Rubber as additives to lower thermal expansion coefficient of plastics: 1. Morphology and properties

Guozhang Wu[a,*], Kouji Nishida[b], Kiyoji Takagi[c], Hironari Sano[d], Hiroshi Yui[a]

[a]*Advanced Research Institute for Science and Engineering, Waseda University, 3-14-9 Okubo, Shinjuku-ku, Tokyo 169-0072, Japan*
[b]*Planning and Development Division, Mitsubishi Engineering Plastics Corporation, 1-1-1, Kyobashi, Chuo-ku, Tokyo 104-0031, Japan*
[c]*Technical Center Hiratsuka, Mitsubishi Engineering Plastics Corporation, 5-6-2, Higashiyawata, Hiratsuka, Kanagawa 254-0016, Japan*
[d]*Mitsubishi Chemical Group, Science and Technology Research Center, Inc., 1, Toho-cho, Yokkaichi, Mie 510-8530, Japan*

Abstract

A substantial approach was proposed to design polymer alloys with very low coefficient of linear thermal expansion (CLTE). The large reduction in CLTE is not based on an addition of *low*-thermal-expansion filler to suppress the bulk expansion, but on the fine control of the polymer alloy's micro-morphology so that the expansion is preferentially toward the thickness direction. In this study, rubber was used as an additive to tune the thermal expansion behavior of various plastics. Although the rubber has a *high* thermal expansion coefficient, it was found that, when the rubber domains are deformed into microlayers and co-continuous with the plastic matrix, the CLTE of the polymer alloy parallel to the microlayer directions could be reduced to a very low level. Various influencing factors including rubber concentration, viscosity ratio, interfacial adhesion as well as the domain size were investigated.
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Keywords: Thermal expansion; Rubber; Polymer alloy

1. Introduction

One of the major issues for polymers in engineering applications is to reduce the thermal expansion coefficient to achieve dimensional stability more comparable with metals. The traditional concept to lower the thermal expansion coefficient of polymers is adding a second component, such as inorganic filler, with relatively *low* thermal expansion coefficient and suppressing the expansion by simple mechanical restraints [1–4]. Numerous studies [1–12] have examined how filler shape, size, concentration and its dispersion influence the thermal expansion of polymer composites. However, since the filled polymer composites often suffer from poor toughness, bad appearance and difficulty in processing, the reduction in the thermal expansion coefficient by this approach remains significant limitations in practical applications.

The objective of this work is to develop a new technology for further reduction of the thermal expansion

coefficient without sacrificing the impact resistance. Rubbers such as ethylene–propylene rubber (EPR) and styrene–ethylene/butylene–styrene triblock elastomer (SEBS), etc. have been widely used as impact or compatible modifiers for improvement of the toughness [13,14]. Generally, an addition of a rubber to a plastic leads to a polymer blend with a high thermal expansion coefficient, as the rubber has a higher thermal expansion coefficient. However, we noticed that the coefficient of linear thermal expansion (CLTE) of plastic/rubber blends could change greatly with the change of the polymer morphology. As described in the next section, when the rubber domains are deformed into microlayers and co-continuous with the plastic matrix, the CLTE in directions parallel to the microlayers might decrease to a very low value, though the CLTE in the thickness direction might increase.

Accordingly, our strategy to lower the CLTE will not be based on the addition of *low*-thermal-expansion filler to suppress the bulk expansion, but on the fine control of the micro-morphology so that the expansion is preferentially toward the thickness direction. Rubber was used as an additive instead of an inorganic filler to mediate the thermal

expansion behavior of various plastics. An injection molding process was employed for deformation of the rubber domains into microlayers.

2. A simplified model

Fig. 1 illustrates our basic considerations to remarkably lower the CLTE of a plastic by the addition of rubber. Generally, rubber has a high CLTE (about $30 \times 10^{-5}/°C$) compared with plastics (from $6 \times 10^{-5}/°C$ to $15 \times 10^{-5}/°C$) [15], and blending of the rubber with the plastic leads to high CLTE mixtures (see Fig. 1(a)). However, when the plastic and the rubber phases are overlapped in a lamellar structure as shown in Fig. 1(b), the CLTE parallel to the lamella direction (X and Y-axis directions) should be reduced to a value close to that of the plastic. This occurs because the Young's modulus of the plastic is 50–1000 times higher than that of the rubber [15], and the expansion of the rubber parallel to the lamella direction should be restricted completely by the plastic layers. Since such a restriction should not change the bulk expansion volume, the rubber will expand transverse to the lamella direction resulting in a high CLTE in the thickness direction (Z-axis direction).

