Effect of PMMA particles on rigid polyurethane foam composites

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Abstract
Rigid polyurethane foam composite was prepared for thermal insulation applications, such as interior foam spraying in building structures by adding polymethylmethacrylate (PMMA) particles and by studying the effect of selected particles sizes of 45, 63, and 75 μm with 5, 10, and 15% wt. content of PMMA particles in some mechanical and physical properties of the produced foam composites. Results show that the flexural strength, flexural modulus, impact strength, and density rise with an increase in weight fraction and decrease in particle size. The hardness increases with an increase in weight fraction and decrease in particle size. The thermal conductivity is enhanced when the added PMMA particles decrease with an increase in the particle weight fraction content and decrease in particle size. SEM confirms the presence of some mechanical enhancement in the resultant foam composite.

Keywords: Rigid polyurethane foam; Foam composite; PMMA particle; Particle size; Weight fraction; Thermal insulation composite; Mechanical properties; Physical properties; Foam density.

1. Introduction
Polymer foams are also identified as sponge polymers, expanded, or cellular. They usually involve a polymer in the solid phase and another in the gaseous phase, which results from a blowing agent. More than one polymer and filler or fiber exists [1]. Depending on their degrees of crystallinity and cross linking and chemical composition, they can be classified as rigid, semi-rigid, or flexible [2]. Foam cells can either be opens (interlinking) or closed. Open-celled foams tend to be flexible, whereas closed-celled foams tend to be rigid [3]. Some polymers can be used to create foams at densities near that of a solid material or at a lower value [1, 2]. The composite material is a multiphase material that reveals an important proportion of the properties of both component phases, such that an enhanced combination of properties is realized [4]. Polymer-matrix composites (PMCs) have fibers or particles that serve as reinforcement or dispersed phase [5]. The mechanical properties of a composite are dependent on many factors but rely largely on the matrix and properties of the reinforcement material; the fractions of each of these phases and the matrix/reinforcement interfacial bonding similarly have an effect on the mechanical properties, as do the impurities and voids that are present in the composite material [6, 7]. For several years, the study of this topic has been extended to the trends of composite foams with a view to the improvement, development, and reinforcement of foams, such as the addition of fibers, fillers, or both [8]. Common fillers include inorganic and organic powders or minerals, metallic particles, whiskers, hollow and solid microspheres, glass or polymer, and nano-particles [9, 10]. Their function is to decrease the cost of foam material and occasionally to reduce also the density of the foam. However, some fillers
have been found to increase the mechanical properties, even when only small volume fractions are added [11]. Reinforced foams have finer cells and are usually more thermally stable than non-reinforced foams [12]. Not all combinations of foam and filler produce better properties [13]. Saint-Michel et al. tested PU foam with calcium carbonate fillers (1-30 microns) and concluded that the particulate reinforcement of the foam is ineffective when the size of the added filler is larger than of the pore size of the foam gas [11]. Vaidya et al. studied the effect of mica on the flexural properties of free rise and integral skin polyurethane foam and found that adding mica in a small amount of 5% v/v increases the flexural modulus of free-rise foam. Moreover, the modulus remains approximately constant with an additional increase in mica concentration when compared at equal densities. The properties of foam also rely on structural parameters, such as skin thickness, core, and corresponding measured densities [10]. Barma et al. modified the rigid polyurethane foam by adding silica particles in the polymer foam matrix and found that these silica particles adjust the mechanical properties of the base foam polymer, aside from the geometrical structure of the foam, where the mechanical properties of foam increase with an increase in silica filler content [14]. Yakushin et al. investigated the effect of hollow glass microspheres (0.5-5% wt.) with a density of 125 kg/m³ on the properties of low-density rigid polyurethane foams (54-90 kg/m³); upon introduction of a small amount of hollow glass microspheres (1-2 wt.%), the characteristics of a polyurethane foam in compression along the rise direction is revealed [15]. Javni et al. prepared rigid polyurethane foams with two types of silica fillers: micro-silica with a mean particle size of 1.5 mm and nano-silica with a mean particle size of 12 nm. The concentration of the fillers varied from 0%-20%. They found that the micro-silica filler does not show any remarkable effect on the density of the rigid foam. Nano-silica increases the density of foams only at a concentration above 20%. It also lowered the compression strength of foam at all concentrations, whereas micro-silica exhibits the same effect at concentrations above 10% [16]. Hongyu et al. investigated the effect of incorporating 1%-7% microsphere and nanoclay fillers on the physical properties of polyurethane (PU) foams and found that foams with fillers show roughly the same thermal conductivity as foams without fillers and that increasing the filler percentage reduces the PU foam density [17]. Poly(methylmethacrylate) (PMMA) particles are uniquely suited to reinforce rigid polyurethane foam composites because they can be easily prepared for traditional manufacturing techniques to produce a product with improved mechanical properties at an acceptable cost. Certain applications for PMMA particle-filled rigid polyurethane foam composites include panels or slabs for certain kinds of roofing and secondary roofing and other interior uses specially as foam spraying in building structures. They may also be utilized for other thermal insulation applications, such as cooling towers and pipes. The present study investigates the effect of PMMA particles with sizes of <75, <63, and <45 µm and weight fractions of 0%, 5%, 10%, and 15% on the various properties of the rigid polyurethane foam that is filled with them, including the mechanical properties of flexural, impact strength, and hardness and physical properties of density and thermal conductivity.

