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Effects of hollow glass microsphere density and surface modification on the mechanical and thermal properties of poly(methyl methacrylate) syntactic foams

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ABSTRACT

Syntactic foams offer low density polymers for insulation and transportation applications with the advantage of having high mechanical properties. In this study, poly(methyl methacrylate) (PMMA) syntactic foams were produced with three different types of hollow glass microspheres (HGMs) as low, medium and high density. It was observed that the density of the syntactic foams was in inverse ratio to the strength properties of the syntactic foams. The lowest measured syntactic foam density was obtained with the addition of high density HGMs into the PMMA matrix without compromising the mechanical properties. Surface coating of HGMs allowed increase in the flexural strength and the impact strength of PMMA syntactic foam by 12% and 17%, respectively, when they were compared with their counterparts with the uncoated HGMs. Addition of HGMs with modified surfaces into PMMA matrix reduced the composite density by 10% with respect to the neat PMMA while had no significant effect on its thermal characteristics.

1. Introduction

Syntactic foams are low density composites which consist of hollow microspheres dispersed in a matrix material such as polymer, ceramic or metal. They are mainly used in thermal insulation and transportation applications due to their low thermal conductivity and light weight [1]. The main advantage of syntactic foams is their tunable properties. By changing the type and composition of microspheres and the matrix material, it is possible to compose a syntactic foam with desired properties. In general, production of syntactic foams with low density and high mechanical properties is a challenging task. Among thermoset plastics, epoxy is the most common matrix material used in the syntactic foam studies since it has been widely applied in transport vehicles. On the other hand, thermoplastic syntactic foams have their own opportunities such as ease of production, moldability, recyclability and higher mechanical properties. As one of the earlier studies on thermoplastic syntactic foams, J-Z Liang used acrylonitrile–butadiene–styrene copolymer (ABS) as matrix material because of its preferable mechanical properties. Addition of HGMs into ABS matrix enhanced both the flexural and tensile strengths due to high interfacial adhesion between the ABS and glass [2]. Addition of HGMs into high-density polyethylene (HDPE) matrix, lowered both the density and thermal conductivity of HDPE and improved its tensile yield strength and modulus. However, low toughness value of these composites led to the necessity of using a compatibilizer, and as a result, higher toughness values were obtained [3].

In syntactic foam studies, several approaches were improved in order to produce foams with low density and high mechanical properties. One of them is selecting the microsphere type and composition which are the main constituents to determine the syntactic foam properties. For example in Doumbia et al.'s study high impact polypropylene (PP) which was composed of PP homopolymer, ethylene propylene rubber (EPR) and a relatively small portion of polyethylene (PE) homopolymer blend is used as matrix material with six types of hollow microspheres [4]. It was found that four types of microsphere shattered during the melt processing and resulted in higher density than the neat polymer. Microspheres with higher thickness over diameter ratio were significantly more durable in melt processing. Mae et al. composed PP syntactic foams by using PMMA microspheres and found out that the yield stress and modulus values decreased with decreasing relative density [5]. Swetha et al. used epoxy as a matrix polymer with three HGM types with different densities. It was observed that the density of the foams decreased linearly with the increasing volume percentage of HGM. High mechanical properties were obtained up to 30 vol% of high-density HGM [6]. Gupta et al. examined the effects of HGM wall thickness and composition on vinyl ester matrix. Authors

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found out that lower HGM volume fractions, and microspheres with higher wall thickness yielded syntactic foams with higher mechanical properties [7].

Another approach for enhancing the mechanical properties of syntactic foam is surface modification of HGMs. Changing the surface group of HGMs improve the compatibility between the components and therefore, the mechanical properties of the syntactic foam. Bharath Kumar et al. treated the hollow microspheres with a silane coupling agent to produce high mechanical HDPE syntactic foams. They stated that improved interfacial bonding between the HDPE and HGM resulted in higher strength for syntactic foams [8]. Li et al. coated the surface of HGMs with styrene butadiene rubber (SBR) latex to be used in the epoxy matrix. While the bending strength of the syntactic foam decreased, the impact resistance increased [9]. Other than the syntactic foam studies, there are several successful examples on increasing the interaction between the polymer matrix and glass substances. In Yi et al.'s study glass fibers, which were coated with PMMA, were dispersed in an acrylic resin and improved its mechanical properties [10].

