. From the Fig. 3, it has shown that the syntactic foam embedded with CT-EM has the highest density compared to the EM and CG-EM. The densities of the syntactic foam depend on the type of coating crumb rubber. As the specific gravity of the type of coating increase, the densities of the syntactic foam increase as well. The densities of the syntactic foam embedded CG-EM has increased by 17.24 % by adding a layer of crumb rubber coated on the EM while the densities of the syntactic foam embedded CT-EM have increased by 20.69 % by adding layers of crumb rubber on the EM. This determines by the specific gravity of the type of coating [7]. The specific gravity of the waste tire rubber crumb is 1.15 whereby the specific gravity of rejected NBR glove crumb is 0.92 therefore as the specific gravity of coating layers increases causes the density of syntactic foam increases.

Furthermore, the coating particle size on macroballoon also affects the density syntactic foam. This is because the finer the size of the coating particles, the higher the area of contact between the macroballoon and the coating layer. Therefore, more number of coating particle will attach to the macroballoon. The size of rejected NBR glove crumb is 1.4 mm (14 mesh) whereby the size of waste tire rubber crumb is 0.4 mm (40 mesh), which is much finer then rejected NBR glove crumb. Therefore more number of waste tire rubber crumb attached on the EM thus contributes to thicker of the wall thickness of the CT-EM and radius ratio decreases which results in higher in the density of syntactic foam [7-8]. Consequently, the thickness of the macroballoon has reduced the concentration of the macroballoons in the matrix of syntactic foams.
3.3 Compressive properties

The compressive properties of the syntactic foams are varied with a different type of crumb rubber layers on macroballoons are shown in Fig. 4. From the Fig. 4, the syntactic foam embedded with CT-EM shows the highest compressive yield strength (14.98 MPa) followed by CG-EM (8.65 MPa) and EM (5.12 MPa). It can be claimed that the presence of crumb rubber layer could absorb deformation energy and delays the crack propagation in syntactic foam during compression process [6]. Therefore, syntactic foam embedded with CT-EM exhibited resistant to compression when a load was applied which resulted in enhanced compressive strength of the syntactic foam. Furthermore, the compressive yield strength of the syntactic foams is depending on the radius ratio, η and size of the coating particles [9]. The decrement of η results in the increment of wall thickness and consequently, it increases the density and thus increases the strength of the syntactic foams. The higher compressive yield strength in syntactic foams embedded with CG-EM and CT-EM have proved that they are stiffer than the syntactic foam embedded with EM. Besides, the epoxy itself is brittle in nature thus reduce the stiffness properties during compression.
The compressive yield strength of the syntactic foam is linearly dependent on the density and concentration of the macroballoon in the syntactic foams. The similar trend can be seen in compressive modulus where the compressive modulus increases in density. The syntactic foams embedded with crumb rubber are having significant higher modulus compared to syntactic foam embedded with EM. This is due to the brittle properties of epoxy, thinner wall thickness and containing high porosity in EM contributes to reducing the stiffness properties. The higher packing of macroballoons in the syntactic foam can result in the higher brittleness in syntactic foams \[6,10\]. Thus the non – permanent deformation of the control EM before the permanent deformation is only 5.12 MPa, while the CG-EM and CT-EM syntactic foam are 8.65 MPa and 14.89 MPa respectively.

Fig. 5 has shown the compressive properties of the syntactic foams up to 60 % deflection. From the Fig. 5, it can be seen that the syntactic foam embedded with CT-EM shows the highest compressive stress as compared to syntactic foam embedded with CG-EM and EM at all compressive strain. This indicated that the inclusive of crumb rubber as coating materials in macroballoons could contribute to the high compressive stress. The sample of the syntactic foam without the aid of crumb rubber (i.e, EM) has the longest and flattest plateau region in the stress-strain curve as compared to the CG-EM and CT-EM which result in slower strain densification. However, the area under the plateau region of the syntactic foam without crumb rubber is the lowest as compared to the coated with crumb rubber syntactic foam. This is due to the aid from crumb rubber tend to reduce the brittleness of the syntactic foam and initiation of stress. The higher energy absorption under the plateau region in the samples of CG-EM and CT-EM syntactic foam is due to ductility of the rubber particles and able to bridging the micro-cracks during compression and higher compression energy can be absorbed \[11-12\].

Furthermore, the high porosity in EM has extended the formation of the plateau regions of the stress -strain curve where there are more spaces in the syntactic foam to be consumed with constant stress \[13\]. From the Fig. 5, has shown the densification strain of the syntactic foam embedded with crumb rubber is seen while the densification strain of the syntactic foam embedded with EM is not that obviously occur.

![Fig. 5. The stress-strain curve of syntactic foam embedded with EM, CG-EM and CT-EM.](image)

### 4 Conclusions

The prepared syntactic foam embedded with CT-EM showed great improvement in compressive properties as compared to syntactic foam embedded with CG-EM and EM. We
found that the produced crumb rubber coated macroballoons had relatively contributes to high compressive modulus, yield strength, and can be used in various engineering applications. Moreover, increment of wall thickness and consequently, it increases the density in high compressive yield strength. The further studies regarding hybridizing coating between rejected NBR glove crumb and waste tire rubber crumb on the macroballoons could be considered in the future to enhance the utilization of these epoxy macroballoons in their desired applications.

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