Thermally conducting aluminum nitride polymer-matrix composites

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Abstract

Thermally conducting, but electrically insulating, polymer-matrix composites that exhibit low values of the dielectric constant and the coefficient of thermal expansion (CTE) are needed for electronic packaging. For developing such composites, this work used aluminum nitride whiskers (and/or particles) and/or silicon carbide whiskers as fillers(s) and polyvinylidene fluoride (PVDF) or epoxy as matrix. The highest thermal conductivity of 11.5 W/(m K) was attained by using PVDF, AlN whiskers and AlN particles (7 μm), such that the total filler volume fraction was 60% and the AlN whisker–particle ratio was 1:25.7. When AlN particles were used as the sole filler, the thermal conductivity was highest for the largest AlN particle size (115 μm), but the porosity increased with increasing AlN particle size. The thermal conductivity of AlN particle epoxy-matrix composite was increased by up to 97% by silane surface treatment of the particles prior to composite fabrication. The increase in thermal conductivity is due to decrease in the filler–matrix thermal contact resistance through the improvement of the interface between matrix and particles. At 60 vol.% silane-treated AlN particles only, the thermal conductivity of epoxy-matrix composite reached 11.0 W/(m K). The dielectric constant was quite high (up to 10 at 2 MHz) for the PVDF composites. The change of the filler from AlN to SiC greatly increased the dielectric constant. Combined use of whiskers and particles in an appropriate ratio gave composites with higher thermal conductivity and low CTE than the use of whiskers alone or particles alone. However, AlN addition caused the tensile strength, modulus and ductility to decrease from the values of the neat polymer, and caused degradation after water immersion. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Thermally conducting, but electrically insulating, polymer-matrix composites are increasingly important for electronic packaging because the heat dissipation ability limits the reliability, performance and miniaturization of electronics. In addition to high thermal conductivity and high electrical resistivity, a low dielectric constant is needed for fast signal propagation and a low coefficient of thermal expansion (CTE) is needed for resistance to thermal fatigue. Applications include encapsulations, die (chip) attach, thermal grease, thermal interface material and electric cable insulation.

In order to provide thermally conducting but electrically insulating polymer-matrix composites, fillers (such as diamond, boron nitride, aluminum nitride, silicon carbide and alumina) which are thermally conducting but electrically insulating are used [1–5].

It is known that the transport of heat in nonmetals occurs by phonons or lattice vibrations. The thermal resistance is caused by various types of phonon scattering processes, e.g. phonon–phonon scattering, boundary scattering and defect or impurity scattering [6]. In order to maximize the thermal conductivity, these phonon scattering processes must be minimized. Phonons travel at the speed of sound. The scattering of phonons in composite materials is mainly due to the interfacial thermal barriers resulting from acoustic mismatch and flaws associated with the filler–matrix interface [4,7,8]. For a given filler composition and volume fraction, there are methods of increasing the thermal conductivity of the composite, namely (i) forming conductive networks through appropriate packing of the filler in the matrix, (ii) decreasing the amount of thermally resistant junctions involving a polymer layer between adjacent filler units by using large filler units with little or no defects and (iii) decreasing the thermal contact resistance at the filler–matrix interface by minimizing the interfacial flaws. The purpose of this study is to develop highly thermally conductive composite materials through (i) the use of aluminum nitride particles and whiskers of different sizes and aspect ratios in order to enhance the formation of a thermally conductive network and (ii) the improvement of the

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Table 1
Types of AlN whiskers and particles

AlN whisker type	I			II		
Whisker content (%)	55			15		
Particulate content (%)	45			85		
Maximum particle size (μm)	12			250		
AlN particle type	F	A	B	M	D	E
Average particle size (μm)	1.5	2.0	4.0	7	56	115

interface between the filler and matrix by surface treatment of the filler.

This work is focused on aluminum nitride due to its combination of high thermal conductivity, low dielectric constant and low cost. Previous work on aluminum nitride (AlN) polymer-matrix composites was limited to the use of epoxy [1] and polyimide [2] as the matrices and AlN particles as the filler [1,2]. Previous work [2] has also included hybrid composites involving AlN particles and SiC whiskers as fillers. The hybrid composites with both AlN particles and SiC whiskers exhibit higher thermal conductivity than those of the composites with SiC whiskers or AlN particles as the sole filler, but the presence of SiC causes the dielectric constant to be undesirably high [2].

In this work, we have investigated the use of AlN in the form of AlN whiskers, with and without the presence of AlN particles. In addition, the effects of the AlN whisker–particle ratio and the AlN particle size were investigated. Furthermore, we have investigated the use of polyvinylidene fluoride (PVDF) as the matrix and found that PVDF gave composites with high thermal conductivity. By the use of AlN whiskers and particles, and PVDF as the matrix, a thermal conductivity up to 11.5 W/(m K) was attained.

