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Yang Hua [a], Qing-Qing Ni [b], Atsuhiko Yamanaka [c], Yoshihiko Teramoto [d] & Toshiaki Natsuki [e]

[a] Department of Materials Science and Engineering, Northeastern University at Qinhuangdao, Qinhuangdao City 066004, P. R. China;, Email: niqq@shinshu-u.ac.jp

[b] Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China, Department of Functional Machinery and Mechanics, Shinshu University, Ueda 386-8567, Japan

[c] Research Center of Toyobo Co., Ltd., 2-1-1 Katata, Otsu, Shiga 520-0292, Japan

[d] Research Center of Toyobo Co., Ltd., 2-1-1 Katata, Otsu, Shiga 520-0292, Japan

[e] Department of Functional Machinery and Mechanics, Shinshu University, Ueda 386-8567, Japan

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The Development of Composites with Negative Thermal Expansion Properties Using High Performance Fibers

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[a] Department of Materials Science and Engineering, Northeastern University at Qinhuangdao, Qinhuangdao City 066004, P. R. China
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[c] Department of Functional Machinery and Mechanics, Shinshu University, Ueda 386-8567, Japan
[d] Research Center of Toyobo Co., Ltd., 2-1-1 Katata, Otsu, Shiga 520-0292, Japan

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Abstract
Almost all solid materials exhibit positive thermal expansivity. However, in many engineering designs, materials with negative thermal expansivity are desirable. The characteristics of high performance fibers, such as high strength, exceptional thermal conductivity and electrical insulation may also include negative thermal expansivity. Therefore, it should be possible to develop fiber reinforced composites with negative thermal expansivity by using an optimum combination of particular fiber reinforcements and a polymer matrix. This paper describes the development of such high performance fiber reinforced composites with negative or low thermal expansivity using four high strength fibers — polyethylene fiber (Dyneema), poly-*p*-phenylenebenzobisoxazole fiber (Zylon), aramid fiber (Technora) and carbon fiber (Torayca). The results showed that the newly developed Dyneema fiber and Zylon fiber composites exhibited significant negative thermal expansivity. Structural products of a stable size over a wide temperature range can be obtained by this method of controlling the coefficient of thermal expansion.

Keywords
Negative thermal expansivity, high performance fiber, TMA, polymer composites

1. Introduction

Machinery can lose precision or be damaged due to differences in thermal expansion between parts. For applications such as precision optical instruments and superconductor coil bobbins [1], the requirements of thermal expansion behavior

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[*] To whom correspondence should be addressed. E-mail: niqq@shinshu-u.ac.jp
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are quite strict. Therefore, in designing precision instruments, controlling thermal expansion is important.

Thermal expansion occurs when heat energy is applied to atoms in a material, and consequently their motion becomes more violent, effectively causing each individual atom to take up more space. This is observed on the macro scale as size increases accompanying a rise in temperature.

Currently only a few negative thermal expansivity materials such as tungsten and zircon oxides are available. However, certain high performance polymer fibers (sometimes called 'super fibers', strength > 2 GPa and Young's modulus > 50 GPa, [2]) with high specific strength and specific stiffness are more widely available and some of these materials exhibit negative thermal expansion due to their crystalline nature or particular chemical structure. Although these materials are readily available, research on negative thermal expansivity materials made from polymer composites is not highly advanced.

For fibers, the phenomenon of negative thermal expansivity was first described [3] in the 1980s. By the 1990s, some research on the negative thermal expansivity of Dyneema [4] and Zylon [4] (Toyobo Co. Ltd., Japan) fiber reinforced composites had started. However, the main research concerned the performance of these fibers at low temperatures. A hybrid multi-fiber structure — for example aramid and carbon fiber — is required to exploit these negative thermal expansivity properties in fiber reinforced composites. Therefore, there is a demonstrable need for systematic research on the properties of negative thermal expansivity in this type of composite material.

