NOTES

Anisotropy in Thermal Expansion in Rubber Toughened Polypropylene—Injection Molded System—

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Rubber toughened Polypropylene (PP) has widely been in industrial use, such as automotive, electric appliance, food packaging, films and sheet applications, due to its superior cost performance and recycling capability over other plastics.¹ PP materials are in use under severe conditions especially in automotive applications. A typical example is thermal condition, where the environmental temperature is between -40°C and 100°C . In this case, dimensional stability, and hence thermal expansion, is one of the most important issues. The coefficient of linear thermal expansion (CLTE) of plastics ($\sim 10^{-5}$ – 10^{-4} m/m $^{\circ}\text{C}$)² is however much greater than other materials, metals and ceramics ($\sim 10^{-5}$ – 10^{-6} m/m $^{\circ}\text{C}$).³ The articles consisting of plastics and metals would thus suffer troubles arising from the dimensional mismatch when the variation of environmental temperature is large. Despite the practical importance of CLTE in PP, few systematic studies were performed.^{4,5} This paper thus focuses on the CLTE of rubber toughened PP with a special emphasis on the anisotropy in CLTE.

EXPERIMENTAL

The materials used in this study were polypropylene homopolymer (PP: PX400A from SunAllomer Ltd.) (MFR = 2.5 dg/min at 230°C , isotactic index = 98.5%) and poly(ethylene-co-octene) (EOR: ENGAGE8200 from DuPont Dow Elastomers L.L.C.) (MFR = 10.0 dg/min at 230°C and specific gravity = 0.870). The blend of PP/EOR = 70/30 w/w was prepared using a twin screw extruder, which was then injection molded to obtain a slab (125 mm $\times$ 20 mm $\times$ 3 mm). A specimen (13 mm $\times$ 5 mm $\times$ 3 mm) was cut out from the central part of the slab. The specimens were then annealed at 100°C for 24 h allowing the secondary crystallization.

Figure 1. Definition of direction, MD, TD and ND, as well as the faces, (a) X-face, (b) Y-face, and (c) Z-face.

The CLTE of the resulting specimen was measured using TMA (MTS9000 from Shinku Riko Co., Ltd.) between -50°C and 100°C under the 5 g of load at the heating rate of $4^{\circ}\text{C}/\text{min}$. The CLTE were monitored as a function of temperature in three directions, MD, TD and ND (Figure 1): each measurement was independently made on a different specimen.

The morphology observations of the specimen from three faces (X-, Y- and Z-face: see Figure 1) were performed by transmission electron microscopy (TEM) (JEM1200EX from JEOL, Ltd.) operated at 120 KV on an ultra thin section stained with RuO_4 .⁶ In addition, the PP crystal orientation from the Z-faces was investigated by wide angle X-Ray diffraction (WAXD) in the reflection mode.

RESULTS AND DISCUSSION

Temperature Dependence of CLTE

Figure 2 showed the CLTE in MD, TD and ND (designated as α_{MD} , α_{TD} and α_{ND} , respectively) as a function of temperature, T . Both α_{MD} , and α_{TD} increased with T with the inflection point at $T \sim 0^{\circ}\text{C}$ when $T < 50^{\circ}\text{C}$, then slightly decreased when $T > 50^{\circ}\text{C}$. On the other hand, α_{ND} increased with T at $T < 0^{\circ}\text{C}$, then somewhat decreased when $0 < T < 30^{\circ}\text{C}$, followed by the increase with T when

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$T > 50^\circ\text{C}$. At $T \sim 0^\circ\text{C}$, the T_g of PP, micro-Brown motion occurred, hence αl_{MD} and αl_{TD} increased due to the inelastic effect; the decrease in αl_{ND} would be the Poisson's effect. In $T > 50^\circ\text{C}$, the elastomer ($T_m \sim 50^\circ\text{C}$) was in a molten state, elastomer domains thus deformed so as to minimize interfacial energy. Retraction thus takes place in both MD and TD, while expands in ND under such circumstances. Consequently, αl_{MD} and αl_{TD} decreased, while αl_{ND} increased, when $T > 50^\circ\text{C}$ as observed in Figure 2.

The deformation based on the difference in modulus between 0°C and 50°C , Δl_{load} , may underestimate CLTE. The deformation ratio, [(deformation by load)/

(thermal expansion)] = $\Delta l_{\text{load}}/\Delta l_{\text{Thermal}} = (F/A(\alpha\Delta T)) \times (1/E_{50^\circ\text{C}} - 1/E_{0^\circ\text{C}})$, was estimated to be 2.6×10^{-3} , being negligible. In this calculation, (load) $F = 4.9 \times 10^{-2}$ (N), (cross section) $A = 1.5 \times 10^{-5}$ (m^2), (CLTE) $\alpha = 5.7 \times 10^{-5}$ ($\text{m}/\text{m}\cdot^\circ\text{C}$), (temperature difference) $\Delta T = 50^\circ\text{C}$, (modulus at 50°C) $E_{50^\circ\text{C}} = 300$ (MPa) and (modulus at 0°C) $E_{0^\circ\text{C}} = 1000$ (MPa).

