

Preparation and Properties of Poly (Silicon-Containing Arylacetylene)/Attapulgite Foams

Jiadong Wu, Shilong Dong and Qiaolong Yuan

Key Laboratory of Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, China
Email: qlyuan@ecust.edu.cn

Abstract. Poly(silicon-containing arylacetylene) (PSA) syntactic foams were prepared by thermally expandable microspheres (EM) in the silicon-containing arylacetylene (SA) resin during curing. The morphology, porosity, thermal and mechanical properties of the foams were studied. Furthermore, the PSA foam was reinforced by attapulgite (ATT) nanoparticles to fabricate the PSA/ATT composite foam. The results display that the density, compressive strength and thermal stability of the PSA foam decrease with increasing EM content in the matrix, but the temperature at 5% weight loss in N_2 is still higher than $560^\circ C$, and the residual yield at $800^\circ C$ is larger than 89%. With addition of 10 g ATT in the 100 g matrix, the average specific compressive and flexural strength of PSA/ATT foam are $31.4 \text{ MPa g}^{-1}\text{cm}^3$ and $33.6 \text{ MPa g}^{-1}\text{cm}^3$, respectively. The thermal conductivity of the composite foam can decrease to $0.064 \text{ W m}^{-1} \text{ K}^{-1}$ and has a density of 319 kg m^{-3} .

1. Introduction

Lightweight, thermal insulating, high strength and heat-resistant polymeric materials have attracted many attentions among researchers and industries. Polymeric foams are widely used in many applications due to their great features, such as thermal and sound insulation, lightening, cushioning as well as low dielectric constant. Polyarylacetylene (PAA) resin possesses high char yield (over 80%). The PAA foam was prepared by blowing PAA prepolymer with pentane and then carbonized to synthesize carbon foams with high mechanical strength and high strength/density ratio [1].

Poly (silicon-containing arylacetylene) is highly heat- and burn-resistant as ceramic, easy-to-process, and light as thermosetting resin with $-C\equiv C-Si-C\equiv C-Ar-$ units. It can be utilized as ablative and heat-protection materials. Itoh and co-workers [2-5] used magnesia to catalyze dehydrogenative coupling polymerization of diethynyl benzenes and hydrosilanes to prepare the poly [(phenylsilylene) ethynylene-1,3-phenyleneethynylene] (called MSP), which has no volatility with cure, high decomposition temperature and high char yield after pyrolysis. Buvat et al [6] prepared a easily processable phenylacetylene terminated poly (silylene ethynylene phenylene ethynylene) (termed BLJ resin) by condensation of dichlorosilane (dichlorophenylsilane) and a mixture of Grignard agents of 1, 3-diethynyl benzene and phenyl acetylene. Huang et al [7] also prepared a silicon-containing arylacetylene resin (SA) by condensation of dichlorodimethylsilane and a mixture of Grignard agents of diethynyl benzene and phenyl acetylene. The resin abbreviated PSA is processable, highly heat resistant and has good mechanical properties as well as stable dielectric property in the range of wide operating temperature and broadband.

The thermally expandable microsphere consists of inert low-boiling liquid hydrocarbon core wrapped by a spherical thermoplastic acrylonitrile copolymer shell to be used as a physical aerating



powder [8, 9]. The liquid core begins to evaporate, and meanwhile the thermoplastic shell becomes soft and starts to swell due to the high internal pressure of the gasified blowing agent in the microsphere when the microsphere is heated to above the glass transition temperature (T_g) of the polymer shell. The thermally expandable microspheres (TEMs) are lightweight fillers that can act as physical blowing agent and adjust the size of closed cells when mixed in the resin and subsequently heated to cause expansion within the matrix to fabricate the composite foam. Wang et al [10] prepared the expandable microspheres/epoxy foams with different densities and microstructures, and found that the precuring process and foaming temperatures affected the cell size, the cell size distribution and the density of the foam.

Poly (silicon-containing arylacetylene) foam will be a promising lightweight material which could be applied as adsorbent materials after pyrolysis. Attapulgit (ATT), a kind of natural fibrillar hydrated magnesium-aluminum silicate clay has been used to prepare polymer/ATT nanocomposites, due to its intriguing properties, low cost, and low density. In this paper, the PSA syntactic foams were prepared by mixing with the expandable microspheres (EMs) and then elevating temperature to cure and foam the SA/EMs resins. Furthermore, a nanorod-like ATT nanoparticles were used to reinforce the PSA syntactic foam. The fabrication of PSA foams, the correlation of structure, thermal and mechanical properties of PSA, and PSA/ATT composite foams were attempted to be investigated in detail.