Negative thermal expansivity materials (see Fig. 1) can be tailored to produce zero thermal expansion by an optimized combination of positive and negative thermal expansivity materials. This implies that for certain applications, negative thermal expansivity materials can be used to control the thermal expansion even to produce zero thermal expansivity materials. To ensure quantifiable and controlled size stability of manufactured products by the use of mixtures of positive and neg-

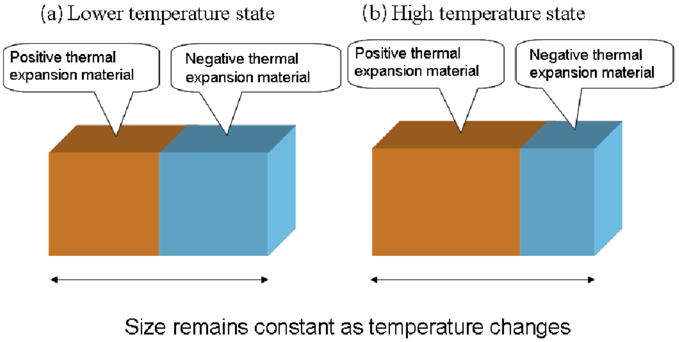

Figure 1. A diagram of the mechanism of zero thermal expansivity. This figure is published in color in the online version.

ative thermal expansivity materials, it is necessary to understand the nature of the response of such materials over a range of conditions.

This paper analyzes four kinds of representative high performance 'super fiber': polyethylene fiber (Dyneema), poly-*p*-phenylenebenzobisoxazole fiber (Zylon), aramid fiber (Technora) and carbon fiber (Torayca). Using an optimized combination of the fiber reinforcements in an epoxy resin polymer matrix, a high performance fiber reinforced composite with negative thermal expansivity was developed. The negative thermal expansion properties of fiber composite reinforcements over a range of temperatures and the relation with mass fractions in the test composites are discussed.

2. Experimental

2.1. Materials

Four types of reinforcing fibers were selected to produce epoxy resin matrix fiber reinforced composites with negative thermal expansivity. Figure 2 shows photographs of Dyneema SK60, Zylon HM, Technora [5] T241J and Torayca [6] T800HB. Table 1 lists the mechanical properties of the selected fibers [7].

Dyneema® SK60 (a registered trademark of Toyobo Co. Ltd. in Japan) is a typical ultra-high molecular weight polyethylene fiber with a specific tensile strength of up to fifteen times that of steel. It floats on water and is extremely durable and resistant to moisture, UV light and chemical attack.

Zylon® HM (a registered trademark of Toyobo Co. Ltd.) is a typical high strength PBO (poly-*p*-phenylenebenzobisoxazole) fiber. It is claimed by the manufacturer [4] to be the strongest organic polymeric fiber.

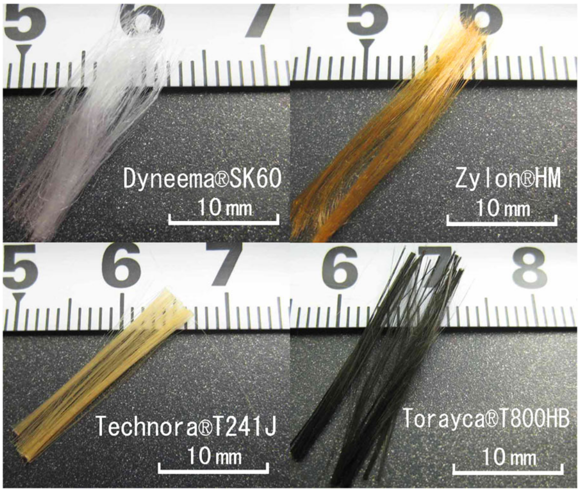

Figure 2. Photographs of Dyneema SK60, Zylon HM, Technora T241J and Torayca T800HB. This figure is published in color in the online version.

Table 1.
High strength and high Young's modulus fibers

	UHMWPE fiber	PBO fiber	Aramid fiber	Carbon fiber
Strength (MPa)	2200–4800	5800	2400–3500	2000–7200
Young's modulus (GPa)	70–175	180–270	55.7–147	230–700
Density (g/cm^3)	0.97–0.98	1.54–1.56	1.39–1.45	1.74–1.97

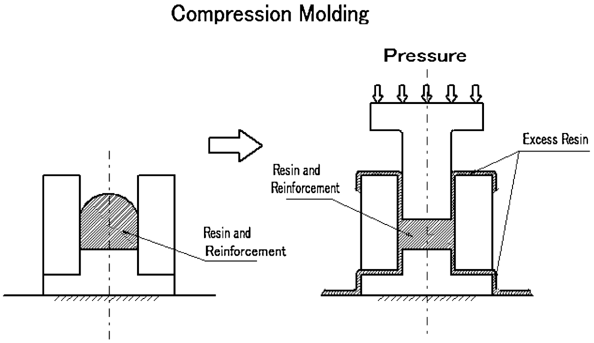

Figure 3. Compression molding method.