2. Experimental

The rigid polyurethane foam used in this study was produced by Baalbaki Chemical Industries and consists of two components of polyol, low-viscosity and light yellow materials. Its density at 25 °C is practically 1.14 g/cc, and isocyanate (MDI) with surfactants and catalysts is mixed, forming a dark brown liquid with a density of 1.29 g/cc at 25 °C. It has a mixing ratio of 1:1 based on volume and on request time to foaming of approximately 1.5 min. After the foaming process, it shows a low density of 0.16 g/cm³. The reinforcing material, which consists of PMMA (PMMA) particles were provided by VERACRIL® and have a particle size of 75 micrometres, density of 1.25g/cm³, and purity of 90–99% [18].

The preparation of the specimen consists of brief steps. The PMMA particles are sieved at different sizes of <75, <63, and <45 µm Figure 1a and are then weighted according to the combined weights of polyl and isocyanate liquids before mixing. The mold is made of wood Figure1b, lined with aluminum foil to prevent the adhesion between sample and mold, and has a core volume of 60×90×220 mm³. To prepare neat foam, polyl and isocyanate are mixed inside the mold at a proportion of 1:1 and volume of 100:100 ml. The mixing process is continued for 15 sec. until the mixture becomes uniform, and the mold is covered while waiting for the foam to rise. The cast is left for 24 hr before it is released from the mold. To produce the PUR foam composite material, PMMA particles are mixed with polyl inside the mold according to the indicated weight fraction. The mixing course is continued until the mixture becomes uniform, and the isocyanate is then added to the blend of polyl and PMMA particles. The mixing
process of isocyanate and polyol and PMMA particles is continued for 20 sec. until the mixture becomes uniform. The mold is then covered while waiting for the foam to rise. The foam composite cast is left for 24 hr before it is released from the mold Figure 1c. The PMMA particles must be mixed with low-viscosity polyol to improve the wetting of particles.

Figure 1. (a) Microscopic 200X sieved PMMA particles at different sizes (<45, <63, <75) µm, (b) Mold of foam composite casting, (c) Samples shape of foam composite casting.