2. Experimental

2.1. Materials

Silicon-containing arylacetylene (SA) resins with ethynyl terminal groups were prepared in our lab according to the procedure shown in reference [7]. The number-average molecular weight (\bar{M}_n) and polydispersity index (PDI) of the silicon-containing arylacetylene resins are 2230 and 1.81, respectively. Ethyl acetate, 99+% was purchased from Shanghai Titan Scientific Co., Ltd., China. The expandable microsphere, DU170 (number-average particle size 25.6 μm , density 1.028 g/cm^3) was received from Crerax Science and Technology Co., Ltd., China. Nano attapulgit (ATT) powder was supplied by Jiangsu Jiuchuan Nano Material Technology Co., Ltd., China. All chemicals were used as received.

2.2. Preparation of PSA Syntactic Foam

50 grams of SA and 220 mL of ethyl acetate were added into the 500 mL three-necked flask with mechanical stirrer, condenser and thermometer. The mixtures were heated to 75°C by oil bath, and were agitated until the SA resin was dissolved in ethyl acetate. The certain amount of DU170 powders were poured into the SA melt after the solvent was evaporated under vacuum. The mixture of SA melt and DU170 was stirred until the powders were evenly dispersed in the melt. The melting SA mixtures were poured into the aluminum boxes with sizes of 25 mm×15 mm ×15 mm and 42 mm×42 mm×5 mm. The mixtures of the SA resin and DU170 were foamed and cured in the hot oven in term of the process, 170°C /2 h, 210°C /2 h and 250°C /4 h. SA resin was crosslinked to form poly(silicon-containing arylacetylene) (PSA) during foaming and curing. The added amount of DU170 and the named PSA foams were listed in Table 1.

Table 1. The Named PSA Foams with Different DU170 Content

Coded foam	DU170 content (phr)	Coded foam	DU170 content (phr)
PSA-1.0	1.0	PSA-3.2	3.2
PSA-2.0	2.0	PSA-3.4	3.4
PSA-3.0	3.0	PSA-3.6	3.6
PSA-4.0	4.0	PSA-3.8	3.8

2.3. Preparation of PSA/ATT Composite Foam

In 500 mL round bottom flask, 220 mL ethyl acetate was poured, and then the ATT powders were

weighed and added with agitation and sonication. After 2 h, the 50 g of SA resin was added into the flask. The dispersion was being agitated and sonicated at room temperature for 1.5 h. And then the dispersion was only heated to 80°C with agitation. The 3.6 parts of DU170 per hundred resin were added into the melted mixture of SA and ATT after the ethyl acetate was partially removed at 80°C for 20 min. The melted mixture was poured into the aluminum box with size of 40 mm × 40 mm × 40 mm until the solvent was evaporated. The mixtures were foamed and cured to achieve the PSA/ATT syntactic foams according to the procedure, 170°C /2 h, 210°C /2 h and 250°C /4 h. With addition of 3.0, 5.0, 7.5, 10.0, 12.5 and 15.0 g of ATT in 100 g of the SA resin, the mixtures were coded as SA/ATT-1, SA/ATT-2, SA/ATT-3, SA/ATT-4, SA/ATT-5 and SA/ATT-6, respectively.

2.4. Characterization

Scanning electron microscopy (SEM, S-4800, Hitachi Company, Japan) was utilized to observe the morphology of the foam samples. Based on Archimedes' principle, the volume density of the PSA foam was tested by drainage method according to the Chinese Standard GB/T 4472-2011. It used the density determination kit for the analytical balance (Mettler Toledo ML204, Switzerland).

The compressive test was done according to Chinese Standard GB/T 8813-2008. The compressive strength of the foams was tested by universal material mechanical testing machine (CMT4204, Shenzhen SANS, China) at room temperature. The testing speed used was 1 mm/min.

Thermal conductivity of the PSA and PSA foams with dimensions of 40 mm × 40 mm × 5 mm was measured by a heat conduction analyzer (TC3000, Xiotech, China).

Thermogravimetric analysis (TGA) was conducted using thermogravimetric analyzer (Mettler-Toledo TGA-DSC1, Switzerland). Nitrogen was used as the purge gas with a flow rate of 50 mL min⁻¹, and a heating rate of 10°C min⁻¹ was used.