Technora® T-241J (a registered trademark of Teijin Co. Ltd.) is a high tenacity para-aramid (aromatic series) fiber. It shows little loss of strength even when abraded, flexed or stretched.

Torayca® T800HB (a registered trademark of Toray Co. Ltd.) is high performance polyacrylonitrile (PAN) type carbon fiber with excellent mechanical properties (high specific strength and specific stiffness) and also displays the notable characteristics of carbon, namely minimal deformation due to thermal effects, heat and chemical resistance and self-lubrication.

The matrix used in this work is a bisphenol-A epoxy resin (Japan Epoxy Resins Co. Ltd.) with high mechanical properties and low thermal deformation. The hardener selected for the system is a saturated aliphatic type with an imidazole accelerator curing agent (Hitachi Chemical Co. Ltd.).

2.2. Method

To maximize the negative thermal expansivity of the test composites, unidirectional orientation of the fibers was used and then the fiber loading was maximized. Compression molding [8] was used to fabricate the fiber reinforced composites. Figure 3 shows a schematic diagram of the compression molding experimental method. The pre-wetted fiber pack was placed in the mold, and compressed to final form. The excess resin escaped through top and bottom vents. The composite was heated and then cured in the mold for about 3 h, and then the mold temperature was

Figure 4. Specimens (from left to right) of DFRP, ZFRP, CFRP, AFRP and the neat epoxy resin. This figure is published in color in the online version.

raised to 130°C for 2 h to post-cure the molding. The hardening and curing process was controlled using a thermo-controller (SOFW-450, Asone Co. Ltd.).

In this paper, the Dyneema composite will be referred to as DFRP, the Zylon as ZFRP, the Technora (aramid fiber) as AFRP and the Torayca (carbon fiber) as CFRP. Figure 4 shows the four samples of unidirectional composite specimens and a neat epoxy resin sample. The specimens were cut at a length of about 10 mm, width and thickness between 5 and 10 mm, and the weight was between 1.6 and 2.5 g.

3. Results

3.1. Microscope Observation

Figure 5 shows optical micrographs of cross-sections of composites made from individual fiber types. In the DFRP cross-sectioned specimens, the interpenetrating nature of the Dyneema fibers can be seen. This morphology is quite clearly different to ZFRP, AFRP and CFRP, where, in a cross-sectional view, the rounded cross-sections of the fibers and the surrounding matrix resin can be seen.

The micrographs indicate that the composites are of high and consistent quality with good matrix adhesion to the fibers, and the defects of composite materials, such as bubbles or cracks, are not found.

3.2. Thermal Expansivity of Fibers and Matrix

The thermal expansivity of the fibers and the fiber reinforced composites were measured over temperatures ranging from 25 to 120°C, by thermo mechanical analysis (TMA) using an EXSTAR6000 TMA rheology system (Seiko Instruments, Inc. SII nano-technology Co. Ltd.). The curves of displacement and temperature were measured under a specified load of about 2 mN.

Figure 6 shows the TMA curves for Dyneema SK60, Zylon HM, Technora T241J and Torayca T800HB.

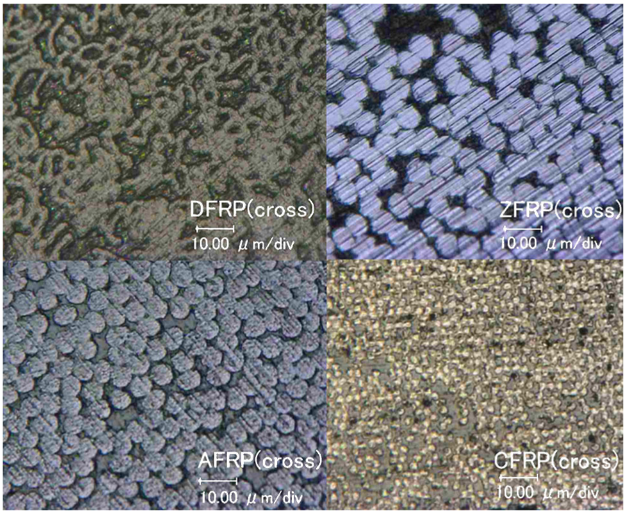

Figure 5. Optical micrographs of cross-sections of composites made from individual fiber types. This figure is published in color in the online version.