Further reduction of CLTE in the X- and Y-axis directions might be achieved when the rubber domains are deformed into microlayers and co-continuous with the plastic matrix (Fig. 1(c)). Assuming that the aspect ratio of the microlayers is so high that the thermal expansion of the rubber in the X- and Y-axis directions is highly constrained by the plastic matrix, then, like the thermal expansion behavior of the lamellar structure in Fig. 1(b), the microlayers have to expand toward the thickness direction. This will, in turn, suppress the thermal expansion of the plastic in the X- and Y-axis directions because the large volume of the rubber expansion should create a strong force exerted in the thickness direction and draw the three-dimensionally continuous plastic matrix toward the thickness direction.
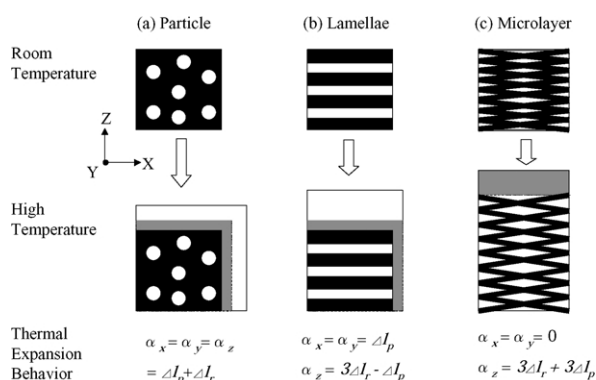

Fig. 1. A schematic of thermal expansion behavior for plastic/rubber blends with various morphologies of rubber domains. α_x, α_y and α_z represent the linear thermal expansion in the x, y and z-axis direction, respectively. Δl_p is the linear expansion per unit from the plastic phase and Δl_r is from the rubber phase.

3. Experimental

3.1. Raw materials and sample preparation

Several groups of model experiments were carried out to support the new idea. Two kinds of widely used polymers, polyamide-6 (PA) and polypropylene (PP) were selected as plastic matrices. They were kneaded with EPR and SEBS, respectively, using a twin-screw extruder (TEX30-2 with a diameter of 30 mm, Nippon Seikosho) at a setting temperature of 250 °C (at 230 °C for PP/EPR blends) with a screw speed of 200 rpm and a feed rate of 10 kg/h. To improve the compatibility between rubber and polyamide, maleic anhydride-grafted EPR (m-EPR) and SEBS (m-SEBS) were used. All grade names, molecular weights and suppliers of these materials are given in Table 1.

The dry pellets of the above compositions were subjected to injection molding using an inline screw-type injection-molding machine (IS-90B Model, Toshiba Kikai Seisakusho) at a cylinder temperature of 280 °C (at 200 °C for PP/EPR blends), an injection pressure of 80 MPa and a mold cooling temperature of 80 °C to prepare $120 \times 130 \times 3$ mm³-thick sheets. For comparison, some of the specimens were hot-pressed at 280 °C for 10 min. These specimens were placed in vacuum desiccators immediately after molding for 4–6 days at 23 °C prior to the thermal expansion testing.

3.2. Thermal expansion measurements

The CLTE was measured according to ASTM D696 using a thermomechanical analyzer (TMA943 by Du Pont). To eliminate the influence of the thermal history, the injection-molded and hot-pressed sheets were annealed at 120 °C for 1 h before the test. They were then cut into rectangular specimens by milling the center part of the annealed sheets to the following dimensions: 3-mm thickness, 5-mm width, and 6-mm height. An average value of CLTE from 23 to 80 °C was calculated.