An average of three specimens was obtained for the flexure test. The mechanical properties of the foams were directed perpendicularly to the rise direction of the foam. Flexure tests were conducted using the Tinius Olsen universal testing machine; model H100KU Figure 2a, at a speed of 5 mm/min. The tests were in accordance to ASTM D 790-03, with dimensions of 200 mm×60 mm×35 mm with span 100 mm Figure 2b [19]. An average of five specimens was obtained for the impact test, which was conducted using an HSM41 Charpy impact tester figure 2c and in accordance to ASTM D 4812-99 for unnotched Izod impact tests with dimensions of 55 mm×15 mm×15 mm with hummer mass 2.5Kg and starting angle 80° [20]. The density of the composite foam was measured according to ASTM D1622-03 [21]. The hardness test involved five readings taken from different places of one foam cast and was conducted using QualiTest HPE Digital Shore a Durometer Figure 2d and in accordance to ASTM F1957-99 [22]. The thermal conductivity was measured using Lee’s disk apparatus Figure 2e with sample dimensions of 40 mm diameter and 5 mm thickness. The heating coil between brass discs 2 and 3 was stationary. The specimen was secured between brass discs 1 and 2, and the applied voltage and current across the terminal of the heating coil were 6 V and 0.2 A, respectively. Heat transfer occurred through the specimen from brass disc 2 to brass disc 1. The temperature of the discs increased slowly until the temperature of all the discs reached the equilibrium.

The morphology of the rigid polyurethane foam composite was examined via SEM (TESCAN VEGA 3) Figure 2f and were observed using selected impact fractured samples. The samples were coated with gold via Cressington sputter coater (108auto) Figure 2g.
Figure 2. Measurement devices for foam composites.
3. Results and discussion

3.1 Flexural test

Figure 3 shows the influence of the weight fraction content of PMMA particles on the flexural strength of polyurethane foam. It reaches the maximum value of 45 μm at 1.415 MPa with 10% wt. and 63 μm at 1.295 MPa and 75 μm at 1.249 MPa) with 5% wt., compared with the PUR of foam at 1.099 MPa. When the PMMA % wt. content is low, the flexural strength of the material is enhanced. When the content is more than 5% wt. for 63 and 75 μm and more than 10% wt. for 45μm, the flexural strength of the rigid polyurethane foams decreases with an increase in the PMMA particle content of neat foams. The gain in strength derives from the interruption in the initiation and combination of the initial cracks during the application of the load. By contrast, when the PMMA % wt. content is low amount, the PMMA particles in the PUR foam matrix (during mixing) can be dispersed homogeneously, and the produced interface can absorb energy in the cells struts. Thus, the surface fracture energy increases, thereby improving the flexural strength. For a higher content of weight fraction, the PMMA particles may be related to a low wettability effect and lead to a weak interface between the particles and matrix and result in a weak foam structure at 63 and 75 μm. PMMA shows a slight reinforcing effect at 5 % wt., which is nevertheless higher than the flexural strength of neat foam. The loss of flexural strength at higher filler % wt. content may be related to the irregularity of cells caused by the imperfections of cells struts due to the presence of large particle sizes. The flexural strength of the samples with 45 μm increases much more than that of the foams with 63 and 75 μm, which may be caused by the enhanced wettability of PMMA particles and large specific surface area of small 45 μm PMMA particles.

Figure 3. Effect of the weight fraction and size of PMMA particles on flexural strength.

Figure 4 shows the effect of the weight fraction and size of PMMA particles on the flexural modulus. The maximum values are 5.989, 5.78, and 5.698 MPa for 45, 63, and 75 μm, respectively, at 15% wt. compared with 4.481 MPa for neat PUR foam. With the addition of PMMA particles, the flexural modulus of PUR foam increases by a reasonable amount with an increase in the PMMA weight fraction. This rise in the flexural modulus can be related to the law of the mixture. At a relative scale, the flexural modulus sharply increases with a decrease in the size of particles, where small particles of 45 μm reach a maximum value, compared with those of 63 and 75 μm, as seen from the figure 4. This effect is explained by the surface area of the interaction of the particles with the PUR matrix. The elasticity of small-sized PMMA particles is also beneficially transferred to the foam composite, along with the elasticity of the PUR foam matrix material. However, as the particles change to a larger size, the relative PMMA particles reduce the specific surface area, thereby weakening the interface surrounding the larger PMMA particles.

