Residual Stress of Particulate Polymer Composites with Reduced Thermal Expansion

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Abstract. Thermal expansion behavior was investigated for tungsten zirconium phosphate (Zr₂(WO₄)(PO₄)₂ (ZWP)) particulate filled poly(ether ether ketone) (PEEK) composite. ZWP is known as ceramic filler with a negative thermal expansion. By incorporating ZWP with 40 volume %, the linear thermal expansion coefficient of the PEEK composite was reduced to almost same value (2.53 X10⁻⁵ K⁻¹) with that of aluminum. This decrease was found to be quite effective for the decrease of the residual stress at the interface between aluminum plate and the composite.

1. Introduction
Thermal expansion behavior is one of the most important thermal properties of the composites. The linear thermal expansion coefficients $\alpha$ of conventional polymers are roughly in the range of $10^{-5}$ K⁻¹, which is far higher than those of metals and ceramics [1]. Assuming the case that polymer was adhered to metal or ceramics, the mismatch of the thermal expansion will induce residual stress at the interface. This residual stress often damages the products seriously through debonding for the adhesives, bending and delamination for the laminates, leak by water uptake for IC, LSI devices. Thus the decrease of the residual stress is very important from the practical usages [2]. The thermally induced residual stress is well known as functions of i) elastic modulus, ii) glass transition temperature and iii) thermal expansion of the material [3]. Thus, the decreases of any of these three factors will contribute to the decrease of the residual stress. However, the former two factors are very important from the mechanical and thermal performance of the materials. Accordingly, the last factor, that is, the decrease of the thermal expansion is the most preferable one to fulfill the purpose.

The thermal expansion behavior of the composite can be controllable by changing the combination of the incorporated fillers/fibers and the matrix, volume fraction, orientation, dispersion and so on. Some of the ceramics are known to show negative thermal expansion. For example, ZrW₂O₈[4], PbTiO₃ [5] are found to show negative $\alpha$ in a wide temperature range. Thus the researchers synthesized micro- and nano-size particles, then incorporated these particles into polymer. They succeeded to reduce the $\alpha$ values of the polymeric composites for epoxy resin [6], poly(methyl methacrylate) [7], polypimide [8], cyanate ester [9]. Zirconium tungsten phosphate, Zr₂(WO₄)(PO₄)₂ (ZWP) also shows negative $\alpha$ of - 3.2 X 10⁻⁶ K⁻¹, which is available commercially.

In this study, we report the particulate polymer composite with reduced thermal expansion, by combining ZWP particles with poly(ether ether ketone) (PEEK). PEEK has found much application as super engineering plastic, where thermal dimensional stability with low $\alpha$ value is highly required. In addition to the thermal expansion behavior, the residual stress of the composite was evaluated.
2. Experimental

2.1 Sample Preparation
Commercial available ZWP particles, kindly supplied from KCM Co., Japan, was mixed with PEEK (Sumitomo Chemical Co. Ltd., 450 G) using a brabender type mixer (Labo Plastomill, Toyo Seiki Seisaku-sho Ltd.) at 400 °C for 10 min. Then the mixture was melt pressed into the sheet shaped composite at 350 °C, 5 MPa for 2 min, followed by quenching into ice water (Quenched). After that, the composite was annealed at 300 °C for 1 h (Annealed). The thickness of the composite was 0.3 mm. The sample preparation scheme is shown in Figure 1 with scanning electron micrographs.

2.2 Measurements
The structure of the composites was investigated by X-ray diffraction using Cu Kα radiation, generated with RINT-2000 (RIGAKU) at 40 kV, 20 mA. Thermomechanical analysis, TMA, was performed using a thermomechanical analyzer (SSC/5200 TMA 120 CU, Seiko Instruments). The tensile stress of 0.1 MPa was applied to the rectangular sample with its original length of 15 mm. Then the sample was heated at 10 °C/min. The thermal expansion coefficient was evaluated from the inclination of the strain vs. temperature curve. The filler volume fraction in the composite was evaluated from the thermal gravimetric trance with the heating rate of 10 °C/min under nitrogen flow. The ZWP particles and the fracture surface of the composite was observed using a scanning electron microscope (SEM) (JSM-5610LVS (JEOL)), at an accelerating voltage of 20 kV. Pt/Pd was deposited on the surface prior to the observation.

