



Thermal expansion adjustable polymer matrix composites with giant negative thermal expansion filler



Koshi Takenaka^{a,b,*}, Masayoshi Ichigo^b

^a Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

^b Department of Crystalline Materials Science, Nagoya University, Nagoya 464-8603, Japan

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ABSTRACT

Polymer matrix composites filled with giant negative thermal expansion (NTE) materials were formed by injection moulding. Antiperovskite manganese nitrides, thermal expansion compensating filler of the composites, exhibit NTE greater than -30 ppm K^{-1} in α (coefficient of linear thermal expansion). This gigantic NTE, several to ten times as large as that of conventional NTE materials, can compensate large thermal expansion of polyamide-imide polymer and thermal expansion of the composites is adjustable in a wide range of α value from positive to even negative. Quantitative analyses reveal that thermal expansion of the composites is less than the estimate based on the volume-weighted sum, which is ascribed to much larger elastic modulus of the nitride filler.

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1. Introduction

Synthetic resin, or polymer, is one of the most familiar materials because of its beneficial features of light weight and high workability, but their large thermal expansion emerges as a shortcoming for which reduction is desired in highly advanced industries. For polymers, the coefficient of linear thermal expansion (CTE) α is at least $30\text{--}40 \text{ ppm K}^{-1}$ or at largest over 100 ppm K^{-1} , which is much larger than those of metals and ceramics in the range of several to 20 ppm K^{-1} . Large thermal expansion of polymers is at present one of the most primary factors suppressing their utility value.

For control of thermal expansion in polymers, polymer matrix composites (PMCs) filled with low-expansion inorganic materials have been designed to date. However, silica (SiO_2) filler, one of the most widely used, has, although low, still positive thermal expansion ($\alpha \sim 0.5 \text{ ppm K}^{-1}$) and hence cannot cancel large positive thermal expansion of polymers. For more active suppression of thermal expansion, we need materials that contract on heating, or *negative* thermal expansion (NTE) materials [1–4]. Beta-eucryptite (LiAlSiO_4) is one of the few practical materials for this purpose, but its NTE is highly anisotropic and the magnitude of the aggregate NTE is at largest -5 ppm K^{-1} , which is not enough for general purposes [1].

Relatively large ($\alpha \sim -9 \text{ ppm K}^{-1}$) and isotropic NTE of ZrW_2O_8 [2] enables us to control thermal expansion to a certain degree. Nevertheless, an extensive practical application is still not realized because of the demerits such as high cost, low stiffness, and existence of a pressure-induced less-negative thermal expansion phase ($\gamma\text{-ZrW}_2\text{O}_8$) [5].

In the field of NTE research, remarkable development has been achieved over the last decade. In particular, after the discovery of gigantic NTE in antiperovskite manganese nitrides Mn_3AN (A: metal or semiconducting element) [6], many giant NTE materials such as $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ [7], $\text{Bi}_{1-x}\text{Ln}_x\text{NiO}_3$ (Ln: lanthanoid) [8,9], and $\text{La}(\text{Fe}, \text{Si}, \text{Co})_{13}$ [10] were discovered successively. The NTE of the antiperovskite manganese nitrides is greater than -30 ppm K^{-1} in α , which can compensate large thermal expansion of polymers and opens a new phase of composite science and technology [11]. Ding et al. [12] and Takenaka et al. [13] reported their attempts to form metal matrix composites (MMCs) containing the antiperovskite and proved that thermal expansion of metals are extremely reduced, even to negative. Huang et al. [14] also reported a pioneer study for reducing thermal expansion of polymers by the antiperovskites. In their study, thermal expansion of epoxy resin was reduced 42% by 32 vol.-%- $\text{Mn}_3\text{Cu}_0.6\text{Si}_{0.15}\text{Ge}_{0.25}\text{N}$ filler loading. Here, we report our attempts to form PMCs filled with antiperovskites by means of injection moulding, which is a conventional manufacturing technique enabling a wide range of industrial applications.

* Corresponding author at: Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan.

E-mail address: takenaka@nuap.nagoya-u.ac.jp (K. Takenaka).