This paper also addresses the third method described above for increasing the thermal conductivity, because this method has received little attention. The value of the third method stems from the tendency for gaps or other flaws to occur at the filler–matrix interface due to the insufficient affinity between filler and matrix. Such interfacial flaws cause a high thermal resistance at the interface, thus reducing the thermal conductivity of the composite. Ref. [3] mentioned the importance of surface modification to the thermal conductivity of BN epoxy-matrix composites, but the method of modification was proprietary and was not disclosed. This paper uses surface treatment of the filler to improve the affinity between filler and matrix, thereby significantly increasing the thermal conductivity of the composite. In particular, this paper uses silane coupling agents for surface treatment. Silane acts as a bridge to connect the ceramic filler and the polymer matrix, because it has two different chemical structures at the two ends of the molecule. One end is chemically reactive with the polymer; the other end is chemically reactive with the surface of the ceramic filler. The surface treatment of AlN may have an additional function; the coating on the surface may protect AlN from the attack of water.

2. Experimental methods

2.1. Materials

The AlN particles (AlN_p), AlN whiskers (AlN_w) and SiC whiskers (SiC) were obtained from Advanced Refractory Technologies (Buffalo, NY). Both AlN_p and AlN_w were made by direct nitridation. The AlN particles used were of six size classes, with average particle sizes shown in Table 1. The AlN whiskers were of two types, labeled I and II, which mainly differed in the whisker content (the balance being particulate) and the particle size of the particulate portion, as shown in Table 1. The mean particle size was 1.5×0.8 μm (aspect ratio = 1.9) for AlN_w (I). The mean AlN_w length and width were 4.86 and 0.70 μm, respectively (aspect ratio = 7.09) for both AlN_w (I) and AlN_w (II). The above mean sizes were determined by image analysis (Olympus Cue-2 Image Analysis System). The SiC whiskers (β-phase) were of length 18.6 μm, diameter 1.4 μm, aspect ratio 13.2, particulate content 15% and whisker content 85%.

The polymers were PVDF (Kynar (R) 721, from Elf Atochem North America, Philadelphia, PA (properties shown in Table 2), the epoxy, Epon (R) Resin 813 and EPI-Cure (R) 3234 Curing Agent were from Shell Chemical (Houston, TX).

The PVDF-matrix composites were fabricated by (i) mixing PVDF powder (5 μm size) and fillers in acetone, (ii) vacuum drying at 70°C for 2 h and (iii) hot pressing at 12.5 MPa and 200°C for 20 min. Two types of silane from Dow Corning, Midland, MI, i.e. Z-6040

$$\overset{\displaystyle O}{\overset{\displaystyle /\ \backslash}{(CH_2CH_2OCH_2CH_2CH_2Si(OCH_3)_3)}}$$

and Z-6020 ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$), were used to treat the surface of AlN particles. The amine group at one end of the silane Z-6020 molecule and the epoxy group at one end of the silane Z-6040 molecule allow coupling to the epoxy matrix. The amine group in the silane Z-6020 serves as a catalyst for the curing of the epoxy and consequently allows the silane coating to fully bond to the epoxy matrix and yields a better interface than in the case of silane Z-6040. Surface treatment for AlN using silanes involved (i) making an ethyl alcohol (200 proof) aqueous solution at a selected concentration, (ii) adding silane to the

Table 2
Properties of PVDF

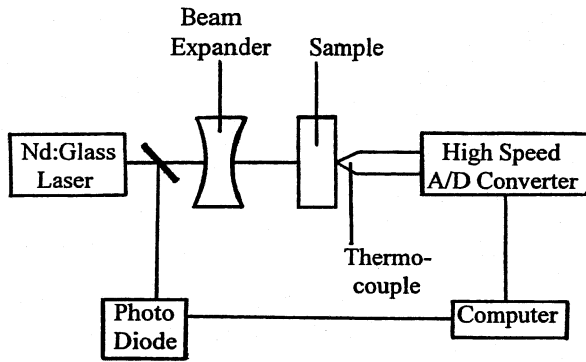|	
Particle size (μm)	5
T_m (°C)	165–172
Density (g/cm³)	1.78
Tensile strength (MPa)	52.0±1.7
Tensile modulus (GPa)	2.22±0.10
Elongation at break (%)	5.0±0.2
Electrical resistivity (Ω cm)	2×10^{14}

Fig. 1. Experimental set-up for thermal diffusivity testing.

solution and stirring for 10 min by using a magnetic stirrer in a flask, (iii) adding AlN particles to the solution made in (ii) and stirring for 20 min, (iv) heating to 80°C and refluxing for 30 min while stirring and then cooling to room temperature, (v) rinsing with alcohol by filtration and (vi) drying at 110°C for 12 h.

The epoxy-matrix AlN (M) composites were fabricated by (i) mixing epoxy resin and curing agent in the weight ratio 100:13, (ii) adding filler and mixing, (iii) pressing at room temperature and 10.5 MPa for 2 h and (iv) heating at 45°C and 10.5 MPa for 1 h to complete polymerization.

2.2. Testing

The AlN particles with and without surface treatment were tested by measuring the weight loss upon heating to 600°C at 20°C/min, using a Perkin–Elmer (Norwalk, CT) TGA7 thermogravimetric analyzer. The weight loss provides an indication of the amount of volatile or decomposable material on the particles. The surface elemental composition of the particles with and without surface treatment was analyzed by electron spectroscopy (ESCA).