3.3. Electron microscopy

Samples for TEM analysis were taken from the skin portion of the specimens parallel to the flow direction and transverse to the flow direction, respectively. They were stained by RuO_4 and OsO_4 vapor at 40 °C for 1 h and then cut into an ultra-thin section (approximately 70 nm in thickness) using an ultra-microtome (Ultracut N, Reicherr). TEM observation was carried out under a Jeol transmission electron microscope (JEM100CX, Nihon Denshi) at an accelerating voltage of 100 kV.

4. Results and discussion

The physical properties of injection-molded specimens are known to depend on the direction within the specimen

Table 1
Materials used

Reference	Grade name	MA content (wt%)	Molecular weight (M_w)	Supplier
PA	MC161	–	65,000[a]	Kanebo
PP	BC1	–	3,500,000	Mitsubishi
EPR	EP02P	–	140,000	JSR
EPR-1	EP912P	–	170,000	JSR
m-EPR	T7711SP	1.0	170,000	JSR
m-SEBS	Kraton G 1901X	1.84	Not available	Shell

[a] Molar mass of number average (M_n).

relative to the flows involved in its formation. Processing directions are commonly described by an orthogonal coordinate system identified by the flow direction (FD), transverse direction (TD) and normal direction (ND, = thickness direction). For better understanding, this nomenclature is used throughout the remainder of this paper.

Figs. 2–4 show TEM micrographs of the injection-molded PA and PP alloys with 40 wt% rubber. The dark areas in the pictures represent the rubber domains that are stained by RuO_4 and OsO_4 vapor. It is observed that both the plastic and rubber phases are elongated and orientated along

FD (see Figs. 2(a), 3(a) and 4(a)), and from the magnified pictures (see Figs. 2(b) and 3(b)), they are co-continuous. Fig. 4(b) shows the morphology of the plastic and rubber phases transverse to FD. Again, we observed the elongated, oriented and co-continuous plastic and rubber microlayers. These pictures clearly illustrate that micro-laminate co-continuous morphologies are formed in the injection-molded samples, at least near the skin portion. Such a morphology is believed to greatly reduce the CLTE of the polymer alloys.

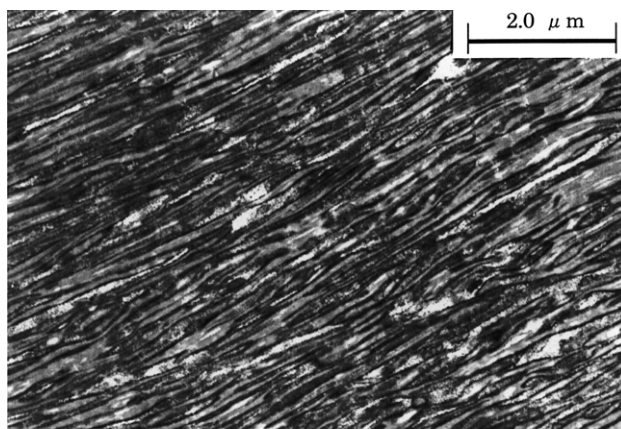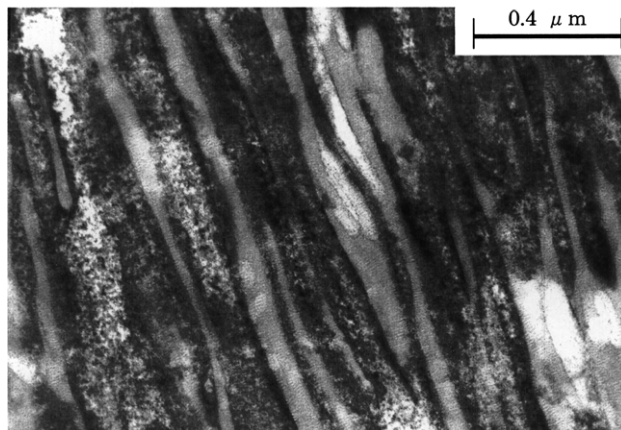Fig. 5 shows a typical plot of the normalized linear
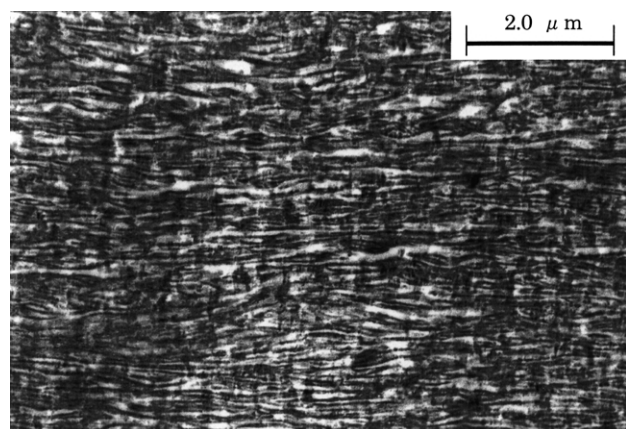
(a)
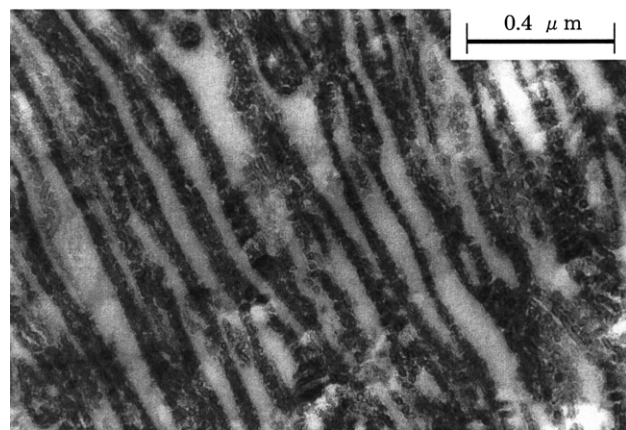
(b)

