

Thermo-mechanical properties of fused borosilicate syntactic foams

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ABSTRACT

The properties regarding thermal stability of syntactic foam such as coefficient thermal expansion, α (CTE) had been investigated in this paper. Determination of CTE in composite materials is commonly used for application in heat exchange transformation. The CTE comparison using kinetic theory model has not really been investigated yet for composite materials. The syntactic foam prepared by mixing fused borosilicate or glass microballoon with matrix resin were considered in this study. The different weight percentage of glass microballoon varied from 2wt.% to 10wt.% were analysed using thermo-mechanical analyser (TMA). The results showed that CTE value became up to 53-63% lower than the pure resin after mixing with different weight percentages (2wt.%-10wt.%) of glass microballoon. Experimental results showed that the CTE decreases when glass microballoons are added into the composites measured at different temperatures ranging from 30°C to 70°C. The CTE from the experimental results were also compared with Turner's modification model for composites for its suitability for thermal expansion of syntactic foams. The results indicate that Turner's modification model exhibits a close correlation with the reduction up to 80% of CTE based on experiment.

Keywords: Coefficient; thermomechanical; composites; syntactic foam; porosity.

INTRODUCTION

Fused borosilicate or glass microballoon particles when mixed with a resin matrix can be considered as a closed cell foam or syntactic foam. Previously numerous works that have been carried out on particular syntactic foam characterized the mechanical properties, and also physical properties such as density, volume fraction, wall thickness and porosity [1-4]. Physical properties such as density syntactic foam, including a radial wall thickness ratio, porosity and voids are most likely to be very effective in tailoring mechanical properties of

syntactic foam [5]. This type of lightweight materials is useful for aerospace [6], marine, thermal insulation and packaging [7] because of their good mechanical properties for the environment. It will lead to a concern subject to high temperatures and thus it is important to determine the coefficient of thermal expansion, α (CTE) [8]. Determination of CTE between the insulation and the substrate is important for use in electronic packaging and thermal insulation because it is necessary to reduce thermal stress and possible failure between two surfaces [8]. Meanwhile, the CTE has also been studied extensively in the aerospace shuttle particularly in the fuel tank to reduce the possibility of failure due to thermal stress [8]. An extensive study was also conducted on the characteristics of CTE of PU foam used as insulation for pipes and cooling gas cooler vehicles [9]. Meanwhile the report on other fillers such as glass microballoon did not include many findings on CTE in the literature review. In the recent study, CTE is decreased for three different types of glass microballoon [8]. Another study [10] also showed that CTE is lower than neat epoxy resins for different glass microballoon weight percentage (0-2% by weight). It is also revealed that the reduction of CTE was reported for different volume fractions of glass microballoon mixed with epoxy resin in syntactic foam [11]. Therefore, these findings were not reported clearly about CTE relationship with the physical characteristics of glass microballoon especially porosity and voids are likely to have the same results with ceramic microballoon. In this study, the gap will be investigated to understand more deeply the effect of CTE of the glass microballoon. In order to improve the understanding of this relationship, several models have been introduced for the purposes of this study. Some report also showed Kerner and Turner model is suitable to be used for comparison with the experimental results of CTE [8]. It is also revealed that some models can estimate a CTE of the particulate composites. While another report also mentioned that several shape memory polymer (SMP) composites exhibited their CTE are comparable with theoretical model [12]. Turner as the founder of this model also assumes that the filler is considered as an isotropic material and thus CTE will not depend on the physical properties of the filler itself [13]. The report also found the changes in the dimensions of the constituent material having the same bulk specimens when associated with temperature, while Kerner with other co-founder of the polymer composite model estimated the CTE considering for shear and isostatic stress occurred in particulate phase composites [14]. Generally, both models use the thermosetting polymer composite matrix resin where CTE is closed to the experimental results within the scope of the wall thickness parameter. Thus, the theoretical and experimental approaches are used in this study to link the CTE with different weight percentages of glass microballoon (2-10 % by weight) in syntactic foam. All physical parameters of glass microballoon will be taken into account, such as syntactic foam density, wall thickness, radius ratio, porosity and voids content towards developing the use of lightweight materials for the application of thermal stability.