The thermal conductivity (W/(m K)) was given by the product of the thermal diffusivity (mm^2/s), specific heat (J/(g K)) and density (g/cm^3). For measuring the thermal diffusivity, the laser flash method was used, as shown in Fig. 1 [9,10]. The pulse type Nd glass laser used for impulse heating was Coherent General (Sturbridge, MA) Everpulse Model 11, which had a pulse duration of 0.4 ms, a wavelength of 1.06 μm and a pulse energy up to 15 J. Adjustment of the capacitor discharge voltage permitted variation of the energy per pulse. The cylindrical sample to be measured was 0.5 in. (13 mm) in diameter, 2.0–3.5 mm in thickness, ground flat on both sides, coated with a thin gold layer on each side and subsequently coated with carbon on the front surface (the side on which the laser beam would hit). The gold layer was used to enhance the thermal contact and to prevent direct transmission of laser beam through the specimen (especially in the case of a transparent polymer sample). The carbon coating served to enhance absorption (as opposed to reflection) of the incident beam. The energy

per pulse was adjusted so that the temperature rise of the specimen was between 0.8 and 1.0°C. The temperature of the specimen at the rear side was measured after the laser flash as a function of time by using a fast response (2–5 ms) and thin (5 μm) type-E thermocouple (Omega Engineering, Stamford, CT, CO2-E), which was attached directly to the rear surface of the sample. The temperature response of the thermocouple was monitored with a high resolution interface card (Omega WB-AAI-B) and with Labtech Notebook data acquisition software. The precision analog/digital interface card was set to measure DC voltage with a resolution of 0.8 μV. The maximum data acquisition rate was 200 Hz. The recording of the temperature rise was triggered by the laser, which was deflected upon firing to a PIN silicon photodiode (Hamamatsu Model S1223-01).

From the temperature vs. time curve, the thermal diffusivity in the direction through the thickness of the specimen was calculated by using an equation in Ref. [6] through an iterative procedure, which was based on the least-squares method and optimization algorithm.

A Perkin–Elmer (Norwalk, CT) differential scanning calorimeter (DSC-7) with UNIX specific heat software was used for measuring the specific heat. A three-curve analysis method was used; it involved obtaining DSC sample, baseline and reference material data. Sapphire was selected as a reference material.

A Perkin–Elmer (Norwalk, CT) thermal mechanical analyzer (TMA-7) was used for measuring the CTE. The temperature range used was from 30 to 150°C and the heating

Table 3
Thermal conductivity and dielectric constant of PVDF-matrix composites with AlN particles, AlN whiskers and SiC whiskers at various volume fractions

Filler	Filler vol.%	Thermal conductivity (W/(m K))	Dielectric constant at 2 MHz
AlN$_p$ (F)	0	0.12	6.60
	50	1.84	–
	55	2.10	–
	60	2.66	–
	65	2.94	–
	70	4.81	–
	73	3.72	–
AlN$_p$ (M)	40	1.86	8.9
	50	3.68	9.40
	55	3.80	9.84
	60	5.56	9.89
AlN$_p$ (A)	55	2.77	8.76
AlN$_p$ (B)	55	2.40	8.07
AlN$_p$ (D)	55	2.79	8.30
AlN$_p$ (E)	55	4.53	7.65
AlN$_w$ (I)	50	2.97	9.40
	60	4.36	8.25
AlN$_w$ (II)	50	4.3	8.40
	60	7.4	8.55
SiC$_w$	50	1.68	14.20
	60	2.04	–

Table 4
Thermal conductivity and CTE of PVDF-matrix composites with AlN whiskers (type II) and AlN particles (type B) in a 1:1 volume ratio and at various total filler volume fractions

Total filler vol.%	Thermal conductivity (W/(m K))	CTE (°C^{-1})
25	1.73	1.1×10^{-4}
35	2.61	9.8×10^{-5}
40	2.86	8.9×10^{-5}
50	3.42	7.1×10^{-5}
55	6.18	6.2×10^{-5}
60	8.16	4.2×10^{-5}

rate was 20°C/min. Before the measurement, the specimens had been annealed in a furnace at 150°C for 2 h.

The tensile properties were measured using a hydraulic mechanical testing system (MTS 810, MTS Systems, Eden Prairie, MN) at a crosshead speed of 1.0 mm/min. The strain was measured by a strain gage (EA-13-120LZ-120, Micro-Measurements Division, Measurements Group, Raleigh, NC) attached to each specimen. The tensile strength, modulus and ductility were measured for the neat PVDF as well as for the PVDF-matrix composite containing 60 vol.% AlN_w (II) and AlN_p (M) in the ratio 1:3 (apparent) or 1:25.7 (true). In each case, the effects of immersing in water for 7 days and of heating in air at 140°C for 7 days were investigated. Five samples of each type were tested for each condition.

A QuadTech (Marlborough, MA), Model 7600 Precision RLC meter with copper-based electrodes was used for measuring the capacitance, which relates to the dielectric constant. The output voltage was 1.0 V and the frequency was scanned from 10 Hz to 2 MHz. The specimen was in the form of a disc with diameter 13 mm and thickness 1–2 mm. The dielectric constant was calculated by using the measured capacitance at a particular frequency.