2. Experimental

Thermal-expansion compensators, antiperovskite manganese nitrides Mn_3AN , were prepared by solid-state reactions using powders of Mn_2N and pure element A (A: Zn, Sn, purity: 99.9%, particle size: 30–50 μm) as starting materials [13,15,16]. The obtained nitrides were pulverized in an agate mortar down to 30–60 μm diameter. For thermal-expansion measurements, the obtained nitride powder was sintered using a spark plasma sintering (SPS) furnace (Syntex Lab; SPS Syntex Inc.). Linear thermal expansion $\Delta L(T)/L$ was measured at temperature $T=100\text{--}500\text{ K}$ using a laser-interference dilatometer (LIX-2; Ulvac). For this class of manganese nitrides, $\Delta L(T)/L$ determined by a dilatometry coincides with the lattice parameters obtained by the neutron diffraction study [17]. The crystal structure was investigated using X-ray powder diffraction (XRD, RINT2000; Rigaku). Specific gravity, or density, was determined by an Archimedes method. The polymer matrix composites were formed by injection moulding (MINI-7; Niigata). Powders of the manganese nitride (particle size: 30–60 μm) and polyamide-imide (AI-polymer; Mitsubishi Gas Chemical) were mixed and extruded into pellets at 280–320 $^\circ\text{C}$. The obtained pellets were moulded by injection under the following condition: cylinder temperature: 300–320 $^\circ\text{C}$, mould temperature: 130–150 $^\circ\text{C}$, extrusion pressure: 80–120 MPa. These parameters were determined with reference to a conventional extrusion condition of polyamide-imide.

3. Results

Fig. 1 displays $\Delta L(T)/L$ for typical NTE manganese nitrides including the thermal-expansion compensators of the present study. The giant NTE of the manganese nitrides was achieved by doping Ge or Sn into A site of Mn_3AN (for example, Mn_3ZnN) as “relaxant” of the sharp volume contraction on heating due to the first-order magnetic transition [18–20]. Therefore, the operating-temperature window ΔT of NTE is limited to a certain T range below the magnetic transition temperature and there is a trade-off between width of the operating-temperature window and magnitude of the negative α . However, we can achieve huge NTE if even a narrow operating-temperature window satisfies purposes. In the case of typical NTE compounds $\text{Mn}_{3+x}\text{Zn}_y\text{Sn}_{1-x-y}\text{N}$, NTE of $\alpha = -25\text{ ppm K}^{-1}$ at $T = 280\text{--}365\text{ K}$ ($\Delta T = 85\text{ K}$) is possible in principle [16]. The thermal-expansion compensators of the present study had larger magnitude of negative α , though the operating-temperature windows were narrower: $\text{Mn}_{3.25}\text{Zn}_{0.5}\text{Sn}_{0.25}\text{N}$ shows

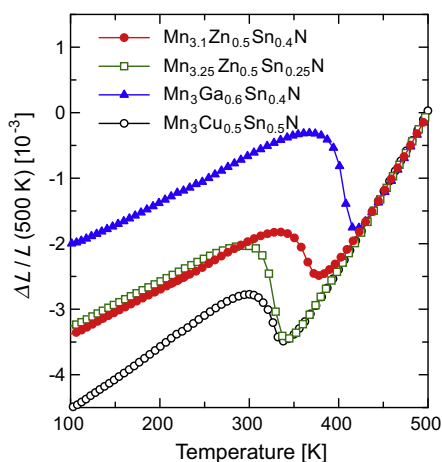


Fig. 1. Linear thermal expansion of typical antiperovskite manganese nitrides showing negative thermal expansion.

NTE of $\alpha = -45\text{ ppm K}^{-1}$ at $T = 305\text{--}340\text{ K}$ ($\Delta T = 35\text{ K}$) and $\text{Mn}_{3.1}\text{Zn}_{0.5}\text{Sn}_{0.4}\text{N}$ shows NTE of $\alpha = -29\text{ ppm K}^{-1}$ at $T = 335\text{--}375\text{ K}$ ($\Delta T = 40\text{ K}$). These thermal-expansion compensators meet the demand for devices in which the evolution of heat is a problem, including an optical or electronic apparatus.

The matrix of the present composites containing the NTE manganese nitrides is polyamide-imide, which has excellent mechanical properties and relatively low thermal expansion ($\alpha \sim 40\text{ ppm K}^{-1}$ at room temperature) among polymer materials. The present composite can be formed by injection moulding, conventional processing of polymers. This is the advantage of the present composites over existing low thermal expansion PMCs in which thermal expansion along only a certain direction is reduced by orientation of the filler and/or the polymers. Instead, the present composites enable us to achieve isotropic and three-dimensional control of thermal expansion by existing facilities for injection moulding.