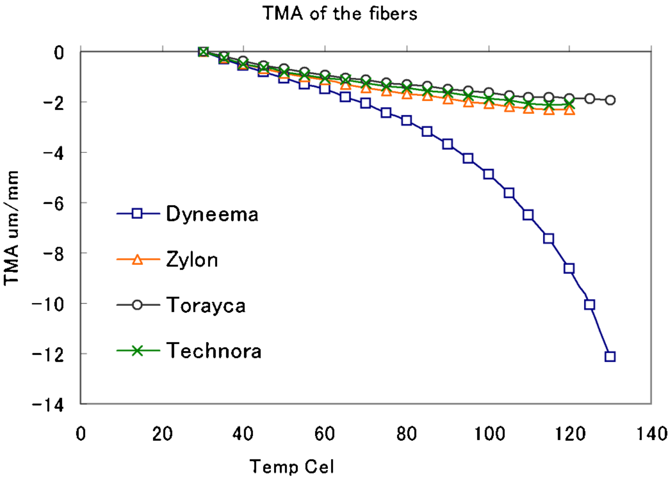

Figure 6. Thermo mechanical analysis results for Dyneema SK60, ZylonHM, Technora T241J and Torayca T800HB. This figure is published in color in the online version.

From Fig. 6, it can be seen that the all of fibers exhibited negative thermal expansivity. Dyneema SK60 exhibits the largest negative thermal expansion coefficient. The other fibers exhibit lower magnitudes, but have similar profiles of negative thermal expansivity.

The average thermal expansion rate α is given by:

$$\alpha = \frac{\Delta L}{L \times \Delta K} \times 10^{-3}\ \text{m/mK}, \tag{1}$$

Table 2.
Average thermal expansion rates of fibers

	TMA (10^{-6} m/mK)	
	25–80°C	25–120°C
Dyneema SK60	−53.7	−92.6
Zylon HM	−23.2	−25.7
Technora T241J	−21.1	−24.8
Torayca T800HB	−19.3	−22.0

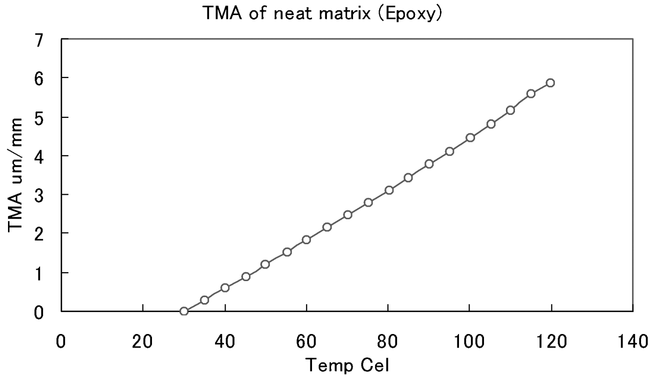

Figure 7. Thermo mechanical analysis of the epoxy resin matrix.

where ΔL is the longitudinal displacement, L is length of the specimen, ΔK is the temperature range.

When the length of the specimen is about 10 mm, from formula (1) it can be seen that the average thermal expansion rate α for the Dyneema between 25 and 120°C is -92.6×10^{-6} m/mK. Eliminating the nonlinear portion of the TMA data, the average thermal expansion rate α for the Dyneema between 25 and 80°C averages -53.7×10^{-6} m/mK. The average thermal expansion rates α of Zylon HM, Technora T241J and Torayca T800HB in different temperature regions are listed in Table 2.

Figure 7 shows the TMA curve for neat epoxy resin under similar TMA measurement conditions to those used to examine the fibers. The thermal expansion rates for epoxy resin between 25 and 120°C show clear positive thermal expansion. The average thermal expansion rate α is $+63.50 \times 10^{-6}$ m/mK.

3.3. Thermal Expansivity of Fiber Reinforced Composites

The mass fractions of fiber (W_f) for DFRP, ZFRP, AFRP and CFRP are denoted as W_f(DFRP), W_f(ZFRP), W_f(AFRP) and W_f(CFRP), respectively. For each fiber, three different fiber mass fraction (high, middle and low) composites were prepared — see Table 3.