3. Results and discussion

Table 3 gives the thermal conductivity of PVDF-matrix composites with various types of AlN_p at various volume

fractions. For a given AlN_p type, the thermal conductivity increased with increasing AlN_p volume fraction, except that the thermal conductivity decreased when the AlN_p volume fraction was increased from 70 to 73% (due to increase in porosity). At a fixed filler volume fraction of 55%, AlN_p (E) gave a composite of higher thermal conductivity than any other type of AlN_p, due to its largest particle size (115 μm). The second highest thermal conductivity was exhibited by the composite with AlN_p (M), even though AlN_p (M) was much smaller in particle size than AlN_p (D). This means that particle size is not the only governing factor. AlN_w (II) gave composites of even higher thermal conductivity than AlN_p (M), probably because of the large particle size in AlN_w (II). AlN_w (I) gave composites of lower thermal conductivity than AlN_p (M); the reason for this is unclear. SiC_w gave composites of the lowest thermal conductivity (even lower than AlN_p (F)), due to the relatively low thermal conductivity of SiC compared to AlN. Table 3 also gives the dielectric constant (relative to that of vacuum) at 2 MHz. For AlN_w (I), the dielectric constant unexpectedly decreased with increasing AlN_w volume fraction. However, for AlN_w (II) and AlN_p (M), the dielectric constant did not vary much with the AlN volume fraction. The dielectric constant is much higher for SiC_w composites than AlN composites, as expected from the high dielectric constant of SiC compared to AlN.

Table 4 gives the thermal conductivity and CTE of PVDF-matrix composites with AlN_w (II) and AlN_p (B) in a 1:1 volume ratio and at various total filler volume fractions. The thermal conductivity increased and the CTE decreased with increasing total filler volume fraction, as expected from the high thermal conductivity and low CTE of AlN compared to the polymer matrix.

Table 5 gives the thermal conductivity, dielectric constant and CTE of PVDF-matrix composites with AlN (II) and AlN_p (B) in various volume ratios and for two different total filler volume fractions. At a fixed total filler volume fraction of 50%, the thermal conductivity was highest for an intermediate AlN_w:AlN_p ratio of 3:1 (apparent, assuming that AlN_w (II) contained no AlN particles) or 1:7.9 (true, accounting for the presence of AlN particles in AlN_w (II)), and the dielectric constant was lowest for the

Table 5
Thermal conductivity, dielectric constant and CTE of PVDF-matrix composites with AlN_w (II) and AlN_p in various volume ratios

AlN_p type	Total filler vol.%	AlN_w:AlN_p volume ratio		Thermal conductivity (W/(m K))	Dielectric constant at 2 MHz	CTE (°C^{-1})
		Apparent	True			
B	50	6:1	1:6.8	3.07	8.00	7.28×10^{-5}
B	50	3:1	1:7.9	4.1	9.00	7.23×10^{-5}
B	50	1:1	1:12.3	3.42	9.20	7.10×10^{-5}
B	50	1:3	1:25.7	2.44	–	–
B	50	1:6	1:45.7	2.32	8.96	6.16×10^{-5}
B	60	1:1	1:12.3	8.16	9.40	4.19×10^{-5}
M	50	1:1	1:12.3	6.09	8.23	5.92×10^{-5}
M	60	1:3	1:25.7	11.51	9.86	3.46×10^{-5}
M	60	1:6	1:45.7	10.36	9.87	3.69×10^{-5}

Table 6
Thermal conductivity, dielectric constant and CTE of PVDF-matrix composites with AlN_w (I) and AlN_p (A) in various volume ratios

Total filler vol.%	AlN_w:AlN_p volume ratio		Thermal conductivity (W/(m K))	Dielectric constant at 2 MHz	CTE ($°C^{-1}$)
	Apparent	True			
50	6:1	1:1.1	2.92	10.00	$7.78×10^{-5}$
50	3:1	1:1.4	3.18	8.55	$7.66×10^{-5}$
50	1:1	1:2.6	3.13	9.45	$7.57×10^{-5}$
50	1:3	1:6.3	3.32	8.50	$6.88×10^{-5}$
50	1:6	1:11.7	2.50	9.40	$6.52×10^{-5}$
60	1:1	1:2.6	3.43	8.80	$4.33×10^{-5}$

highest AlN_w:AlN_p ratio of 6:1 (apparent, assuming that AlN_w (II) contained no AlN particles). At a fixed AlN_w (II):AlN_p ratio of 1:1 (apparent), the dielectric constant increased with increasing total filler volume fraction; this trend is consistent with that for the case of AlN_w (II) being the sole filler (Table 3). Table 5 also shows the thermal conductivity of PVDF-matrix composites with AlN_w (II) and AlN_p (M) in various volume ratios and at different total filler volume fractions. The change from AlN_p (B) to AlN_p (M) increased the thermal conductivity, as shown for the case of AlN_w:AlN_p in the 1:1 ratio and a total filler volume fraction of 50%. This is consistent with the higher thermal conductivity of AlN_p (M) compared to AlN_p (B), as shown in Table 3. With AlN_w:AlN_p (M) in the 1:3 ratio (apparent) or 1:25.7 ratio (true) and at a total filler volume fraction of 60%, the thermal conductivity was 11.51 W/(m K), the highest value among all the composites of this work. The CTE decreased with increasing total filler volume fraction, but varied only slightly with the AlN_w:AlN_p ratio. Table 6 gives similar results for composites with AlN_w (I) and AlN_p (A) in various volume ratios. At a fixed total filler volume fraction of 50%, the thermal conductivity was highest and the dielectric constant was lowest for an intermediate AlN_w:AlN_p ratio of 1:3 (apparent) or 1:6.3 (true). Although Tables 5 and 6 differ in both AlN_w type and

AlN_p type, the true AlN_w:AlN_p volume ratio that gave the highest thermal conductivity at a total filler volume fraction of 50% was quite close in both tables. Both Tables 5 and 6 show that the CTE decreased slightly with decreasing AlN_w:AlN_p ratio, probably because of the relatively large particles in AlN_w.