Fig. 2. TEM micrographs of injection-molded PA alloys with 40 wt% m-SEBS. (a) × 10,000; (b) × 50,000.

(a)

(b)

Fig. 3. TEM micrographs of injection-molded PA alloys with 40 wt% m-EPR. (a) × 10,000; (b) × 50,000.

thermal expansion for press-molded PP/EPR (40 wt%) was isotropic and its CLTE is 16.2×10^{-5}/°C. It is clear that the specimen formed by injection molding has a low CLTE in FD and TD and a very high CLTE in ND compared with those of the press-molded samples. The bulk expansion coefficient is 48.6×10^{-5}/°C for the press-molded sample and 47.8×10^{-5}/°C for the injection-molded one, which is calculated by adding the linear coefficients in the three directions, i.e. $\gamma = \alpha_{FD} + \alpha_{TD} + \alpha_{ND}$. These results strongly demonstrate that: (1) injection molding can greatly reduce the CLTE of PP/EPR alloys in FD and TD; (2) injection molding does not change the bulk expansion coefficient; and (3) the great reduction of the CLTE in FD and TD for injection-molded polymer alloys occurs because of the high expansion in the thickness direction (ND).

Fig. 6 shows the rubber concentration dependence of the CLTE for various polymer alloys in FD. It can be seen that, compared to the linear increase in CLTE for press-molded PA/m-EPR blends (Fig. 6(a)), the CLTE of the injection-molded samples drastically decreases when the m-EPR concentration is higher than 40 wt%. Note that the CLTE for
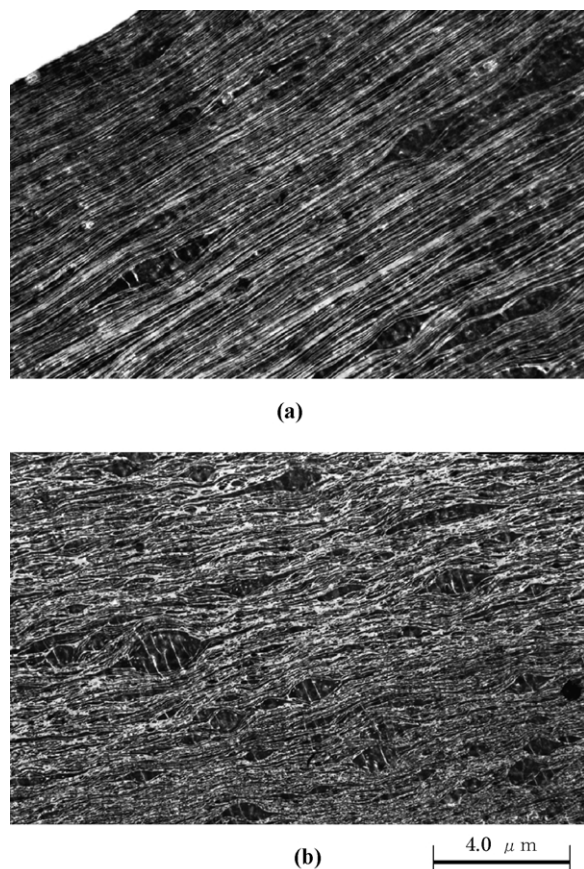