METHODS AND MATERIALS

Investigation on Thermogravimetric analysis (TGA)

TGA testing was carried out using NETZSCH TG 209F1 Libra equipment. The weight of the specimens were between 4 mg to 8 mg, and different weight percentage of glass microballoon, were used for the analysis. The specimens were heated from 30°C to 800°C at a rate of 10°C/min. A differential thermogravimetric analysis (DTGA) curve was achieved

from the TGA analysis. The heating conditions were maintained constant along the experiment.

Investigation on Thermomechanical analysis (TMA)

The linear dimension at different temperatures for the thermal expansion characteristics of the prepared specimen were evaluated by a thermomechanical analyser (TMA) using TA Instrument (Model TGA Q500), as shown in Figure 1. An expansion type probe was used to measure the temperature-dependent dimensional changes. A preload loading of 0.02 N was applied in all tests. A minimum of 3 coupons were prepared for each compositions. The samples were cut into pieces with dimensions L: 3 mm x W: 3 mm x t: 2 mm. The external gas air input was used for cooling the TA unit system after finishing the testing. The heating rate in each run was kept at 3°C/min and the temperature range was changed from ambient to 80°C. Time, temperature and change in specimen height were recorded during the test. The slope of tangent, also called coefficient of thermal expansion (CTE), between Dimension change-temperature plot was determined and predicted as shows in Equation (1) [8, 9].

$$\alpha = \left(\frac{1}{l}\right) \left(\frac{\Delta l}{\Delta T}\right) \quad (1)$$

where l initial length of specimen, $\frac{\Delta l}{\Delta T}$ slope of the graph.

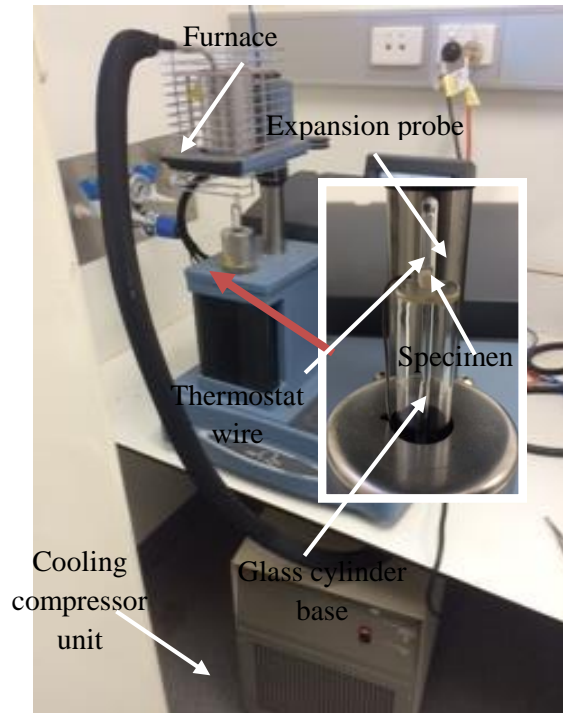


Figure 1: Overview of the thermomechanical analyser (TMA) machine

ANALYTICAL CALCULATION

The Coefficient of Thermal Expansion (CTE) model, α

The rule of mixture (ROM) is commonly used to obtain upper bound of various properties of composites material. Shunmugasamy et al. [8] have duplicated the relationship equation between ROM and CTE, as shown in Equation (2) below:

$$\alpha = \alpha_m \beta_m + \alpha_g \beta_g \tag{2}$$

where α_m, α_g is CTE for matrix resin and glass microballoon, respectively. The mixture of specimens in this study was weight percentage (wt.%), therefore β_m, β_g used wt.% of matrix resin and wt.% glass microballoon, instead of using volume fraction [8].

Kerner’s and Turner’s models have been modified from previous reports by Shunmugasamy et al. [8] to include the physical parameters of glass microballoon, such as wall thickness and radius ratio, but excluding the porosity and voids. Therefore, in this study additional parameters have been included, starting with the derivation from Turner’s model, as shown in Equation (3) below:

$$\alpha = \frac{\alpha_m \beta_m K_m + \alpha_g \beta_g K_g}{K_m \beta_m + \beta_g K_g} \tag{3}$$

$$K = \frac{E}{3(1-2\nu)} \tag{4}$$

Where K is a bulk moduli composite, considering K_m, K_g , modulus of elasticity for matrix resin and glass microballoon, while E is Young’s modulus and ν is Poisson’s ratio of glass microballoon, respectively. An effective modulus of elasticity of glass microballoon can be assumed if the glass microballoon sphere has the same properties as the hollow glass microballoon, which is modified with porosities and voids content in syntactic foam, as shown in Equation (5) [15] and [16] below:

$$E_{\text{eff}} = \frac{E_g (1-2\nu)(1-\phi_g^3)(1-\phi_m)(1-\phi_v)}{(1-2\nu) + \left(\frac{1+\nu}{2}\right)\phi_g^3 + \left(\frac{1+\nu}{2}\right)\phi_m + \left(\frac{1+\nu}{2}\right)\phi_v} \tag{5}$$

where ϕ_g, ϕ_m , and ϕ_v are percentages of cavity porosity, matrix porosity and voids content, respectively. In order to have a mutual understanding about the existing model, the standard specification has been used. Proposed value for modulus of elasticity glass microballoon E_g can be used at 60 GPa [17]. The final modified Turner model can be written up and divided by three equations as below in Equations (6), (7) and (8):

$$\text{Cavity porosity, } \alpha_{\phi_g} = \frac{\alpha_m \beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_g^3 \right] + \alpha_g \beta_g E_g (1-2\nu_m)}{\beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_g^3 \right] + \beta_g E_g (1-2\nu_m)} \tag{6}$$

$$\text{Matrix porosity, } \alpha_{\phi_m} = \frac{\alpha_m \beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_m^3 \right] + \alpha_g \beta_g E_g (1-2\phi_m^3)(1-2\nu_m)}{\beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_m^3 \right] + \beta_g E_g (1-2\phi_m^3)(1-2\nu_m)} \quad (7)$$

$$\text{Voids, } \alpha_{\phi_v} = \frac{\alpha_m \beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_v^3 \right] + \alpha_g \beta_g E_g (1-2\phi_v^3)(1-2\nu_m)}{\beta_m E_m \left[(1-2\nu_g) \left(\frac{1+\nu_g}{2} \right) \phi_v^3 \right] + \beta_g E_g (1-2\phi_v^3)(1-2\nu_m)} \quad (8)$$

where ν_g is Poisson's ratio of glass microballoon, which can be used as 0.21, while the modulus of elasticity, E_m vinyl ester matrix resin, is used as 22.82 GPa [4] and ν_m is Poisson's ratio as 0.35 [18]. In this prediction, the void content can be ignored from the modelling in Turner's model because air/gas trap in syntactic foam is not required for higher percentages (< 5%) in terms of its contribution to the evaluation. Thus, the CTE values investigation only focused on radius ratio's (η), cavity porosity (ϕ_g) and matrix porosity (ϕ_m).

Theoretical Study on Kinetic Energy for Polymer Degradation

The kinetic energy for polymer degradation commonly uses the Equation (9) introduced by Flynn [19].

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (9)$$

where α represents conversion factor ($\alpha=0-1$), t is the time, $k(T)$ is temperature rate constant and $f(\alpha)$ is the reaction model, which describes the dependence of the reaction rate on the extent of the reaction. The temperature dependence of $k(T)$ could be represented by the Arrhenius Equation (10).

$$\frac{d\alpha}{dt} = A e^{\frac{-E_a}{RT}} f(\alpha) \quad (10)$$

where E_a is activation energy of the process. A is the pre-exponential factor, R is the universal gas constant and $f(\alpha)$ depends on the decomposition mechanism. The simplest and most frequently used model for $f(\alpha)$ is shown in Equation (11),

$$f(\alpha) = (1-\alpha)^n \quad (11)$$

where n is order of reaction, while the rate of conversion, $d\alpha/dt$ can be written as,

$$\frac{d\alpha}{dt} = k = k(T) f(\alpha) \quad (12)$$

The combination of Equation (10 – 12) gives the following relationship, as shown in Equation (13),

$$\frac{d\alpha}{dt} = k = (1-\alpha)^n A e^{\frac{-E_a}{RT}} \quad (13)$$

and the first order reaction (n =1) and Equation (13) can be expressed as,

$$\frac{d\alpha}{dt} = k = Ae^{\frac{-E_a}{RT}} \quad (14)$$

Therefore, the Arrhenius equation can also be shown as Equation (14) above. In a chemical kinetics reaction, the rate constant quantifies the speed of a chemical reaction. It is also quantified by a frequency factor or a factor is the pre-exponential constant in the Arrhenius equation, which can be expressed as in Equation (15),

$$\ln(k) = \frac{-E_a}{RT} + \ln(A) \quad (15)$$

Then, a reaction obeys the Arrhenius equation as a plot of ln(k) versus T⁻¹ will give a straight line, or slope and an intercept can be used to determine E_a and A. The final activation energy can be defined as (-R) multiplied by the slope of the graph.