3.2 Hardness

Figure 5 shows the effect of the weight fraction and size of PMMA particles on the hardness. The hardness increases with the addition of PMMA particles, and the maximum values are 72.6, 72.7, and 73.3 for 45, 63, and 75 μm, respectively, at 15% wt. compared with 70.2 for neat PUR foam. This result can be related to the PMMA particles, which are comparatively harder than the PUR foam, possibly because of the PMMA particles accumulate and are distributed to resist the penetration of the applied load. Foam densification is also affected by the particles. By contrast, large particles of 75 μm, compared
with 63 and 45 μm, have a maximum value, as seen from Figure 5. The hardness increases with an increase in PMMA particle size, where the larger-sized PMMA particles come into contact with one another as they accumulate in cell struts, when compared with smaller-sized particles.

![Image 1](image1.png)

Figure 4. Effect of the weight fraction and size of PMMA particle of the flexural modulus.

![Image 2](image2.png)

Figure 5. Effect of the weight fraction and size of PMMA particles on hardness.

### 3.3 Impact strength test

Figure 6 show the effect of the weight fraction and particle size of PMMA particles on impact strength. The impact strength of the materials reveals their capability to resist high-speed fracture. The impact strength of the PU composites Figure 6 increases with an increase in PMMA content and with a decrease in particle size. The impact strength reaches the maximum value at 5.28, 4.38, and 3.86 KJ/m² for 45, 63, and 75 μm, respectively, at 15% wt., as compared with 2.76 KJ/m² for neat PUR foam. This improvement in the impact strength of the prepared composite foam can be related to the PMMA particles, which share part of the impact stress, and to the interaction between the PUR foam matrix and PMMA particles. These particles also function as barrier for crack propagation in cell struts (walls), which makes the crack take a long and irregular path. As a result, the fracture surface area of cell walls increases, and the impact strength of the foam composites increases with the PMMA particle % wt. content. Small particles of 45 μm have a maximum value, compared with those of 63 and 75 μm, as seen from Figure 6. The decrease in the impact strength the particle size increases may be due to the difficulty in the diffusion of a large particle in the resin during mixing. This reduces the interaction between the prepared foam composite. As a result, a large flaw in the cell wall, whose function is related to stress intensity, is created. In turn, the absorbed impact energy value is reduced, thereby increasing the speed propagation of the crack. The spasm also fails at lower impact strength.

### 3.4 Density

Figure 7 show the effect of the weight fraction and particle size of PMMA particles on density. For foam structural consideration, pore size, porosity, and density are generally adjusted together to obtain the
preferred strength of the foam. Figure 7 shows that the density of the foam composite increases regularly with the inclusion of and increase in PMMA particle wt% content for three different particles sizes. The maximum values are 0.1801, 0.1782, and 0.1757 g/cm$^3$ for 45, 63, and 75 μm, respectively, at 15% wt., compared with 0.1682 g/cm$^3$ for neat PUR foam. This increase in density may be related to the law of mixture and to the denser PMMA particles. Furthermore, the presence of PMMA has an effect on the foaming process. Specifically, it increases the viscosity of foam resin (polyol), thereby diminishing the foamability of resin by an obvious degree. Thus, the foam porosity is affected (i.e., decrease in cell size) because the PMMA particles are induced, and the density is increased. The size of the PMMA particles also affect the density of the foam composite, where small particles of 45 μm have a maximum value, in contrast to those of 63 and 75 μm, as seen from the figure. When the particle size decreases, the density rises. This can be related to the decrease in particle size, which changes the amount of particles per unit volume. This also has an effect on the resultant pore and cell size, where the number of cell nucleation increases more than the cell expands, thereby also increasing the density.