Fig. 4. TEM micrographs of injection-molded PP alloys with 40 wt% EPR. (a) observed in the edge direction; (b) observed in the end direction.

expansion (dL/L) in three directions as a function of temperature for injection-molded PP alloys with 40 wt% EPR. The average CLTE over a temperature range from 20 to 80 °C in FD, TD and ND was calculated to be 6.3×10^{-5}/°C, 6.8×10^{-5}/°C and 34.7×10^{-5}/°C, respectively. The

$$\alpha_{FD} = 6.3 \times 10^{-5} \text{ /°C}$$
$$\alpha_{TD} = 6.8 \times 10^{-5} \text{ /°C}$$
$$\alpha_{ND} = 34.7 \times 10^{-5} \text{ /°C}$$
$$\alpha_{Press} = 16.2 \times 10^{-5} \text{ /°C}$$
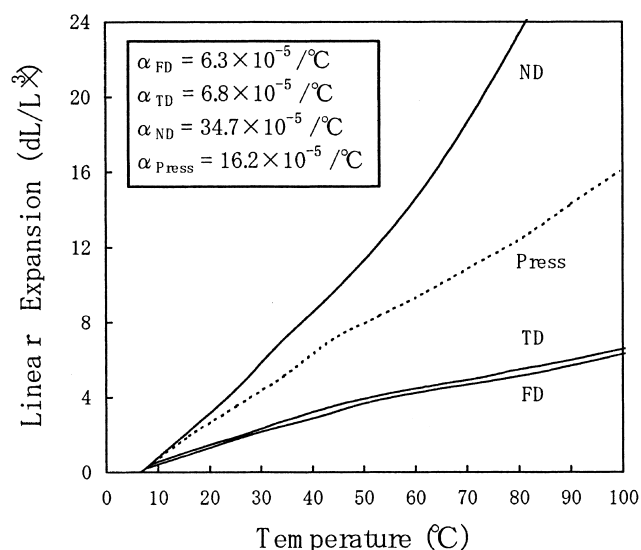
Fig. 5. Temperature dependence of the linear expansion for injection-molded and press-molded PP/EPR (40 wt%) in different directions.
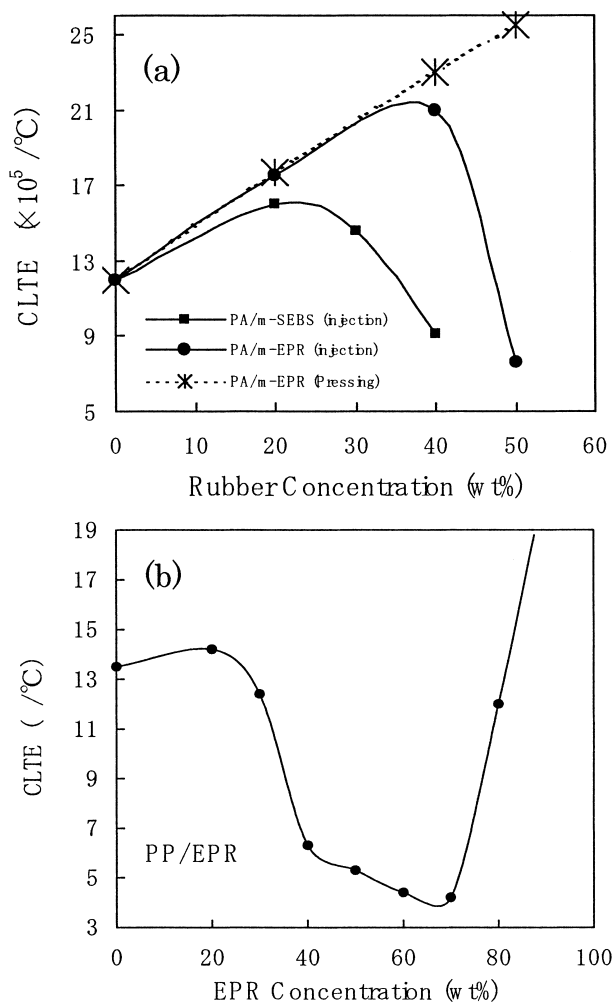