3. Results and Discussion

3.1 Structure of PEEK / ZWP Composites
The ZWP particles were crushed shape and the size was widely distributed from 0.1 to several μm. The ZWP particles were homogeneously dispersed in the PEEK matrix as shown in Fig.1. Figure 2 shows the X-ray diffraction profiles of quenched, annealed PEEK and annealed PEEK / ZWP (40 vol %) composite. The quenched PEEK is amorphous, however, it crystallized after annealing. In addition, the diffraction peaks assigned as ZWP were overlapped to the amorphous halo and the crystalline peaks from PEEK for the composite. These reveal that the crystalline state of the composites changed drastically by annealing.
3.2 Thermal Properties and Residual Stress of PEEK/ZWP Composites

Figure 3 shows the relationship between the thermal strain and temperature of the PEEK films and the composite from the TMA measurements. With increasing temperature, all of them showed thermal expansion. Especially, the quenched PEEK film showed nonlinear large expansion due to the amorphous state. After annealing, the inclination of the curve decreased, then by incorporating ZWP, it decreased further. Here, the $\alpha$ value is defined from the linear part of the curve between 50 and 80°C as shown in the figure.

Figure 4 shows the relationship between the $\alpha$ value and the volume fraction of ZWP for the quenched and annealed ZWP particulate PEEK composites. The $\alpha$ values of some metals and PEEK/SiO$_2$ (40 vol %) composite were also superimposed on the figure. With increasing the volume fraction of ZWP particles, the $\alpha$ value decreased linearly. The absolute $\alpha$ value of the annealed composite was lower than those of the quenched ones. This is reflected by the $\alpha$ value of each matrix. Above 20 vol % for the annealed composite (corresponding to the 35 vol % for the quenched composite), the $\alpha$ values were lower than that of Zn, and it reached to that of Al ($2.36 \times 10^{-5}$ K$^{-1}$) at 40 vol % for the annealed composite. This value is far lower than that of SiO$_2$ particulate filled composites, in which the $\alpha$ value of SiO$_2$ is $1.3 \times 10^{-5}$ K$^{-1}$. Thus the incorporation of the particles with low (negative) $\alpha$ value is quite effective for lowering the thermal expansion of the composite. As the first-order approximation to the overall calculation, the calculated $\alpha_{\text{calc}}$ value can be evaluated using the simple rule of mixture as follows:

$$\alpha_{\text{calc}} = \alpha_f \phi + \alpha_m (1 - \phi)$$

where, $\phi$ is the volume fraction of filler, and $\alpha_f$, $\alpha_m$ are the $\alpha$ values of the filler and the matrix, respectively. The $\alpha_{\text{calc}}$ values for the quenched and annealed composites with $\phi$ = 40 vol % are $4.2 \times 10^{-5}$ K$^{-1}$, $3.3 \times 10^{-5}$ K$^{-1}$, respectively, which were higher than the observed values. The equation simply predicts the $\alpha$ value without considering dispersivity of the ZWP particles in the matrix and/or the interfacial interaction between ZWP and PEEK. Further investigations will be needed to reproduce the observed ones. The extrapolating of the red line for the annealed composite to the volume fraction of 60%, the $\alpha$ value reached to that of Fe. However, the volume fraction of 40 % of ZWP was the maximum attained value by the brabender mixing so far we investigated. Further improvement of the dispersivity of the particles should be considered.
Figure 5 shows the photographs of the laminates composed of (upper) quenched PEEK sheet / Al plate, and (lower) annealed PEEK / ZWP (40 vol %) composite / Al plate. The PEEK sheet and the composite sheet were adhered to the Al plate (thickness: 0.3 mm) using the epoxy resin, respectively, then cured at 140 °C followed by rapidly cooling to room temperature.

![Figure 5](image.png)

**Figure 5** Photographs of the laminates composed of (upper) quenched PEEK sheet / Al plate, and (lower) annealed PEEK / ZWP (40 vol %) composite / Al plate.

The laminate of quenched PEEK and Al was bended with the PEEK sheet inside. This is because the thermal shrinkage of the PEEK film is higher than that of the Al plate during cooling from the curing temperature to room temperature. It is clear from these photographs, the radius of the curvature decreased for the composite. This reveals that the residual stress could be reduced by the decreased of the thermal expansion of the polymer composite. The residual stress $\sigma_{\text{calcd.}}$ can be calculated as 20.1 MPa, 1.4 MPa for the quenched PEEK and the annealed composite, respectively, by considering the elastic modulus of the quenched PEEK sheet (1.7 GPa) and the annealed composite (4.1 GPa) [10]. This corresponds to the observed ones shown in Fig.5.

4. Conclusions

By incorporating ZWP particles with negative thermal expansion, the thermal expansion coefficient of the PEEK composite could be reduced to almost same value with that of Al. These decreases of the thermal expansion coefficient were quite effective for the decrease of the residual stress at the interface.

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