Fig. 2 displays $\Delta L(T)/L$ of 75 wt.-%- $\text{Mn}_{3.25}\text{Zn}_{0.5}\text{Sn}_{0.25}\text{N}$ /polyamide-imide composite. Because specific gravities of the matrix and the filler are respectively 1.4 and 6.9, the volume fractions of the matrix and the filler are respectively 62 vol.-% and 38 vol.-% and the specific gravity of the composite is 3.5. The huge NTE of $\text{Mn}_{3.25}\text{Zn}_{0.5}\text{Sn}_{0.25}\text{N}$ strongly reduced the thermal expansion of polyamide-imide, resulting in NTE ($\alpha = -3\text{ ppm K}^{-1}$ at $T = 315\text{--}327\text{ K}$) for the composite. Displacement in $\Delta L(T)/L$ is less than 160 ppm at $T = 303\text{--}333\text{ K}$, equivalent to the averaged CTE of 5.3 ppm K^{-1} . Huang et al. also reported that the $\text{Mn}_3\text{Cu}_{0.6}\text{Si}_{0.15}\text{Ge}_{0.25}\text{N}$ filler highly reduced CTE of epoxy resin, but the $\Delta L(T)/L$ of their composites showed rather monotonous T dependence and the remarkable reduction – the negative slope – like the present composites was not confirmed at the T region where the nitride filler exhibited NTE behaviour [14].

Although large difference in the specific gravity between the matrix and the filler might cause uneven distribution of the components, the microscope observation denies it. Fig. 3 is a microscopic image of 38 vol.-%- $\text{Mn}_{3.25}\text{Zn}_{0.5}\text{Sn}_{0.25}\text{N}$ /polyamide-imide composite. Matte-gray and glossy-gray regions represent respectively the matrix and the filler. Indeed, we confirmed that the $\Delta L(T)/L$ data obtained on different specimens were identical to each other and they were reproducible after several times repeated thermal cycling. We also confirm that the diameter of the nitride filler is about several 10 μm . This observation also shows that there are not remarkable voids at the interface between the matrix and the filler.

4. Discussion

The obtained thermal expansion of the composites was analysed using models in which particles of an isotropic thermal-expansion-compensating filler are uniformly dispersed in an iso-

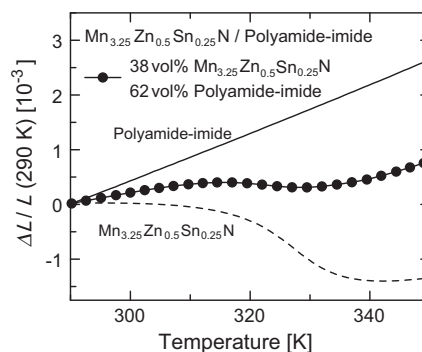


Fig. 2. Linear thermal expansion of 38 vol.-%- $\text{Mn}_{3.25}\text{Zn}_{0.5}\text{Sn}_{0.25}\text{N}$ /polyamide-imide composite formed by injection moulding.

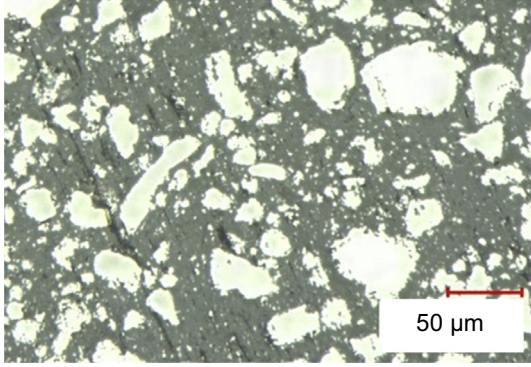


Fig. 3. Microscopic image of 38 vol.-%-Mn_{3.25}Zn_{0.5}Sn_{0.25}N/polyamide-imide composite formed by injection moulding.

tropic matrix [11,21]. Here, E , ν , K and G , respectively, represent Young's modulus, Poisson ratio, bulk modulus, and shear modulus. Subscripts c, m and f, respectively, represent the composite, matrix, and filler. For an isotropic elastic material, the independent constants are reduced to two: $K = E/[3(1 - 2\nu)]$ and $G = E/[2(1 + \nu)]$. Poisson ratio ν is weakly dependent on the materials and in most cases can be treated as a constant in the range of 0.3–0.4 in the case of metals and polymers. Therefore, we can estimate K and G from E , which is often easier to measure. We summarize the parameters (Table 1) and results (Table 2) for thermal-expansion analyses of the present composites. Here, ν was assumed to be 0.3 for the matrix as well as the filler.