The flexural properties of the foams were performed on an electronic universal testing machine (CMT4204, Shenzhen SANS, China) at room temperature. The flexural properties of the samples were tested according to Chinese Standard, GB/T 1499-2005. The cross-head speed was 2 mm min⁻¹ and the resulting fracture surfaces were used for the SEM observations.

3. Results and Discussions

3.1. PSA Foaming

The morphology of the PSA syntactic foams with different DU170 content displays that the rigid PSA syntactic foam can be obtained during crosslinking and expanding. The most of foams have closed cell structure, and the amount of spherical cells increases with addition of DU170 content in the PSA. The cell wall of the PSA syntactic foam becomes thinner and the cells squeeze and collapse with each other when the 4 parts DU170 per hundred PSA matrix are added. The increase of the cell density can decrease the density of the PSA syntactic foam. Figure 1 shows the fractured surfaces of the PSA syntactic foams with the content of DU170 from 3.2 to 3.8 phr. The spherical cells are evenly dispersed in the PSA matrix. The PSA syntactic foam with high content of closed cells presents the low density and the proper mechanical property.

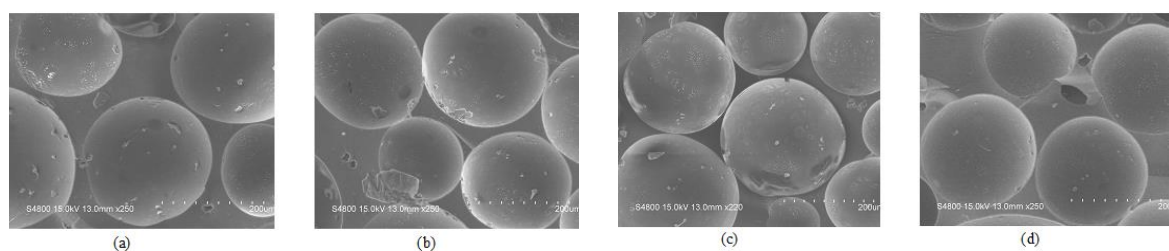


Figure 1. SEM Images of PSA-3.2 (a), 3.4 (b), 3.6 (c) and 3.8 (d) Foams

3.2. Structure and Compressive Strength

The density and compressive strength of the PSA syntactic foams with different DU170 content were

listed in Table 2. The results show that the density of PSA syntactic foam decreases with increase of DU170 content. Meanwhile, the compressive strength of PSA syntactic foam decreases from 10.3 MPa to 4.0 MPa. The decrease of the density of the foam results in the increase of porosity of the foam. The compressive strength of the foam reduces because the wall of the closed cells becomes thinner. However, there is an optimal value, 25.6 MPa g⁻¹ cm³ for the specific compression strength of the foam when the content of DU170 is 3.6 g in 100 g of PSA matrix. The density of the PSA foam with 4.0 g DU170 in 100 g PSA can reach 296 kg m⁻³, but the compressive strength of the foam declines to 4.0 MPa since the collapse of the cells occurs in the foam (see Fig. 1(d)).

Table 2. Density and Compressive Strength of PSA Foams with Different DU170 Content

Foam	ρ (g cm ⁻³)	σ_c (MPa)	σ/ρ (MPa g ⁻¹ cm ³)
PSA-3.0	0.511±0.021	10.32±0.22	20.20
PSA-3.2	0.433±0.011	9.92±0.11	22.90
PSA-3.4	0.361±0.006	9.11±0.06	25.23
PSA-3.6	0.341±0.008	8.74±0.09	25.63
PSA-3.8	0.323±0.013	6.07±0.14	18.80
PSA-4.0	0.296±0.004	4.03±0.05	13.62

3.3. Thermal Stability and Conductivity

The effect of DU170 microspheres on the thermal stability of the PSA syntactic foams are shown in Table 3. The results show that the temperature of 5% weight loss (T_{d5}) of the cured SA, namely PSA decreases with addition of DU170 microspheres. However, the T_{d5} of PSA syntactic foams is still higher than 560°C in N₂, and the residual yield at 800°C (Y_{r800}) of the foams and the cured SA are greater than 89%. The PSA syntactic foam still sustains high heat-resistance. The weight loss of the foams is higher than that of the cured SA, and increases with rising temperature since the gases in the cells escape from the foam. There is a first decomposition temperature for the PSA syntactic foams around 330°C. It results from the decomposition of the polymeric shell of DU170 microspheres. The second weight losses are attributed to the decomposition of the PSA. The thermal conductivity of the PSA syntactic foam is in the range of 0.08~0.09 W m⁻¹ K⁻¹, which is lower than 0.2 W m⁻¹ K⁻¹ of the cured PSA.