$$E_a = -R \left(\frac{\Delta \ln(k)}{\Delta \ln\left(\frac{1}{T}\right)} \right) \quad (16)$$

Studying kinetic energy, particularly activation energy, can be described in the form of many methods. There are several methods that can determine kinetic energy [20]. The well-known method called the Broido Method is useful to determine the kinetic parameters, which can be derived from mass loss versus temperature [21]. Equation (17) shows the derivation of the Broido Method [22],

$$\ln\left(\ln \frac{1}{Y}\right) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln\left(\frac{R}{E_a} \cdot \frac{Z}{R_H} \cdot T_m^2\right) \quad (17)$$

where (1/Y) is the fraction of the number of initial molecules not yet decomposed, R is the universal gas constant (8.31451JK⁻¹mol⁻¹), T_m is the temperature of the maximum decomposition rate unit Kelvin (K), R_H is the heating rate (Kmin⁻¹) and Z is frequency factor s⁻¹.

RESULTS AND DISCUSSION

Coefficient of Thermal Expansion (CTE), α physical properties

From the experimental results, CTEs were analysed and compared to understand the effect of the physical parameters of syntactic foam on CTE. The CTE result for all specimens, including pure vinyl ester, is shown in Figure 2. It shows that the CTE of glass microballoon syntactic foam decreased when the glass microballoon in syntactic foam was increased. This graph reveals a 30-70% decrease in the CTE of syntactic foams compared to the neat resin result. The lowest CTE value was observed for 10wt.% glass microballoon, which contained the lowest average wall thickness, as shown in Table 4. The reduction of CTE related to the physical properties of glass microballoons, such as wall thickness, radius ratio, porosities and voids, which were interesting to discover for a more concrete understanding of how to obtain the quantitative parameters in this study. The percentage reduction of the CTE can be determined with a different (ratio) starting from pure vinyl ester and a specimen of 2wt.%, which is also shown in Table 1. Incorporation of filling with glass microballoon resulted in

up to a 63 % reduction and it kept decreasing to 53% for a temperature change from 30°C to 70°C.

Table 1: CTE syntactic foam at different temperature

Specimens	T: 30°C		T: 50°C		T: 70°C	
	CTE α ($\mu\text{m}^\circ\text{C}^{-1}$)	Δ (%)	CTE α ($\mu\text{m}^\circ\text{C}^{-1}$)	Δ (%)	CTE α ($\mu\text{m}^\circ\text{C}^{-1}$)	Δ (%)
Pure VE	100.18	-	-	-	-	-
2wt.%	63.70	-36.41	68.59	-31.53	69.50	-30.62
4wt.%	59.15	-40.95	58.99	-41.12	45.80	-54.27
6wt.%	41.58	-58.49	56.88	-43.22	32.80	-67.25
8wt.%	38.89	-61.18	45.38	-54.69	57.06	-43.04
10wt.%	36.71	-63.35	44.61	-55.46	46.77	-53.31

The CTE values between 4wt.% and 6wt.%, and between 8wt.% and 10wt.% did not have much difference between them, whereas they were almost 5% and 1% if compared to each other, respectively. This gap could be contributed to the porosity and voids content occurring in the syntactic foam with a debris of glass microballoons. The thermal flow through these kinds of mechanism will affect the CTE value in the syntactic foams and can be seen in the SEM photo in Figure 3. The specimen with 2wt.% had the highest CTE value, which also corresponded to the lower glass microballoon. This trend was also detected by Shunmugasamy et al. [8] who also noted that the CTE value decreased when glass microballoon was added (with a 30-60% volume fraction) into the vinyl ester matrix resin.