A bound of α_c is given, assuming that thermally induced stress is uniform everywhere in a composite. This is equivalent to the assumption that the matrix and the thermal-expansion compensator exhibit their own thermal expansion independently. Consequently, the thermal expansion of a composite is given by the volume-weighted sum of the contributions from the matrix and the dispersed filler.

$$\alpha_c = v_m \alpha_m + v_f \alpha_f. \quad (1)$$

Here, v_m and v_f are the volume fractions of the matrix and the filler, respectively, and $v_m + v_f = 1$, which is called the rule of mixture (ROM).

Another bound is given by the approximation that thermally induced strain is uniform everywhere in a composite, as first proposed by Turner:

$$\alpha_c = \frac{v_m E_m \alpha_m + v_f E_f \alpha_f}{v_m E_m + v_f E_f}. \quad (2)$$

In Eq. (2), the element with the larger elastic modulus contributes more to the thermal expansion of the composite. In the case of $\alpha_m > \alpha_f$ and $E_m < E_f$, Eq. (1) gives the upper bound and Eq. (2) gives the lower bound for α_c .

Schapery derived a more realistic estimation, in which inner stress arising from differences between α_m and α_f in a composite is determined under the condition of minimum free energy:

$$\alpha_c = v_m \alpha_m + v_f \alpha_f - \frac{\frac{v_m}{K_m} + \frac{v_f}{K_f} - \frac{1}{K_c}}{\frac{1}{K_m} - \frac{1}{K_f}} (\alpha_m - \alpha_f). \quad (3)$$

When deriving this equation, it was assumed that $K_m < K_f$ and $G_m < G_f$. In this scheme α_c is determined by the bulk modulus of the composite K_c . Adopting Hashin and Shtrikman's estimation of K_c , Eq. (3) gives the upper and lower bounds of Schapery's α_c , corresponding to K_{c1} and K_{c2} , respectively. In this case, Schapery's upper limit corresponds to Kerner's estimation.

$$K_{c1} = K_m + \frac{v_f}{\frac{1}{K_f - K_m} + \frac{v_m}{K_m + 4G_m/3}} \quad (4a)$$

$$K_{c2} = K_f + \frac{v_m}{\frac{1}{K_m - K_f} + \frac{v_f}{K_f + 4G_f/3}} \quad (4b)$$

Within the present case, the values of α_c estimated with different models decrease in the following order: ROM, Schapery's upper limit (Kerner's estimation), Schapery's lower limit, and Turner's estimation. In the following, thermal expansion of the composites is evaluated also based on $\Delta L(T)/L$ (integral of α) in addition to α , because α of these composites drastically changes around the operating temperature of NTE.

Fig. 4 displays a plot of the $\Delta L(T)/L$ experimental values as well as curves calculated assuming ROM, Schapery upper limit, Schapery lower limit, and Turner's moles for 38 vol.-%-Mn_{3.25}Zn_{0.5}Sn_{0.25}-N/polyamide-imide composite. It is noteworthy that the obtained $\Delta L(T)/L$ is in between the ROM and the Schapery upper limit; in the operating-temperature window, it is close to the Schapery upper limit. This reflects much larger E of the nitride filler (200 GPa) than the matrix (5 GPa). This is in contrast to the MMCs filled with the NTE nitrides [13], in which $\Delta L(T)/L$ is reduced to ROM at most. The suppressed performance of the NTE manganese nitrides in the MMCs may be ascribed to relatively larger Young's modulus of the metal matrices ($E \sim 100$ GPa) than the polymer matrix. It also suggests better interfaces between the matrix and the filler in the PMCs. For MMCs, residual voids at the interfaces may degrade the performance of the NTE nitrides [13].