Table 3. TGA Analysis of the Cured PSA and PSA Foams (in N₂)

DU170 content in 100 g of PSA (g)	T_{d5} (°C)	Y_{r800} (%)
0.0	622.0	89.1
3.0	573.4	90.9
3.2	583.0	91.0
3.4	584.1	90.9
3.6	560.8	89.3
3.8	569.2	89.9
4.0	564.3	89.5

3.4. PSA/ATT Composite Foams

The effect of ATT content on the mechanical properties of the PSA/ATT composite foams are presented in Table 4. The density of the composite foam decreases gently with increasing ATT loading. It probably belongs to the hydrated pristine ATT nanoparticles, which can participate in the foaming with DU170 to reduce the density of the composite foams compared with the neat PSA foam. The nearly free zeolitic water filling up the empty channels which parallel to the ribbons in two silicon-oxygen tetrahedron layers and one octahedral layer of metal cations, escapes firstly during heating dehydration [11, 12]. The escape of water can be gasified and held by the PSA to form the bubble cells in the matrix. The remaining solvents and water resulting from polycondensation reaction were used as blowing agent to prepare polyimide foams [13]. The average specific compressive and flexural

strength of PSA/ATT composite foam are higher than that of the neat PSA foam, and increase with increase of ATT loading, and can reach $31.4 \text{ MPa g}^{-1} \text{ cm}^3$ and $33.6 \text{ MPa g}^{-1} \text{ cm}^3$, respectively, when the 10 phr of ATT loading are added in the matrix. The epoxy foams expanded by microspheres at 175°C foaming temperature exhibited specific compressive strength of $32.5 \text{ MPa g}^{-1} \text{ cm}^3$ [10]. The maximum values obtained are attributed to the formation of physical network of ATT nanoparticles in the PSA matrix. The unmodified attapulgite nanosized particles could be well-dispersed in the phenolic (PF) matrix and had the supporting effect in PF foam cell wall to improve the tensile strength and the compressive strength of PF foam nanocomposites [14]. The thermal stability of the PSA/ATT-4 composite foam is also higher than that of the PSA foam ($T_{d5} 589^\circ\text{C}$, $Y_{r800} 92.8\%$). Moreover, the specific strength of the composite foam decreases evidently with addition of higher content of ATT nanoparticles. The fractured surfaces of the PSA/ATT-4 and PSA/ATT-5 composite foams and wall of cells in the foams are shown in Figure 2. The ATT nanoparticles can be evenly dispersed in the cell wall of PSA/ATT-4 composite foam (see white prominent dots in Figure 2(b)). The strength of the PSA/ATT composite foam with higher than 10 phr ATT loading in PSA matrix drops down because of existence of the agglomeration of the filler (as indicated in the black cycle in Figure 2(d)). The flexural modulus of the PSA/ATT composite foam decreases slowly with increasing ATT loading. The decrease of the density of the PSA/ATT composite foam causes the reduction of the thickness of wall of cells which will lead to the decrease of the modulus of the foam. Similarly, the flexural strength of the cured SA was augmented with addition of montmorillonite (MMT) or organically modified montmorillonite (OMMT), but the flexural modulus of the cured SA decreased slightly [15].

Table 4. Mechanical Properties of PSA/ATT Composite Foams with Different ATT Loadings

ATT (phr)	ρ (g cm^{-3})	σ_c (MPa)	E_c (MPa)	σ_f (MPa)	E_f (GPa)
0.0	0.341 ± 0.003	8.74 ± 0.03	284.53 ± 26.31	8.12 ± 0.44	2.45 ± 0.14
3.0	0.337 ± 0.007	9.15 ± 0.18	311.67 ± 19.64	8.27 ± 0.03	2.38 ± 0.11
5.0	0.333 ± 0.010	9.41 ± 0.33	373.37 ± 33.88	8.71 ± 0.12	2.35 ± 0.17
7.5	0.326 ± 0.001	9.87 ± 0.28	447.72 ± 14.67	9.41 ± 0.24	2.25 ± 0.08
10.0	0.319 ± 0.001	10.02 ± 0.78	599.66 ± 97.44	10.72 ± 0.55	2.22 ± 0.10
12.5	0.311 ± 0.004	8.44 ± 0.34	212.80 ± 26.57	5.88 ± 0.68	1.40 ± 0.22