Table 7 gives the thermal conductivity and CTE of PVDF-matrix composites with SiC_w and AlN_p (F) in various volume ratios and for two different total filler volume fractions. Due to the 15% particulate content in the SiC_w lot, SiC particles (SiC_p) were present along with SiC_w. Thus, two types of particles were involved in Table 7, namely SiC_p and AlN_p. At either total filler volume fraction, the thermal conductivity was highest for an intermediate SiC_w:SiC_p:AlN_p ratio of 1:0:6 (apparent) or 0.85:0.15:6 (true) and the thermal conductivity was higher when AlN_p was the sole filler than when SiC_w was the sole filler. This means that AlN_p was more effective than SiC_w in enhancing the thermal conductivity, though the presence of a small proportion of SiC_w helped through improving the connectivity among the filler units. The CTE depended on the total filler volume fraction much more than the SiC_w:SiC_p:AlN_p ratio. At a given total filler volume fraction, the CTE was lowest at an intermediate SiC_w:SiC_p:AlN_p ratio of 3:0:1 (apparent) or 2.55:0.45:1 (true) for 50 vol.% total filler and 1:0:3 (apparent)

Table 7
Thermal conductivity and CTE of PVDF-matrix composites with SiC_w and AlN_p (F) in various volume ratios

Total filler vol.%	SiC_w:SiC_p:AlN_p volume ratio		Thermal conductivity (W/(m K))	CTE ($°C^{-1}$)
	Apparent	True		
50	1:0:0	0.85:0.15:0	1.68	$6.09×10^{-5}$
50	6:0:1	5.1:0.9:1	1.58	$5.96×10^{-5}$
50	3:0:1	2.55:0.45:1	1.45	$5.47×10^{-5}$
50	1:0:1	0.85:0.15:1	1.72	$6.06×10^{-5}$
50	1:0:3	0.85:0.15:3	2.00	$5.62×10^{-5}$
50	1:0:6	0.85:0.15:6	2.06	$5.89×10^{-5}$
50	0:0:1	0:0:1	1.84	$5.89×10^{-5}$
60	1:0:0	0.85:0.15:0	2.04	$3.85×10^{-5}$
60	6:0:1	5.1:0.9:1	1.85	$3.89×10^{-5}$
60	3:0:1	2.55:0.45:1	2.23	$3.12×10^{-5}$
60	1:0:1	0.85:0.15:1	2.14	$3.23×10^{-5}$
60	1:0:3	0.85:0.15:3	2.83	$2.87×10^{-5}$
60	1:0:6	0.85:0.15:6	2.92	$3.30×10^{-5}$
60	0:0:1	0:0:1	2.66	$3.53×10^{-5}$

Table 8
CTE of PVDF-matrix composites with AlN_p (F) at various volume fractions

Filler vol.%	CTE (°C^{-1})
0	1.37×10^{-4}
50	5.99×10^{-5}
55	4.62×10^{-5}
60	3.53×10^{-5}
65	1.81×10^{-5}
70	1.53×10^{-5}
73	1.29×10^{-5}

Table 9
Measured and calculated dielectric constant (2 MHz) of polymer-matrix composites with 60 vol.% AlN

Matrix	Calculated		Measured
	Series[a]	Parallel[b]	
PVDF	7.60	7.74	8.25–9.87
Epoxy	6.16	6.84	8.01

[a] Model based on capacitors in series.
[b] Model based on capacitors in parallel.

or 0.85:0.15:3 (true) for 60 vol.% total filler. This is reasonable, since connectivity among the filler units is important for a high thermal conductivity, but not important for a low CTE.

Table 8 gives the CTE of PVDF-matrix composites with AlN_p (F) as the sole filler at different volume fractions. The CTE greatly decreased when the AlN volume fraction increased from 0 to 55%. The CTE monotonically decreased with increasing AlN_p volume fraction up to 73%. At 65 vol.% AlN_p, the CTE was lower than any of the values (Table 7) obtained at 60 vol.% total filler ($SiC_w + AlN_p$).

The porosity (as calculated from the measured density) of PVDF-matrix composites did not vary much with the types of AlN_w and AlN_p or with the volume ratio of AlN_w to AlN_p, but it increased with increasing total filler volume fraction. It is 0.4–0.7 and 1.0–1.4 vol.% at total filler volume fractions of 50 and 60%, respectively.

The dielectric constant of composites was calculated using the model based on capacitors in series and the model based on capacitors in parallel. In the series model, the dielectric constant of a composite with a volume fraction of AlN being V_i is given by

$$\varepsilon = \frac{\varepsilon_1 \varepsilon_2}{V_i + \varepsilon_2(1 - V_i)} \tag{1}$$

where ε_1 is the dielectric constant of matrix (6.60 and 4.36 for PVDF and epoxy, respectively, as measured at 2 MHz) and ε_2 the dielectric constant of AlN (8.5, as estimated).