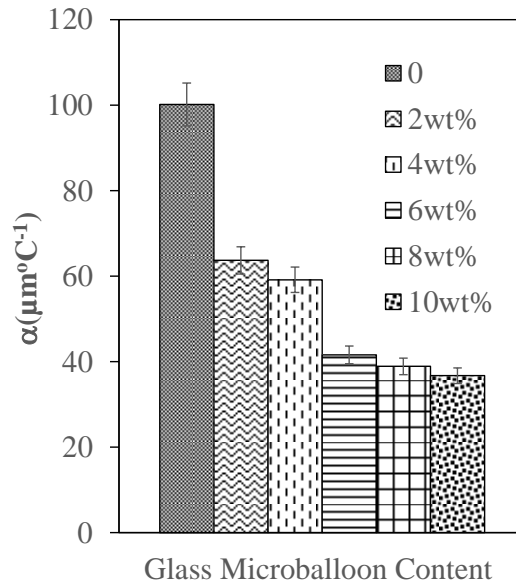


Figure 2: Experimental CTE measured values for neat resin and syntactic foam

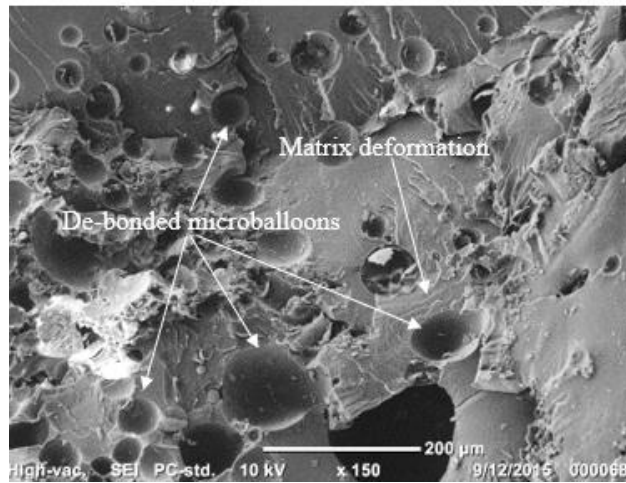


Figure 3: SEM images of the fracture surface of the specimens after being immersed in water

Comparative study on CTE using Turner’s model

The CTE in the experimental result was analysed and plotted to be normalised in the CTE vinyl ester resin as shown in Figure 4. The CTE function was considered at different weight percentages of (wt.%) glass microballoons at temperatures of 30°C, 50°C and 70°C. Generally, the normalised CTE steeply decreased when glass microballoon was added from lower to higher temperature conditions. According to the graph, normalised CTE at a temperature of 70°C shows to be more stable when compared to other temperatures, particularly in combination with more than 4wt.% of glass microballoon. It shows that a lower thermal heat resistance application was also useful and not only for weight saving composite material, with varied wall thickness as reported by Shunmugasamy et al. [8]. Starting from 2wt.%, the behaviour showed a more polymerised condition with 20%, which is different from pure resin CTE. The variation between three different temperatures did also have almost no gap between 1 to 5%, when close to each other. Normalised CTE rapidly changed at between 6–8wt.% but until 10wt.% it was suitable to be used for lower heat transfer applications at 30°C.

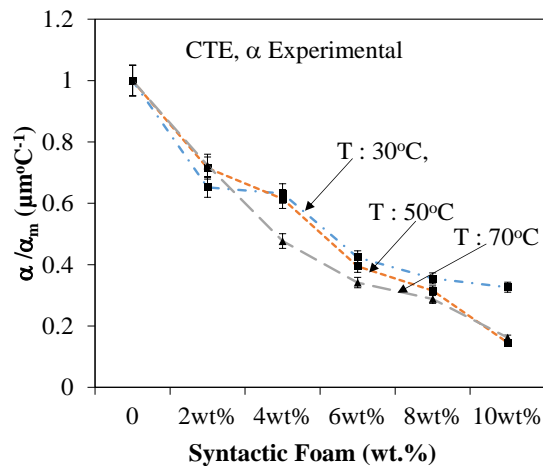


Figure 4: Normalised CTE function of wt.% glass microballoon.