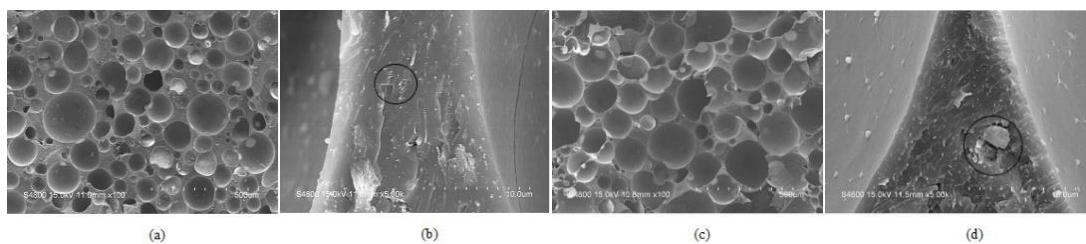


Figure 2. SEM Images of Fractured Surface of PSA/ATT-4 and PSA/ATT-5 Composite Foams

The attapulgite powders could be hot-pressed to form a dehydrated attapulgite with porosity of 45.7%, and exhibited that the thermal conductivity of the attapulgite is as low as $0.34 \text{ W m}^{-1} \text{ K}^{-1}$ at 50°C [16]. This suggests the potential of hot-pressed attapulgite as a candidate for thermal barrier materials. The effect of ATT nanoparticles on the thermal conductivity of the PSA composite foam is presented in Table 5. The results show that the thermal conductivity of the PSA/ATT composite foams are lower than that of the PSA foam, and decreases with increase of ATT loading. It can descend to $0.0642 \text{ W m}^{-1} \text{ K}^{-1}$ when 10 g ATT nanoparticles without premodification are added into 100 g PSA matrix. The thermal conductivity of the microsphere-expanded epoxy foam was about $0.05\sim 0.07 \text{ W m}^{-1} \text{ K}^{-1}$ when the expandable microspheres were added in the range of 3wt%~4wt% [17]. The thermal conductivity of the PSA foam can further be improved by adding ATT nanoparticles in the matrix.

Table 5. Thermal Conductivity of the PSA/ATT Composite Foams

ATT content (phr)	ρ (g cm ⁻³)	K (W m ⁻¹ K ⁻¹)
0.0	0.341±0.008	0.0821
3.0	0.337±0.007	0.0753
5.0	0.333±0.010	0.0724
7.5	0.326±0.001	0.0688
10.0	0.319±0.001	0.0642

4. Conclusions

Thermally expandable microspheres (EM) were added into the silicon-containing arylacetylene (SA) resin to prepare the SA/EM mixtures. The melted mixtures were swollen with expanding of microspheres during curing to form the poly(silicon-containing arylacetylene) (PSA) syntactic foams. Furthermore, the PSA foam was reinforced by attapulgite (ATT) nanoparticles to fabricate the PSA/ATT composite foam. The results show that the foams can form at initial curing temperature of SA resin, and harden to achieve the rigid foams with spherical closed cells after the foams are post-cured. With increasing EM content in the PSA matrix, the density, compressive strength, and thermal stability of the PSA foam decrease, but the T_{d5} of PSA syntactic foam in N₂ is still higher than 560°C, and the Y_{r800} is larger than 89%. The specific compressive strength of the PSA syntactic foam can reach 25.6 MPa g⁻¹ cm³. The thermal conductivity of the foam changes from 0.08 to 0.09 W m⁻¹ K⁻¹. With addition of 10 g ATT in the 100 g matrix, the average specific compressive and flexural strength of PSA/ATT foam are 31.4 MPa g⁻¹ cm³ and 33.6 MPa g⁻¹ cm³, respectively. In addition, the thermal conductivity of the PSA syntactic foam can reduce to 0.064 W m⁻¹ K⁻¹ when the composite foam has a density of 319 kg m⁻³. A highly heat-resistant poly (silicon-containing arylacetylene) foam is lightweight and heat-insulating syntactic foam for aerospace application, and a promising precursor for preparing carbon foam to be used as an absorbent material.

5. References

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