In the parallel model,

$$\varepsilon = (1 - V_i)\varepsilon_1 + V_i\varepsilon_2 \tag{2}$$

As shown in Table 9 for the case of $V_i = 0.6$, the measured dielectric constant was higher than the values calculated by

both models and the parallel model gave calculated values that were closer to the measured values than the series model. Similar behavior was present at $V_i = 0.55$ and 0.50, though not shown in Table 9. The large values of the measured dielectric constant, the calculated ones, are probably due to the contribution of the interface between AlN and matrix to the dielectric constant.

Table 10 shows that AlN addition decreased the tensile strength and ductility, but increased the tensile modulus. Water immersion for 7 days decreased the tensile strength and ductility slightly for the PVDF matrix, but decreased the tensile strength and ductility greatly for the PVDF-matrix composite. Heating in air at 140°C for 7 days had negligible effects on the tensile properties of neat PVDF, but increased the tensile ductility of the PVDF-matrix composite. Hence, heating did not degrade the composite, but water immersion did. The degradation by water immersion is attributed to the reactivity of AlN with water, as PVDF did not degrade after water immersion.

Table 11 gives the fractional loss in weight of silane-treated AlN upon heating to 600°C. The volatile/decomposable materials on the silane Z-6040 and silane Z-6020 treated particles were higher than that of the as-received AlN particles, indicating that treatments involving silane resulted in a coating on the particles. The fractional loss in weight of silane-treated AlN particles did not change much with the concentration of silane in the treatment solution. This is due to the relatively smooth AlN particle surface and the limited amount of active sites on the AlN surface.

Table 12 shows the ESCA results of AlN particles with and without treatment. The as-received particle surface has

Table 10
Tensile properties of PVDF and PVDF-matrix composite containing 60 vol.% AlN (AlN_w (II) and AlN_p (M) in the ratio 1:3 (apparent) or 1:25.7 (true))

Material	Condition	Strength (MPa)	Modulus (GPa)	Ductility (%)
PVDF	As-fabricated	52.0±1.7	2.22±0.10	5.00±0.20
PVDF	After water immersion for 7 days	50.5±0.9	2.16±0.12	4.20±0.23
PVDF	After heating in air at 140°C for 7 days	51.5±1.3	2.01±0.15	4.80±0.15
PVDF/AlN	As-fabricated	30.0±1.3	15.51±0.75	0.165±0.026
PVDF/AlN	After water immersion for 7 days	13.1±1.2	–	0.096±0.014
PVDF/AlN	After heating in air at 140°C for 7 days	32.0±1.5	14.30±0.55	0.250±0.030

Table 11
Fractional loss in weight of AlN particles upon heating to 600°C

As-received	0.11%
Silane Z-6040 treated	0.35%
Silane Z-6020 treated	0.80%

Table 12
Surface elemental composition (at.%) of AlN

Element	As-received	Silane Z-6040 treated	Silane Z-6020 treated
Al	33.9	28.4	25
N	15.5	12.2	15.8
C	26.8	22.4	30.2
O	23.8	35.5	23.7
Si	–	1.5	5.3

Table 13
Charge corrected binding energies (eV) and possible assignment for silane Z-6020 treated AlN

Energy level	Binding energy (eV)	Assignment
C_{1s}	285.0	$(CH_2)_n$
Si_{2p}	102.1	Organic silicone
Al_{2s}	120.2	AlN
Al_{2p}	74.1	AlN, Al_2O_3
O_{1s}	531.7	Si–O
N_{1s}	397.0	AlN

oxygen, probably in the form of aluminum oxynitride. Compared with the as-received AlN particles, the Z-6040 treated particle surface has more silicon atoms, fewer nitrogen atoms, fewer aluminum atoms and more oxygen atoms. This is consistent with the fact that the surface is partly covered by the silane coating and that Z-6040 contains Si and O atoms. Compared with the as-received AlN particles, the Z-6020 treated particle surface has more silicon atoms, fewer aluminum atoms and slightly more nitrogen atoms. This is consistent with the fact that the surface is partly

covered by the silane coating and that Z-6020 contains Si, N and O atoms. Compared with silane Z-6040 treated AlN particles, the silane Z-6020 treated AlN particle surface has less aluminum atoms, more carbon atoms and more silicon atoms results from that silane Z-6020 treated AlN particle surface has been coated by more silane (which contains Si and C), as shown by the thermogravimetric analysis (Table 11). That the silane Z-6020 treated AlN particle surface contains more nitrogen atoms and less oxygen atoms than the silane Z-6040 treated AlN particle surface is due to each silane Z-6020 molecule containing two nitrogen atoms and each silane Z-6040 molecule containing no nitrogen atom but more oxygen atoms. Table 13 shows the charge corrected binding energies of silane Z-6020 treated AlN particles, confirming the existence of silane groups on the particle surface. Tables 11–13 indicate that AlN particles have been coated by silane molecules after either silane treatment.

The thermal diffusivity, specific heat and thermal conductivity are shown in Table 14 for composites with different volume fractions of AlN (M) particles (with and without treatment). The thermal conductivity increased with increasing filler volume fraction and the specific heat decreased with increasing filler volume fraction for each type of filler particles, due to the high thermal conductivity and low specific heat of the filler compared with those of the polymer.