Table 3.
Mass fraction of fiber in specimens

	High (%)	Middle (%)	Low (%)
W_f(DFRP)	55.9	38.5	18.2
W_f(ZFRP)	58.6	40.7	19.1
W_f(AFRP)	76.4	64.4	28.9
W_f(CFRP)	72.5	49.7	21.2

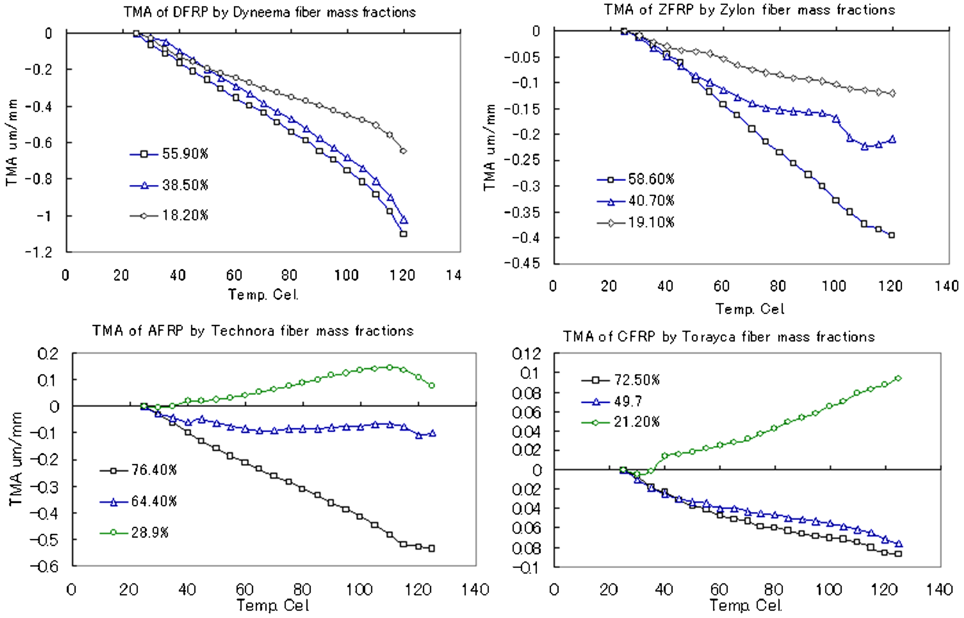

Figure 8. Thermo mechanical analysis results for DFRP, ZFRP, AFRP and CFRP. This figure is published in color in the online version.

Figure 8 shows the relationship between displacement and temperature in the direction of fiber orientation for different fiber mass fractions between 25 and 120°C. All of the composite specimens exhibited negative thermal expansivity at higher fiber mass fractions. Moreover, the DFRP and ZFRP specimens exhibited the desired negative thermal expansivity. DFRP has the largest negative thermal expansion coefficient, and negative thermal expansivity increases with fiber mass fraction. The AFRP and CFRP specimens with higher fiber mass fractions also exhibited negative thermal expansivity, but at lower fiber mass fractions the composites exhibited positive thermal expansivity.

Based on TMA displacement *vs.* temperature curves for DFRP, when the fiber mass fraction W_f(DFRP) is 55.9%, the average thermal expansion rate α(DFRP)

Table 4.
Average thermal expansion rates of composites

	Mass fraction (%)	TMA (10^{-6} m/mK)	
		25–80°C	25–120°C
DFRP	55.9	−9.87	−11.57
	38.5	−8.62	−10.73
	18.2	−6.35	−6.80
ZFRP	58.6	−4.27	−4.18
	40.7	−2.80	−2.19
	19.1	−1.55	−1.26
AFRP	76.4	−5.69	−5.56
	64.4	−1.51	−0.99
	28.9	+1.59	+0.76
CFRP	72.5	−1.08	−0.91
	49.7	−0.84	−0.76
	21.2	+0.77	+0.93

between 25 and 120°C can be obtained from formula (1) as follows:

$$\begin{aligned}\alpha(\text{DFRP}) &= \frac{\Delta L}{L \times \Delta K} \times 10^{-3}\ \text{m/mK}\\ &= \frac{-1.099}{1 \times 95} \times 10^{-3}\ \text{m/mK} \approx -11.57 \times 10^{-6}\ \text{m/mK}.\end{aligned}$$

In the same way, the average thermal expansion rates α(DFRP) are -10.73×10^{-6} and -6.80×10^{-6} m/mK, respectively, for fiber mass fractions W_f(DFRP) of 38.5 and 18.2%.