The dimension changed at various temperatures, which shows that a temperature of 30°C, obtained from a specimen with 2wt.%, had a lower expansion rate, with the highest slope of dimension change-temperature plot at 0.2006 $\mu\text{m}/^\circ\text{C}$. This characteristic behaviour made polymeric resin the dominantly crystallised influence in syntactic foam. Furthermore, the specimen of 4wt.%, between temperatures 30°C and 50°C, exhibited a similar CTE value of $\alpha = 58 \mu\text{m}^\circ\text{C}^{-1}$. The modified Turner's model was used to predict the CTE values function with different glass microballoon (wt.%), as shown in Figure 4. The CTE value also varied within a different parametric investigation, whereby radius ratio (η), cavity porosity (ϕ_g), and matrix porosity (ϕ_m) were estimated at three different temperatures: 30°C, 50°C and 70°C. Generally, the CTE value decreased when the glass microballoon content was increased at different temperatures, thus following the experimental values. Similar work has also revealed that a parametric study on the wall thickness of glass microballoons decreased their CTE values when the filler content was increased in syntactic foam [8]. From the graph, it can be predicted that Turner's model showing CTE values was varied in terms of radius ratio, η and syntactic foam for different wt.% of glass microballoons. The CTE decreased from 70 - 37 $\mu\text{m}^\circ\text{C}^{-1}$, which led to a milder effect on the radius of the glass microballoon. Turner's model CTE trend value closely matched the experimental results, particularly specimens 4, 8 and 10wt.% for a temperature at 30°C. At temperatures of 50°C and 70°C, Turner's CTE model values were nearest to the experimental results at 4wt.% glass microballoons. In conjunction with additional glass microballoons, the estimation of CTE in Turner's model will have a reduction from 66% to 36% with varied temperature conditions, as shown in Table 2.

Turner's prediction model, when related to porosity in this study, revealed that the CTE trend for both cavity porosity and matrix porosity were close to each other. This is also evidence that both porosities were present in all specimens and that it increased their percentage in Table 1 when many fractured glass microballoons in the syntactic foam occurred. At a temperature of 30°C, Turner's model predicted a lower CTE when compared to the experimental result. Within this behaviour, α was decreased from 28 $\mu\text{m}^\circ\text{C}^{-1}$ to 19 $\mu\text{m}^\circ\text{C}^{-1}$ but still below the α experimental with 38 $\mu\text{m}^\circ\text{C}^{-1}$. Also in this model, many CTE values were much higher than the experimental CTE value with elevated temperature conditions especially at 50–70°C. This model could predict that the CTE value was close to the experiment for the composition of glass microballoons of between 2wt.% and 4wt.%, while a higher composition of glass microballoon thus contributed more porosity. As a result, a gap occurred between the experimental CTE result and Turner's porosities model especially at a temperature of 70°C with large gap CTE, α : 48 -57 $\mu\text{m}^\circ\text{C}^{-1}$. The reduction of the CTE could be calculated by using this model from 78% to 44% and 80% to 45% for cavity porosity and matrix porosity, respectively as shown in Table 2. Therefore, this model predicted that the CTE was higher in porosity at a high temperature even though there was a decreasing trend towards being inclusive in terms of glass microballoon content.

In this study, the average diameter glass microballoon, with a range of 72-75 μm was used with the average r_o and r_i that could be estimated at a range of between 36-38 μm size, respectively. Hence, the wall thickness of this microballoon could be calculated by using the equation introduced by [23]. The thermal stability of this syntactic foam could be varied in terms of wall thickness, due to a different radius of glass microballoon. Similar results have also been detected in previous studies where the thin wall thickness $(1-\eta) < 0.4$, decreased

the CTE sharply, which was similar in this report. This could be happening when the porosities regime was dominantly in the syntactic foam, which was contributed to an increase in the CTE value. Therefore, porosity also contributed to a change in phase- transformation, which occurred internally in the syntactic foam. It can be seen in Figure 5 that the dimensional change occurred nonlinearly up to a glass transition temperature, T_g of syntactic foam. Beyond this temperature, the behaviour of syntactic foam totally changed in terms of the dimensional variation and it changed to a fairly linear graph. Saha et al. [24] also found similar results for epoxy resin composite. The potential changes in phase with the dimensional stability of the various types of glass microballoon when mixed with an epoxy resin [25].