At a fixed AlN volume fraction, the thermal conductivity was increased by either silane treatment. Table 15 shows that the fractional increase in thermal conductivity due to surface treatment is high for all three AlN volume fractions, especially for 40 vol.% AlN. At the same AlN volume fraction, silane Z-6020 treatment was more effective than silane Z-6040 treatment for enhancing the thermal conductivity.

Figs. 2–3 show plots of the dielectric constant vs. frequency from 100 Hz to 2 MHz for selected AlN polymer-matrix composites. The dielectric constant decreased with increasing frequency for all composites, as expected. Fig. 2 is for the PVDF-matrix composite with AlN_w (II) and AlN_p

Table 14
Thermal conductivity, specific heat and thermal diffusivity of AlN epoxy-matrix composites. The standard deviations are shown in parentheses

AlN filler (vol.%)	Thermal diffusivity (mm²/s)	Specific heat (J/(g K))	Density (g/cm³)	Thermal conductivity (W/(m K))
As-received				
40	0.68 (0.022)	0.940 (0.020)	2.03	1.30 (0.108)
50	1.74 (0.045)	0.921 (0.021)	2.20	3.52 (0.316)
60	3.31 (0.05)	0.875 (0.027)	2.41	6.99 (0.668)
Silane Z-6040 treated				
40	1.13 (0.05)	0.941 (0.02)	2.03	2.16 (0.23)
50	2.19 (0.065)	0.923 (0.025)	2.20	4.45 (0.43)
60	3.58 (0.072)	0.894 (0.02)	2.41	7.71 (0.067)
Silane Z-6020 treated				
40	1.34 (0.046)	0.942 (0.022)	2.03	2.56 (0.26)
50	2.60 (0.052)	0.925 (0.03)	2.20	5.29 (0.47)
60	5.18 (0.067)	0.88 (0.03)	2.41	10.98 (0.97)

Table 15
Percentage increase in thermal conductivity of AlN epoxy-matrix composites due to AlN surface treatment

	Percentage increase in thermal conductivity due to silane surface treatment		
	40 vol.% AlN	50 vol.% AlN	60 vol.% AlN
Z-6040 treated	66.5	26.4	10.3
Z-6020 treated	96.9	50.3	57.1

(M) in the ratio 1:3 (apparent) or 1:25.7 (true) and at a total filler volume fraction of 60%. As shown in Table 5, this composite is the one with the highest thermal conductivity among all composites of this work. Fig. 3 is for the epoxy-matrix composite with 60 vol.% AlN_p (M); this composite is the one with the highest thermal conductivity among all epoxy-matrix composites of this work.

The thermal conductivity of the composites was estimated by using the models of Cheng and Vachon [11], Lewis and Nielson [12] and Russell [13], with the thermal conductivity of the polymer matrix at 0.2 W/(m K). The calculated values for AlN composites are all much lower than the measured values. The ineffectiveness of these models is due to the relatively large particle size and non-equiaxed shape of the particles.

4. Conclusions

1. The thermal conductivity increases with increasing filler volume fraction regardless of the filler type among the various types of AlN_p at a fixed volume fraction, the type with the greatest mean particle size (115 μm) gives composites with the highest thermal conductivity. However, the porosity of the composites increases with increasing AlN_p particle size.

2. The combination of AlN_w (II) and AlN_p (M) as fillers in an appropriate ratio gives the highest thermal conductivity. By using the AlN_w (II) and AlN_p (M) in the ratio 1:3 (apparent) or 1:25.7 (true) at a total filler volume fraction of 60%, a PVDF-matrix composite with a highest thermal conductivity of 11.5 W/(m K) and a dielectric constant (2 MHz) of 9.86 was obtained. Changing the whisker–particle ratio to 1:6 (apparent) or 1:45.7 (true) decreases the thermal conductivity to 10.4 W/(m K), while not affecting the dielectric constant. Decreasing the total AlN filler volume fraction from 60 to 50% decreases the thermal conductivity significantly and decreases the dielectric constant slightly.

3. The addition of fillers (either AlN or SiC) to the polymer increases the dielectric constant and the change of the filler from AlN to SiC_w greatly increases the dielectric constant.

4. The CTE of PVDF-matrix composites decreases with increasing filler volume fraction, whether the filler is AlN_p or SiC_w. The use of SiC_w and AlN_p at a volume ratio 1:3 and a total filler volume fraction of 60% gives composites of slightly lower CTE than the use of AlN_p alone or SiC_w alone.