PMMA is a good candidate for the syntactic foam studies since it has relatively low density with high toughness and rigidity, and low thermal conductivity [11]. The unique properties of PMMA such as high resistance to UV light and water, and excellent transparency facilitate its use in thermal insulation and transportation applications. However, PMMA is seldom mentioned in the area of syntactic foam applications, which requires enhancement of foam properties with the addition of suitable hollow microspheres. To our knowledge, there has been only one study on PMMA syntactic foams in the literature, in which Kinra and Ker mixed thin-walled glass microspheres with PMMA at different volume fractions. It was found out that while the densities of the composites were higher than the theoretical values due to the mechanical deformation of HGMs, they were still lower than that of the neat PMMA [12]. In the present study, PMMA syntactic foams were produced by dispersing three different types of HGMs as low, medium and high density at various HGM compositions in the range of 5–15% by weight. The effects of HGM density and concentration were examined on the mechanical and thermal properties as well as the morphology of PMMA syntactic foams. Since high mechanical properties are crucial for their applications, the effects of coating of the HGMs were also studied. Surface of the HGMs were coated with PMMA to be used in the PMMA matrix to improve the interactions at the matrix-filler interface, and to enhance the mechanical properties.

2. Experimental method

2.1. Materials

PMMA Altuglas V825-T (density of 1.19 g/cm^3) was purchased from Hayim Pinhas A.Ş., Turkey. Three different hollow glass microspheres (HGMs) were used. Low density HGM (LD-HGM), HGS-21 (Larand Chemical Corporation) was supplied by Konuray A.Ş., Turkey, and medium density HGM (MD-HGM), K-37 (3M) and high density HGM (HD-HGM), iM30K (3M) were obtained from Kemiropa A.Ş., Turkey. The properties of HGMs are given in Table 1. Acetone, which was used in the coating process of HGMs, was reagent grade and purchased from Sigma Aldrich.

Table 1
Properties of the hollow glass microspheres from the manufacturer data.

	Density (g/cm^3)	Particle size (μm)	Crush Strength (MPa)	Thermal Conductivity (W/mK)
LD-HGM	0.12*	70	9.48	0.036
MD-HGM	0.37**	45	20.68	0.124
HD-HGM	0.60**	18	193.05	0.200

* Bulk density.
** True density.

2.2. Surface coating of HGMs

A 4 wt% PMMA acetone solution was prepared by sonication for 1 h. After that 60 g of HD-HGMs were mixed with 100 ml of this solution and the mixture was kept at room temperature for 1.5 h. After the filtration, HGMs were dried at 90 °C for 3 h. The agglomerates of HGMs were mechanically disrupted into smaller particles using a muller, which were then sieved.

2.3. Processing

PMMA syntactic foams were produced through extrusion of PMMA and hollow glass microspheres using a Thermo Prism TSE 16 TC twin screw extruder with co-rotating screw configuration at a screw speed of 80 rpm. The temperature profile in the extruder was 235–235–235–245–245 °C from hopper to die. While the PMMA pellets were supplied to the extruder through the main feeder, HGMs were added from the side feeder. The HGM-PMMA syntactic foams were produced with each HGM type with various HGM concentrations as 5%, 10% and 15% by weight.

The syntactic foam pellets which were obtained by the extrusion process were shaped by the injection molding. Rectangular shape materials with the dimensions of 80 × 10 × 4 mm^3 were obtained using a DSM Xplore, laboratory scale micro injection molding device with mold and melting barrel temperatures of 98 °C and 235 °C, respectively. The maximum applied pressure was 13 bars. In order to be used in the thermal conductivity measurement, disc shape specimens with diameter of 50 mm and thickness of 2 mm were produced by compression molding at a melt temperature of 190 °C and applied pressure of 120 bars.

2.4. Density measurement

The densities of the syntactic foams were measured using the bar shaped specimens. The weights of the samples were divided by the volumes of these samples, and the average of five measurements was calculated. The theoretical densities were calculated based on the rule of mixtures which is given in Eq. (1):

$$\rho_{theor} = \rho_{HGM} \cdot V_{HGM} + \rho_P \cdot (1 - V_{HGM}) \quad (1)$$

where ρ_{theor}, ρ_P and ρ_{HGM} are the theoretical density of the composite, densities of the polymer and the HGM (g/cm^3), and V_{HGM} is the volume fraction of HGMs in the composite, respectively [4].

2.5. Mechanical characterization

The flexural analyses of PMMA syntactic foams were carried out according to ISO 178 standard using a Shimadzu Universal Testing Machine. For impact measurements, a Ceast Resil Impactor was used with a hammer of 7.5 J. The analyses were carried out using rectangular shape specimens according to ISO 179.

2.6. Thermal characterization

The glass transition temperature (Tg) of the syntactic foams were determined from the differential scanning calorimetry (DSC) analyses using a Shimadzu DSC-60A. The thermal degradation behavior of the syntactic foams was examined with a Shimadzu, DTG-60H Thermal Gravimetric Analyzer under nitrogen atmosphere. The degradation temperatures at the maximum weight loss were determined from the first derivative of the weight loss vs. temperature curves. The thermal conductivity measurements of the syntactic foams were carried out with an Anter Unitherm™ Model 2022 Thermal Conductivity Meter according to ASTM E1530.