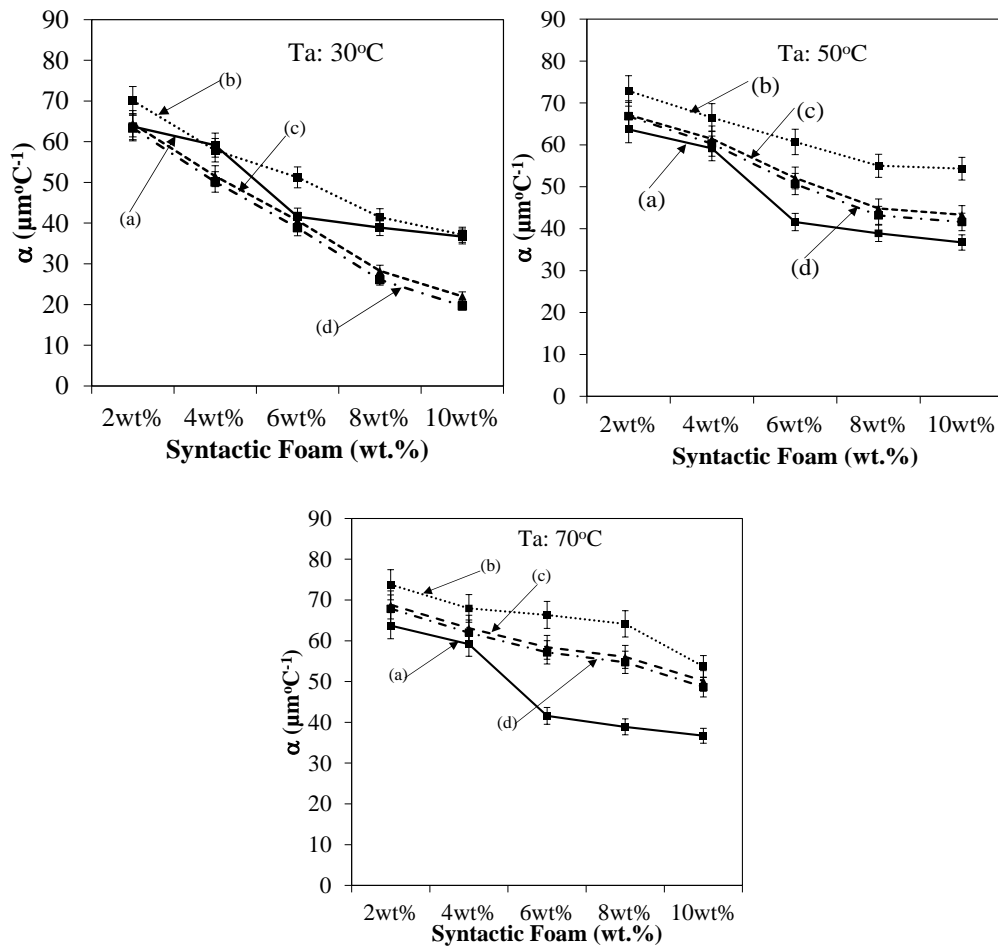


Figure 5: Typical comparison of CTE values using Turner's model (a) Experimental (b) Radius ratio (η), (c) Cavity porosity (ϕ_g), (d) Matrix porosity (ϕ_m)

Table 2: Difference (Δ) of α CTE Turner's model at temperature 30°C, 50°C and 70°C.

Specimen	Tuner's Model Radius ratio, η	Tuner's Model Cavity Porosity, ϕ_g	Tuner's Model Matrix Porosity, ϕ_m
Different at 30°C	Δ (%)	Δ (%)	Δ (%)
2wt%	-30.08	-35.70	-36.77
4wt%	-42.21	-48.55	-49.99
6wt%	-48.84	-59.45	-61.24
8wt%	-58.63	-71.79	-73.97
10wt%	-62.93	-78.02	-80.38
Different at 50°C	Δ (%)	Δ (%)	Δ (%)
2wt%	-27.26	-32.97	-33.32
4wt%	-33.63	-38.69	-39.83
6wt%	-39.43	-47.99	-49.44
8wt%	-45.10	-55.23	-56.91
10wt%	-45.78	-56.76	-58.48
Different at 70°C	Δ (%)	Δ (%)	Δ (%)
2wt%	-26.39	-31.32	-32.26
4wt%	-32.19	-37.03	-38.12
6wt%	-33.79	-41.70	-42.95
8wt%	-35.97	-44.04	-45.38
10wt%	-46.42	-49.93	-51.44

CONCLUSIONS

In this study, the linear dimension stability, also called coefficient of thermal expansion α (CTE), decreased when the glass microballoon content increased. An addition with glass microballoon resulted in up to a 63% reduction of CTE and it kept decreasing to 53% for a temperature change from 30°C to 70°C. The modification of Turner's model was applied in this study for a comparison of CTE in three different temperatures (30°C, 50°C and 70°C) for syntactic foams. The modification included parametric study involvement into the effect of radius ratio, porosity and void content in syntactic foams. Moreover, additional glass microballoons can also comparatively estimate CTE in Turner's model having a reduction from 66% to 36% with varied temperature conditions. The reduction of the CTE from this model could also be reduced from 78% to 44% and 80% to 45% for cavity porosity and matrix porosity in syntactic foams.

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