Fig. 6. Rubber-concentration dependence of the CLTE in the flow direction (FD) for injection-molded (a) PA/m-EPR and PA/m-SEBS and (b) PP/EPR.

the 50 wt% m-EPR specimen is about three times lower than that of the press-molded one, and this value is nearly one-half of the PA. A similar tendency is observed for PA/m-SEBS alloys, except for a lower rubber concentration necessary for the drastic reduction of CLTE. The increase in CLTE at low concentrations should be attributed to the noncontinuous rubber domains in the plastic matrices, though they were also deformed into microlayers during the injection molding.

Fig. 6(b) shows the variation of CLTE for PP/EPR alloys over the entire EPR concentration range [16]. A 'well-shaped' curve is observed where the CLTE increases at concentrations lower than 20 wt% and then experiences a significant decrease with EPR concentrations from 20 to 70 wt%. For samples with the concentration higher than 70 wt%, the CLTE rapidly increases to EPR value $(30 \times 10^{-5}/°C)$ due to a phase inversion of EPR domains into the matrix as detected by TEM. Thus, by the addition of EPR rubber, the CLTE of PP can be reduced from $13.5 \times 10^{-5}/°C$ to $4.3 \times 10^{-5}/°C$. It is worth pointing out that the latter value is lower than that of 30 wt% talc-filled PP composites $(5.0 \times 10^{-5}/°C)$ and is comparable with 30 wt% glass fiber filled PP $(3.5 \times 10^{-5}/°C$, in FD) and aluminum metals $(2.4 \times 10^{-5}/°C)$ [17].

Further experimental results demonstrated that the reduction of CLTE was significantly influenced by the viscosity ratio and the interfacial adhesion between the rubber and the plastic. As shown in Fig. 7, a decrease in the viscosity ratio and the interfacial adhesion between the rubber and the plastic leads to a lower CLTE of the polymer alloy. This is significant because a polymer component with a lower viscosity and interfacial adhesion is easier to deform into microlayers during the injection molding [18]. It is found in Fig. 7(a) that there exists a critical value of the viscosity ratio, lower than that the CLTE reduces drastically. This should be related to a phase inversion in the polymer alloy. According to Paul and Barlow [19,20], a low viscosity ratio of rubber to plastic will reduce the critical rubber concentration necessary for evolution from a 'sea-island' structure to a co-continuous two-phase morphology. Therefore, the different critical rubber concentration, where the CLTE starts to reduce drastically, among PA/m-EPR, PA/m-SEBS and PP/EPR should partially be attributed to their different viscosity ratio.

The thickness of the plastic domains is another influencing factor. It can be expected that thinner 3-D continuous plastic layers should result in a lower CLTE in FD and TD. This may partially explain the continuous reduction of CLTE for PP/EPR in a rubber concentration range from 40 to 70 wt%. Because of this, the relationship between the CLTE and the interfacial adhesion was found to be quite complex. A low interfacial adhesion might be good for microlayer deformation, however, this accompanies with a poor compatibility between the two polymers, resulting in big domains either for the rubber or for the plastic.