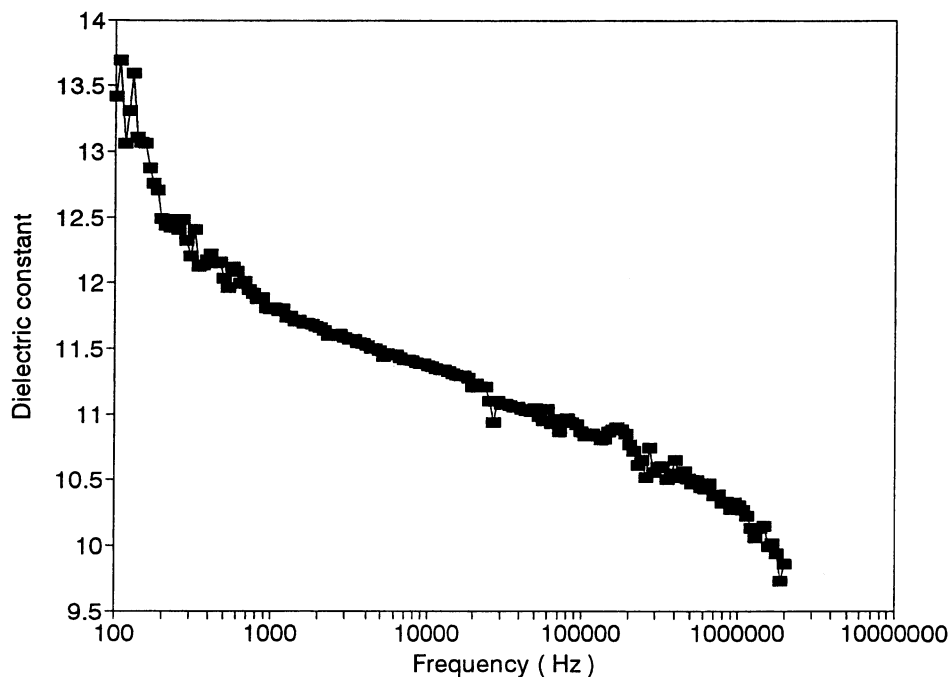5. For AlN_w and AlN_p at a total filler volume fraction

Fig. 2. Variation of the dielectric constant with frequency for a PVDF-matrix composite with AlN_w (II) and AlN_p (M) in the 1:3 (apparent) or 1:25.7 (true) ratio and a total filler volume fraction of 60%.
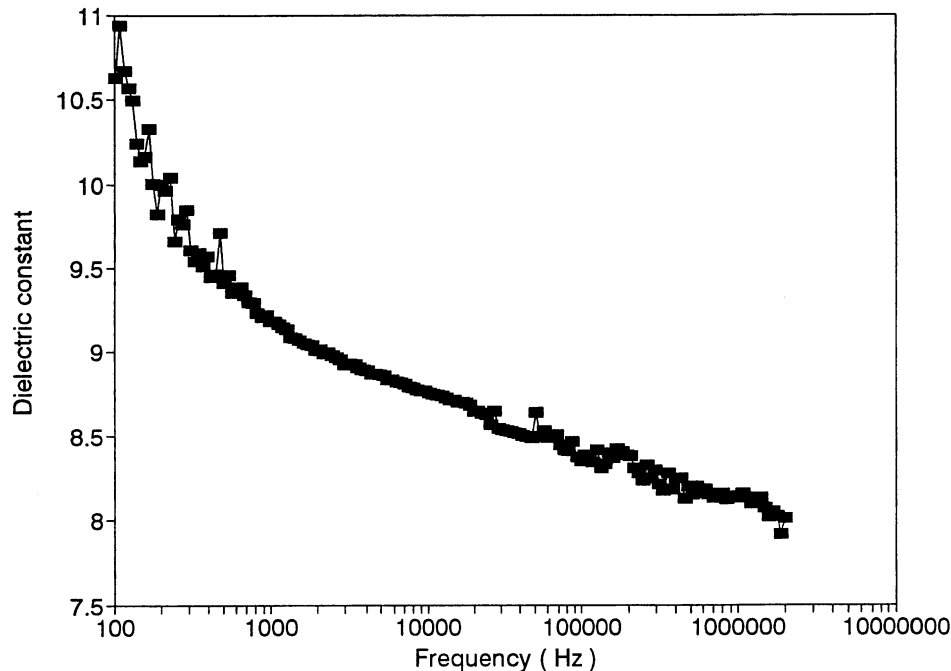
Fig. 3. Variation of the dielectric constant with frequency for an epoxy-matrix composite with 60 vol.% AlN_p (M).

of 50%, a whisker–particle volume ratio (true) ranging from 1:6.3 to 1:7.9 gives PVDF-matrix composites with the highest thermal conductivity.

6. The use of SiC_w and AlN_p at a volume ratio of 1:6 gives PVDF-matrix composites of higher thermal conductivity than the use of AlN_p alone or SiC_w alone. However, the thermal conductivity is lower than that obtained by the use of AlN_w and AlN_p.

7. With the same AlN filler type and volume fraction, PVDF gives a composite with a significantly higher dielectric constant than epoxy composites, due to the inherently higher dielectric constant of PVDF.

8. The tensile strength, modulus and ductility are decreased by AlN addition to a polymer. The AlN PVDF-matrix composite does not degrade after heating at 140°C, but degrades after water immersion.

9. Surface treatment of AlN particles is useful for increasing the thermal conductivity of AlN particle epoxy-matrix composite by up to 97%. Both silane Z-6020 and Z-6040 treatments are effective for AlN epoxy-matrix composites, but silane Z-6020 treatment is more effective than silane Z-6040 treatment for AlN particles in enhancing the thermal conductivity. At 60 vol.% AlN treated by Z-6020, the thermal conductivity is 11.0 W/(m K).

10. The effectiveness in enhancing thermal conductivity by surface treatment is due to the decrease in the thermal contact resistance at the filler–matrix interface.

Acknowledgements

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