Then, we investigated $\Delta L(T)/L$ of the composites filled with Mn_{3.1}Zn_{0.5}Sn_{0.4}N, which has the higher and wider operating-temperature window of NTE. Fig. 5 displays a plot of the $\Delta L(T)/L$ experimental values as well as curves calculated assuming the above four models for (a) 23 vol.-% and (b) 45 vol.-%-Mn_{3.1}Zn_{0.5}Sn_{0.4}N/polyamide-imide composite. The obtained $\Delta L(T)/L$ is suppressed below the ROM estimation for both composites; α at $T = 355$ – 370 K is 16 ppm K^{-1} , close to the Schapery upper limit for the 23 vol.-%-composite, and -6 ppm K^{-1} , lower than the Schapery upper limit for the 45 vol.-%-composite.

Thermal expansion of a composite is determined by elastic interactions between a matrix and a filler via the interfaces. In the scheme of the Turner's model, thermal expansion of the composite reflects more strongly thermal expansion of the component with higher stiffness, manganese nitrides in the present case. However, if the amount of the manganese nitrides is extremely small, the condition of *uniform strain* assumed in the Turner's model becomes unreasonable and hence thermal expansion of the composite deviates from Eq. (2) to (1). In short, thermal expansion of the matrix far from the interface cannot be suppressed by small amount of the nitride filler. This trend is supported by the present results (Fig. 6). We evaluated performance of the thermal-expansion compensator by the parameter a , defined as the following equation:

Table 1

Parameters for thermal-expansion analysis. The densities d were determined by an Archimedes method. The Young's moduli E were determined from the reported values. The Poisson ratios ν were assumed to be 0.3. The bulk moduli K and the shear moduli G were estimated using the above E and ν .

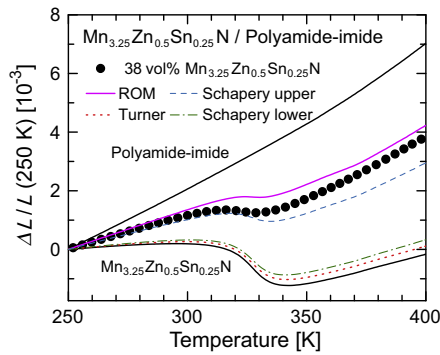
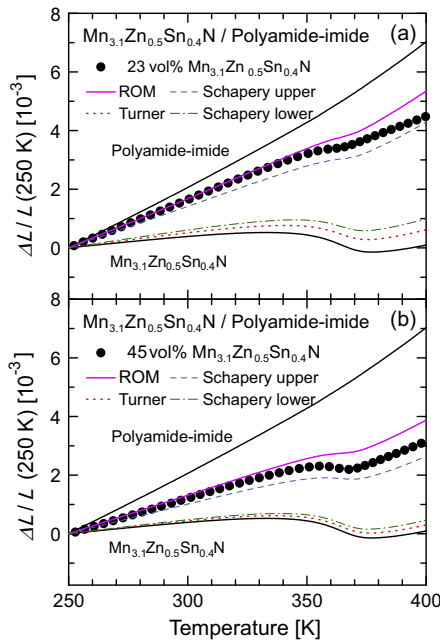
Material	Density d (g/cm ³)	Young's modulus E (GPa)	Poisson ratio ν	Bulk modulus K (GPa)	Shear modulus G (GPa)
Polyamide-imide (matrix)	1.4	5 ^a	0.3	4.2	3.6
Mn–Zn–Sn–N (filler)	6.9	200 ^b	0.3	166.7	142.9

^a Refs. [22,23].

^b Ref. [24].

Table 2Analysis of CTE (α ; ppm K⁻¹) in the operating-temperature window.

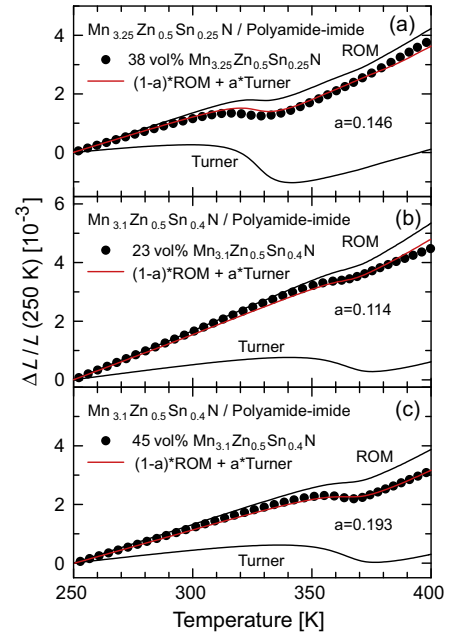
Composite	Schapery						
	Measured	Matrix	ROM	Upper	Lower	Turner	Filler
38 vol.-%-Mn _{3.25} Zn _{0.5} Sn _{0.25} N	-3	44	11	-6	-39	-41	-45
23 vol.-%-Mn _{3.1} Zn _{0.5} Sn _{0.4} N	16	51	26	15	-20	-23	-29
45 vol.-%-Mn _{3.1} Zn _{0.5} Sn _{0.4} N	-6	51	10	-3	-25	-27	-29