It should be pointed out that the CLTE showed strong anisotropy, *e.g.*, $\alpha l_{\text{MD}} = 5.7 \times 10^{-5}$ ($\text{m}/\text{m}\cdot^\circ\text{C}$), $\alpha l_{\text{TD}} = 8.2 \times 10^{-5}$ ($\text{m}/\text{m}\cdot^\circ\text{C}$) and $\alpha l_{\text{ND}} = 35.0 \times 10^{-5}$ ($\text{m}/\text{m}\cdot^\circ\text{C}$), respectively, being discussed later.

TEM Observations

Figures 3a, 3b and 3c showed TEM micrographs of X-, Y- and Z-face, respectively. In X- and Y-face, the elastomer domains were highly elongated, while in the Z-face, elastomer domains were disorderly located. The shape of the elastomer domains was thus slab, the normal vector of which was parallel to ND.

TEM micrographs at a higher magnification revealed that PP crystal lamellae aligned normal to the elastomer domains (Figures 4a and 4b), while rectangular pattern was observed in Z-face (Figure 4c). Similar morphologies were reported in a PP/EPR/talc system.^{4,5} It should be noted that no shish-kabab structure was observed in PP crystal. Somani *et al.* showed that in isotactic PP, shish-like structure appeared under flow at a high crystallization temperature ($T_c = 165^\circ\text{C}$),⁷ while only lamella structure was observed at lower temperature $T_c = 145^\circ\text{C}$.⁸ In the present case, the mold temperature was 40°C . T_c would thus be $<145^\circ\text{C}$, suggesting no shish-like structure.

Anisotropy of CLTE

The anisotropy in CLTE arises from the anisotropy in morphology as well as from that in the three components, PP (crystal and amorphous) and EOR.

The CLTE of the PP/EOR system can be given by

Figure 2. CLTE as a function of temperature for MD, TD and ND.

Figure 3. TEM images; (a) X-face, (b) Y-face, and (c) Z-face. The arrows in (a) and (c) show flow direction.

Figure 4. TEM images at high magnification; (a) X-face, (b) Y-face and (c) Z-face.

Figure 5. WAXD (reflection mode) pattern from Z-face.

Eqs 1 and 2,⁹ where all components are assumed to be isotropic.

$$\alpha l_{MD}(\text{calc}) = \alpha l_{TD}(\text{calc}) = \frac{\alpha l_{PP} E_{PP} \phi_{PP} + \alpha l_{EOR} E_{EOR} \phi_{EOR}}{E_{PP} \phi_{PP} + E_{EOR} \phi_{EOR}} \quad (1)$$

$$\alpha l_{ND}(\text{calc}) = (1 + \nu_{PP}) \alpha l_{PP} \phi_{PP} + (1 + \nu_{EOR}) \alpha l_{EOR} \phi_{EOR} - (\nu_{PP} \phi_{PP} + \nu_{EOR} \phi_{EOR}) \alpha l_{MD} \quad (2)$$

The subscripts PP and EOR represent PP and EOR, respectively. E , ν and ϕ represent Young's modulus, Poisson's ratio, and volume fraction, respectively. Inserting $\alpha l_{PP} = 17.0 \times 10^{-5}$,¹⁰ $\alpha l_{EOR} = 26.0 \times 10^{-5}$ (m/m $^{\circ}$ C) (measured), $E_{PP} = 2000$ (MPa), $E_{EOR} = 20$ (MPa), $\phi_{PP} = 0.696$, $\phi_{EOR} = 0.304$, $\nu_{PP} \sim 0.45$, and $\nu_{EOR} \sim 0.5$ into Eqs 1 and 2, we obtained $\alpha l_{MD}(\text{calc})$ ($= \alpha l_{TD}(\text{calc})$) and $\alpha l_{ND}(\text{calc})$ to be 17.0×10^{-5} and 21.0×10^{-5} (m/m $^{\circ}$ C), respectively. These

results still show massive difference from those observed, suggesting that the anisotropy in PP (crystal and amorphous phases) as well as in EOR would be conceivable.