Eliminating the nonlinear portion of TMA (temperatures between 25 and 80°C), the average thermal expansion rate α(DFRP) for DFRP are -9.87×10^{-6}, -8.62×10^{-6} and -6.35×10^{-6} m/mK for fiber mass fractions of W_f(DFRP) 55.9, 38.5 and 18.2%, respectively.

The variations of average thermal expansion rates α of the ZFRP, AFRP and CFRP composites with fiber mass fraction at temperatures from 25 to 80°C and from 25 to 120°C are shown in Table 4.

4. Discussion

4.1. The Comparison of Thermal Expansivity

From Table 2, it is obvious that the thermal expansion rate α of Dyneema SK60 shows the largest negative thermal expansion rate of the materials examined. The average thermal expansion rate α of Dyneema SK60 is about 2.3 times larger than those of the other fibers between 30 and 110°C (the linear element) reaching nearly 5 times higher at 120°C (including the nonlinear part). The other three fibers also exhibit small but clear negative thermal expansivities. As expected, the epoxy resin matrix has a positive thermal expansivity (see Fig. 7).

The thermal expansivity of the fiber reinforced composites largely resulted from the thermal expansivity of the fiber reinforcement. Figure 9 shows the relationship of thermal expansivity between reinforcing fibers and the composites reinforced by those fibers. Clearly, there is crucial contribution to the thermal expansivity of the fiber reinforced composites by the fiber reinforcement. Figure 10 shows the change in negative thermal expansivity rate α against fiber content. As the reinforcing fiber content increases, so does the negative thermal expansivity of the fiber reinforced composite. The negative thermal expansivity is broadly proportional to the amount of fiber in the composite, particularly in DFRP composites.

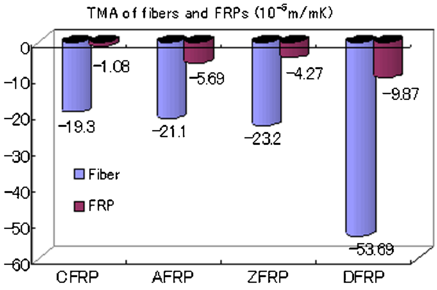

Figure 9. Thermo mechanical analysis of the fibers and their composites. This figure is published in color in the online version.

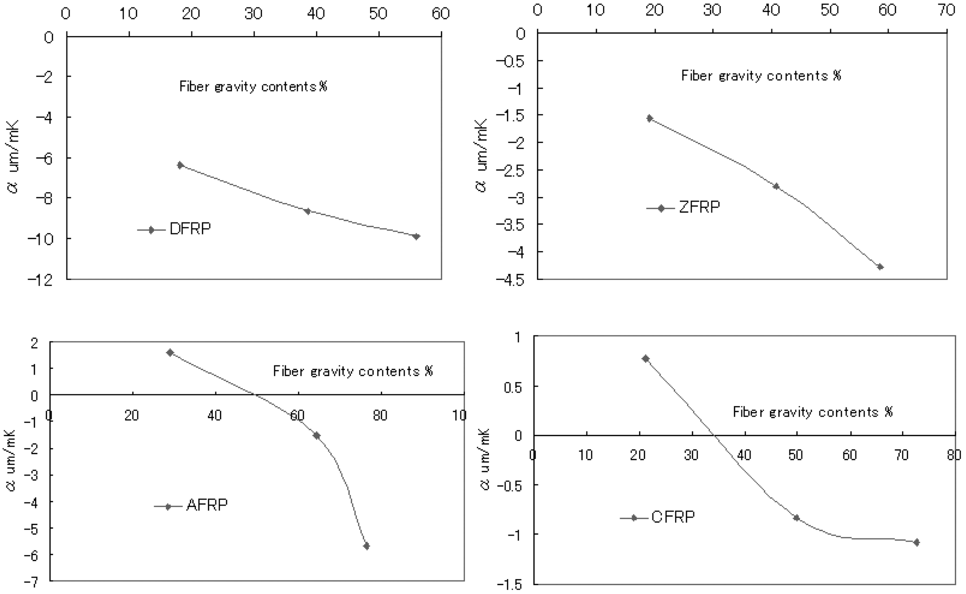

Figure 10. Thermal expansion rates of composite for different fiber contents.