![Figure 6. Effect of the weight fraction and particle size of PMMA particles on impact strength.](image)

3.5 Thermal conductivity

Figure 8 shows the effects of the size and weight fraction content of PMMA particles on the thermal conductivity of PUF. The thermal conductivity decreases when the PMMA particle content increases and reaches the minimum values of 0.02373, 0.02678, and 0.02855 W/m.$^\circ$C for 45, 63, and 75 μm, respectively, at 15% wt. compared with 0.03031 W/m.$^\circ$C for neat PUR foam. This decrease in the thermal conductivity of the foam composite may be due to the low conductivity of PMMA and the higher porosity of the PUR foam composite system, resulting in thin porous walls enclosed in bubbles. The distribution of the cell size is also even, and the foam composite structure effectively inhibits heat transfer. The size of PMMA particles also has an effect on the thermal conductivity of the PUR foam.

![Figure 7. Effect of the weight fraction and particle size of PMMA particles on density.](image)
composite, where small particles of 45μm have minimum values, in contrast to those of 63 and 75 μm, as seen from Figure 8. Small particles can rise from the number of nucleation within the foam matrix and reduce the pores, and cell size develops the pore structure of the foam matrix. Hence, the thermal conductivity of the PUR foam composite is reduced.

Figure 8. Effect of the weight fraction and size of PMMA particles on thermal conductivity.

4. SEM morphology examination
The impact fracture surfaces of the PMMA particle-reinforced rigid polyurethane foam composites with selected PUR foam at 63 and 75 μm and weight fractions of 5% and 10% wt. were located under SEM and are shown in Figure 9a. According to the SEM morphology, the fractured surface of the neat rigid polyurethane foam is characterized by matrix homogeneity, uniform fracture structure, and non-corrugated crack path. Figure 9b shows that the addition of PMMA changes the matrix, such that small and large cells and voids form in the small-sized particle. This may be related to the uniform distribution in the matrix, where the majority of the particles are in the small-sized region, indicating that PMMA particles impede cell growth by physically affecting the bubble rise and growth. Figure 9b also shows that the crack takes a long (corrugated) path, which has an effect on the mechanical properties of the foam composite. Figure 9c shows the PMMA particles in the matrix and the particle debonding on the surface of the cell wall. This can be related to the lack of wettability at high particle content, which may in turn lead to weak interface and interaction between the PUR foam matrix and PMMA particles. Figure 9c also shows a corrugated crack path.

Figure 9. Continued.
Figure 9. SEM image of selected samples of rigid polyurethane foam with PMMA particle composite: (a) PUR foam, (b) 63 μm with 5% wt, and (c) 75μm with 10% wt.

5. Conclusions
1. The flexural strength and flexural modulus are improved using a small PMMA size and the maximum amount of particles in % wt. content can be added to obtain the optimum flexural loading, which is 5% wt. for 63 and 75μm and 10% wt. for 45μm. This phenomenon is related to the weakening of the interfacial bonding between the particles and the rigid polyurethane foam matrix with a higher content of PMMA.
2. The impact strength increases with an increase in PMMA % wt content and with a decrease in particle size.
3. Hardness increases with an increase in the PMMA particle content and with an increase in particle size. This phenomenon is related to the effect of particle distribution.
4. PUR foam density increases with the amount of particles and with a decrease in particle size.
5. The thermal conductivity decreases with an increase in the particle content and with a decrease in particle size.
6. In general, a clear improvement occurs in the properties, and the maximum properties are gained using 45μm with 10% wt.
7. For foam structural consideration, the mechanical strength, physical properties, and cost are adjusted. We prefer and recommend using a PMMA particle size of 63 μm with 5 % wt.
8. The SEM images confirm decent particle dispersion, distribution, and interaction between the PMMA particles. The dewetting and debonding in the PUR foam matrix can also be observed in samples with high particle content.

References