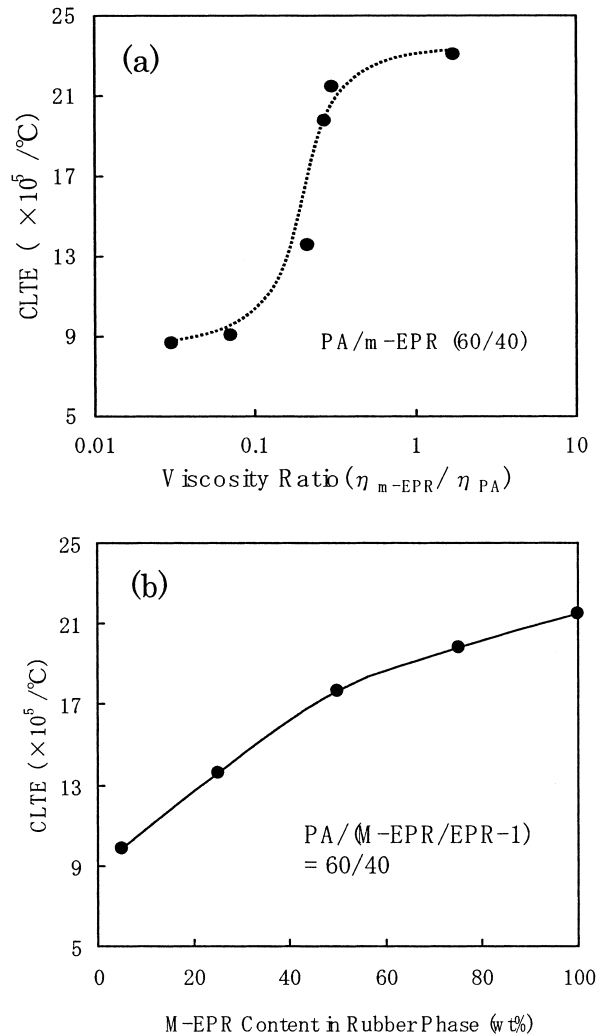It is natural to consider whether or not the reduction of

Fig. 7. Influence of (a) viscosity ratio and (b) interfacial adhesion between the rubber and plastic on the CLTE of injection-molded PA alloys with 40 wt% m-EPR. To change the interfacial adhesion, EPR-1 was blended with m-EPR.

CLTE arises from an orientation of the plastic chains and thus the orientation of its crystalline structure during the injection molding [5,21]. Two experimental facts can clarify the question. One is that the large reduction of CLTE requires co-continuous microlayers either for the rubber or for the plastic as shown in Fig. 6. However, this is not the necessary condition for the orientation of the polymer chains or the crystalline structure. Another fact is that we did not find a remarkable reduction of CLTE in PA/high-density polyethylene (HDPE) and PP/HDPE alloy systems. As we known, HDPE has a polymer chain near to EPR, and PA/HDPE and PP/HDPE blends are easy to deform into co-continuous microlayers during injection molding. If the reduction of CLTE is mainly due to the orientation of the polymer chains and the polymer crystalline structure, then the reduction should also take place in these systems. In our view, no remarkable reduction of CLTE occurs in these systems because HDPE has a value of thermal expansion

coefficient and Young's modulus comparable to those of PA and PP; accordingly, there is no driving force to reduce the CLTE.

Finally, we have to mention that the co-continuous microlayer morphology mainly existed near the skin portion in the injection-molded polymer alloys. In the core part, the polymer domains are less oriented. This is the so-called skin-core effect. The reduction of CLTE should arise from the skin constraints in the 'skin-core-skin sandwich' structure. It is believed that with decreasing the thickness of injection-molding specimens and thinning the un-orientated portion, the thermal expansion coefficient of the polymer alloys in FD and TD should be further reduced to a very low value.

5. Conclusions

We discovered that the CLTE of injection-molded polymer alloys could be significantly reduced by addition of a rubber component. The reduction was not due to the suppression of the bulk expansion coefficient, but to the control of the thermal expansion anisotropically toward the thickness direction. It was confirmed that 3-D co-continuous microlayer morphologies both for the plastic and rubber are essential for constraining the expansion along FD and TD.

As mentioned previously, rubber is often used as an impact modifier. The reduction in CLTE by the addition of rubber provided a substantial way to design polymer alloys having high impact resistance and low thermal expansion coefficient simultaneously, which is of great importance in practical applications.

Acknowledgements

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