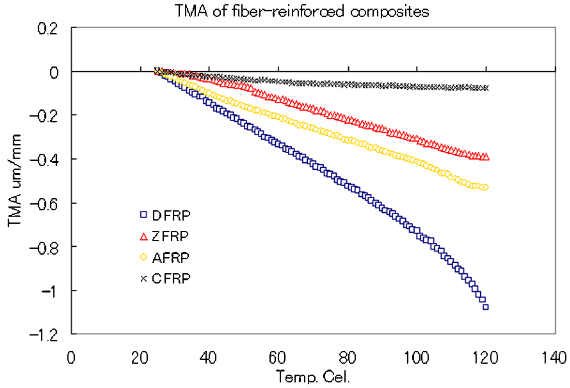

Figure 11. Thermo mechanical analysis of fiber reinforced composites with high mass fraction. This figure is published in color in the online version.

Figure 11 shows the TMA curves for fiber reinforced composites with the highest fiber content. It is found that the magnitude of average negative thermal expansion rates for DFRP is about twice that of ZFRP and AFRP, and about 10 times larger than CFRP.

4.2. The Mechanism of Negative Thermal Expansion of High Performance Fibers

Generally for this type of high performance fiber, the molecular chains are cross-linked by C–C bonds, and the C–C bond is much stronger than other intermolecular forces such as van der Waals forces [9, 10]. Greater energy is needed to elongate or shorten these chains, because the C–C bonds that hold adjacent carbons in the fundamental unit of the molecular chain are much stronger than those between two adjacent molecular chains (allowing lateral motion). Therefore, the thermal motion associated with molecular chains is limited to lateral motion, and the chain is relatively inextensible.

High performance ultra-high molecular weight polyethylene (UHMW-PE) fiber Dyneema is a high molecular weight polymer which has highly crystalline molecular orientation. The molecular orientation of Dyneema is more than 95% in the longitudinal direction, while the molecular orientation of normal UHMW-PE has less than 85% in the longitudinal direction and its molecular crystal orientation is multi-directional [11, 12].

An intuitive model of the molecular chain suggests that an increase in the amplitude of lateral motion with temperature can cause a shortening in the chain direction, and this effect could explain the observed negative thermal expansion along the chain direction of the crystalline polymer. Similarly, the lateral thermal motion of atoms in an inextensible polymer chain could cause a shortening along the chain direction. It has been suggested that the out-of-plane motion of a planar zigzag chain could account for the thermal contraction of polyethylene crystallites. The amplitude of out-of-plane motion can be characterized by the rotation angle between consecutive planes. These are defined by pairs of C–C bonds in the molecular structure of Dyneema.

The lateral thermal motion model considers a linear chain made up of atoms joined together by inextensible segments. Under lateral displacement, the chain effectively buckles causing a shortening in length. Experimental measurement indicates that the lateral motion model yields results in broad agreement with theoretical predictions. Therefore, the high molecular crystal orientation in a longitudinal direction is likely to cause negative thermal expansion along the chain direction of a polymer crystal. Research conducted by Toyobo Co. Ltd. [13] indicates that there is similarly high molecular crystal orientation in the longitudinal direction in Dyneema and Zylon, offering a possible explanation of the negative thermal expansivity of these fibers.

5. Conclusions

In this work, representative high performance fibers and an epoxy resin matrix, were chosen to develop materials with negative or low thermal expansivity. Four types of unidirectional composites and an epoxy bulk specimen were fabricated and their thermal expansivities measured. The resulting composites of DFRP, ZFRP, AFRP and CFRP exhibited significant negative thermal expansivity. Therefore, the development of the high performance fiber reinforced composites with a controllable coefficient of thermal expansion (CTE) obtained by an optimized combination of high performance fiber reinforcements in a polymer matrix was demonstrably successful. It is expected that these materials will find applications in the manufacture of high thermal stability, high strength industrial parts. Moreover, it is likely that the continued development of hybrid structures using high performance composites will lead to further novel tailoring of material properties.

Acknowledgements

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