**Fig. 4.** Experimental plots of linear thermal expansion as well as curves calculated by ROM, Schapery upper limit, Schapery lower limit, and Turner's model for 38 vol.-%-Mn_{3.25}Zn_{0.5}Sn_{0.25}N/polyamide-imide composite formed by injection moulding.**Fig. 5.** Experimental plots of linear thermal expansion as well as curves calculated by ROM, Schapery upper limit, Schapery lower limit, and Turner's model for (a) 23 vol.-%- and (b) 45 vol.-%-Mn_{3.1}Zn_{0.5}Sn_{0.4}N/polyamide-imide composite formed by injection moulding.

$$\Delta L/L_c = (1 - a) \times \Delta L/L_{[ROM]} + a \times \Delta L/L_{[Turner]}. \quad (5)$$

The parameter a obtained by the fitting analyses using Eq. (5) decreases with decreasing filler loading ($a = 0.193$, 0.146 , and 0.114 for 45 vol.-%, 38 vol.-%, and 23 vol.-%-composites, respectively).

In the scheme of the above models, perfect interfaces are assumed. For more detailed arguments about the performance of the thermal-expansion compensators, information on interfaces

**Fig. 6.** Fitting analysis of linear thermal expansion of the Mn-Zn-Sn-N manganese nitrides/polyamide-imide composites.

and residual voids is necessary, but unfortunately they are yet to be explored. For example, Duan and Karihaloo discussed that the averaged CTE in the presence of imperfect interfaces is strongly dependent on the size of the filler [25]. The filler-size dependence of the CTE is one of the most important future issues for the present composites.

The giant NTE over $\alpha = -30$ ppm K⁻¹ of the manganese nitride expands our capability of thermal-expansion control and achieves widely various α , even negative values, in PMCs. Fine tuning of α in the negative region is possible because the negative α is realized using lower filler loading than that of other NTE materials. The filler loading quantity necessary for negative α was less than 40 vol.% in the present PMC. In many cases, it is difficult for other NTE materials to achieve negative α in a PMC. For example, there are many attempts to fabricate PMCs using ZrW₂O₈, one of the conventional NTE materials with relatively large negative α (~ -9 ppm K⁻¹) [26]. Thermal expansion of polyimide [27], phenolic resin [28], and epoxy resin [29], which have almost the same α (~ 40 ppm K⁻¹) as polyamide-imide, is reduced less than the ROM estimation by forming composites with ZrW₂O₈. However, α became 10 ppm K⁻¹ at last for the 50 vol.% filler loading.

A possible demerit of manganese nitride filler is to degrade light transmittance of a matrix because light does not penetrate the metallic manganese nitrides. Light transmitting polymers are widely used for optical parts such as a window and a lens. In order to retain light transmittance of composites, down-sizing of the manganese nitride particles to wavelength of visible light has been attempted [30]. However, Song et al. reported that the fine-grained manganese nitrides lose their NTE properties [31]. A technique to

control NTE and grain size simultaneously is necessary for the manganese nitride filler.

5. Conclusion

We have successfully controlled thermal expansion of polyamide-imide over a wide range from positive to even negative by forming composites using the manganese nitride filler. Analyses using models describing thermal expansion of a composite verify that thermal expansion of polyamide-imide matrix is suppressed less than the estimate based on the volume-weighted sum, which is ascribed to much larger elastic modulus of the nitride filler. A remarkable merit of the present composite is three-dimensional isotropic reduction of thermal expansion by conventional injection moulding, which is in contrast to existing low thermal expansion polymer matrix composites that exhibit suppressed in-plane thermal expansion but uncontrolled out-of-plane thermal expansion. The present technique removes the demerit of polymers that limits their utility value.

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