Figure 5 showed the WAXD spectra from Z-face. The (040) peak was very strong in comparison with others, suggesting that the b axis of PP crystal oriented parallel to the ND in the present system. Nomura *et al.* demonstrated in the PP/EPR/talc system that the b axis of PP crystal had strong orientation along the ND when the MFR ratio, $\text{MFR}_{PP}/\text{MFR}_{EPR}$, was small, where the shape of EPR domains were slab.⁴⁻⁶ Diez-Gutierrez *et al.* also reported similar type of the b axis orientation in a PP/surface treated talc system.¹¹

Yamada *et al.* have reported that the CLTE of PP crystal along the b axis was 2.6 folds greater than that along the a axis. Additionally, the CLTE along the c axis was $\sim 10\%$ of the a axis, and hence much smaller than that along the b axis.¹² The CLTE of a specimen in a direction parallel to the b axis is therefore greater

than other directions. In the present case, the *b* axis corresponds to ND as mentioned in the above. Indeed, Choy *et al.* reported in the stretched film PP that the CLTE showed anisotropy associated with PP crystal orientation, where the higher the draw ratio (λ) the greater the anisotropy when $\lambda < 4$.¹³

In the case of PP amorphous, the anisotropy between MD and TD (not between MD and ND) would be the largest since molecular chains (*c* axis) tend to align parallel to the MD under flow. In addition, EOR was observed to be isotropic ($\alpha_{\text{MD}} = \alpha_{\text{TD}} = \alpha_{\text{ND}}$) when specimens were prepared under the same conditions. Thus, the anisotropy neither in the PP amorphous phase and EOR could be operative mechanisms. The orientation of PP crystals would thus be one of the operative mechanisms for the anisotropy in CLTE ($\alpha_{\text{ND}} \gg \alpha_{\text{MD}}$ and α_{TD}). For more detailed analysis, precise knowledge on the orientation of PP seems to be necessary, deserving for the future work.

CONCLUSIONS

The coefficient of linear thermal expansion, (CLTE), of a polymer blend of polypropylene (PP) and poly(ethylene-co-octene) (EOR) was investigated by TEM and WAXD. The CLTE depended strongly on the directions, *e.g.*, the CLTE in MD, TD and ND were observed to be $\alpha_{\text{MD}} = 5.7 \times 10^{-5}$, $\alpha_{\text{TD}} = 8.2 \times 10^{-5}$ and $\alpha_{\text{ND}} = 35.0 \times 10^{-5}$ (m/m $^{\circ}$ C), respectively.

TEM observations revealed that the shape of the EOR domains was “slab”, the normal vector of which was parallel to the ND. The anisotropy in morphology was found to account well for the largest CLTE in the ND direction. In addition, WAXD analysis revealed

that the *b* axis of PP crystals grew between the EOR domains toward the direction parallel to the ND, resulting in the largest CLTE in ND. (Note that the CLTE of PP crystal along the *b* axis was 2.6-folds greater than the *a* axis and that along the *c* axis was negligibly small.) Two conceivable mechanisms, anisotropy in morphology and PP crystal orientation, would be operative for the anisotropy in CLTE.

REFERENCES

1. E. P. Moore, Jr., Ed., “Polypropylene Handbook,” Carl Hanser Verlag, Munich, 1996.
2. J. Brandrup and E. H. Immergut, Ed., “Polymer Handbook,” 3rd ed., Wiley, New York, N.Y., 1989.
3. “Landolt Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik,” 6 Aufl., II Band, 1 Teil, S. 379–448, Springer-Verlag, Berlin, 1971.
4. T. Nomura, Ph.D. Thesis Nagoya University, 1994.
5. T. Nomura, T. Nishio, H. Taniguchi, I. Hirai and N. Hisamura, *Kobunshi Ronbunshu*, **51**, 505 (1994).
6. T. Nomura, T. Nishio, H. Tanaka, and K. Mori, *Kobunshi Ronbunshu*, **52**, 90 (1995).
7. R. H. Somani, L. Yang, and B. S. Hsiao, *Physica A*, **304**, 145 (2002).
8. R. H. Somani, L. Yang, B. S. Hsiao and H. Fruitwala, *J. Macromol. Sci., Part B: Phys.*, **42**, 515 (2003).
9. R. A. Shapery, *J. Composite Mater.*, **2**, 380 (1968).
10. P. Zoller and D. J. Walsh, “Standard Pressure–Volume–Temperature Data for Polymers,” Technomic Publishing Co., Inc., Lancaster, U.K. 1995.
11. S. Diez-Gutierrez, M. A. Rodriguez, J. A. De Saja, and J. I. Velasco, *J. Appl. Polym. Sci.*, **77**, 1275 (2000).
12. F. Gu, M. Hikosaka, A. Toda, S. K. Ghosh, S. Yamazaki, M. Arakaki, and K. Yamada, *Polymer*, **43**, 1473 (2002).
13. C. L. Choy, F. C. Chen, and E. L. Ong, *Polymer*, **20**, 1191 (1979).