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Article

Structural Evolution of Two-phase Blends of Polycarbonate and PMMA by Simultaneous Biaxial Stretching

Takumi Kobayashi[1] and Hiromu Saito[1]*

[1] Department of Organic and Polymer Materials Chemistry; Tokyo University of Agriculture and Technology; Koganei-shi, Tokyo 184-8588; Japan
* Correspondence: hsaitou@cc.tuat.ac.jp

Abstract: We investigated the structural evolution of the two-phase blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) at various blend compositions by simultaneous biaxial stretching using optical microscopy and SEM observation. The spherical PMMA domains and PC matrix in 30/70 PC/PMMA were enlarged uniformly at all in-plane direction, while the anisotropic-shaped co-continuous structure in 50/50 PC/PMMA was deformed to crosshatched one by in-plane bimodal orientation. In 70/30 PC/PMMA, the phase inversion was found to occur by simultaneous biaxial stretching; i.e., the spherical PMMA domains were changed to crosshatched matrix by in-plane bimodal orientation due to coalescence of the PMMA domains during the stretching. Owing to the phase inversion, the surface hardness estimated by pencil hardness test became harder from 2B to 2H with increasing the strain from 1.0 to 2.0.

Keywords: Biaxial stretching; blend; polycarbonate; PMMA; phase inversion; surface hardness

1. Introduction

Biaxially stretched polymer films are often used as packaging materials for food and industrial products because the mechanical and gas barrier properties can be improved by biaxial stretching in the manufacturing process [1]. The structure of polymer films obtained by biaxial stretching are investigated in various aspects [2-34]. Isotropic plane film can be produced by simultaneous biaxial stretching in which films are stretched to X and Y directions at the same time, so that the properties of the stretched specimen thus produced are isotropic in the in-plane direction [19,29,31]. This indicates that uniform orientation at all in-plane direction is caused by simultaneous biaxial stretching; i.e., polymer chains and crystalline lamellae are uniformly oriented at all in-plane direction. The *in-situ* polarized infrared spectroscopic study by Nitta et al. suggests that molecular chain is elongated uniformly at all in-plane direction by simultaneous biaxial stretching of isotropic polypropylene [24,33]. Though the uniform orientation without preferred orientation is considered in the simultaneous biaxial stretching, bimodal orientation to the stretching directions of X and Y is also suggested by wide angle x-ray diffraction study in crystalline polymers such as polyethylene terephthalate (PET) and polyethylene naphthalate [4,29]. However, it is difficult to clarify the bimodal orientation of the structure in neat polymers because of the difficulty for the observation of the stretched structure.

In this paper, to observe the stretched structure obtained by simultaneous biaxial stretching, we investigated the evolution of the two-phase structure of polymer blends by simultaneous biaxial

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stretching using optical microscopy and SEM observation. When the two-phase structure obtained after simultaneous stretching is isotropic, it is considered that the domain structure is enlarged uniformly at all in-plane direction, for instance. We chose the blends of bisphenol-A-polycarbonate (PC) and poly(methyl methacrylate) (PMMA) because various two-phase structure having a size of micrometer scale can be obtained at different blend composition; e.g., spherical domain structure is obtained at 30/70 composition while co-continuous structure is obtained at 50/50 composition. Hence, various structural evolution by simultaneous biaxial stretching can be observed by the microscopic observation. The result of the surface hardness estimated by the pencil hardness test was also presented to discuss the structure change by stretching.

2. Materials and Methods

The PC and PMMA specimens used in this study were commercial polymers. The PC was bisphenol-A polycarbonate supplied by Mitsubishi Gas Chemical Company, Inc; Iupilon S-2000N, Mw = 2.4 x 10^4 g mol^{-1}. PMMA was supplied by Kurarey Co., Ltd; Parapet G, Mw = 1.0 x 10^5 g mol^{-1}.

PC and PMMA were melt-mixed at temperature of 250 °C and at rotor speed of 90 rpm for 5min in a mixing chamber of a miniature mixing machine (Imoto IMC-18D7). The melt mixed blend was extruded and chopped into pellets. The pellets were then melt pressed in a vacuum hot-press machine (Imoto IMC-11FD) at 250 °C and 10 MPa for 5 min to obtain the unstretched film with a thickness of about 100 μm and then was cooled to room temperature. The unstretched film was cut into square-shaped specimen of 65 mm × 65 mm to employ the biaxial stretching.

Biaxial stretching was performed by a biaxial stretcher equipped with a temperature controller (IMC-1A94, Imoto Machinery Co., Ltd.). The film specimen was gripped on each side by 2 pairs of 5 clamps (Figure 1) and the initial gauge area before stretching was 50 mm x 50 mm. Then the specimen was heated to 140 - 160 °C, which was about 10 °C higher than the glass transition temperature of the blends. After keeping the heating temperature for 5 min, the specimen was biaxially stretched to various draw ratios at a draw speed of 100 mm min^{-1} by moving the clamps simultaneously in two stretching directions (X and Y directions as shown by arrows in Figure 1) at the same speed and to the same draw ratio. Then the stretched specimen was cooled to room temperature for the observation.

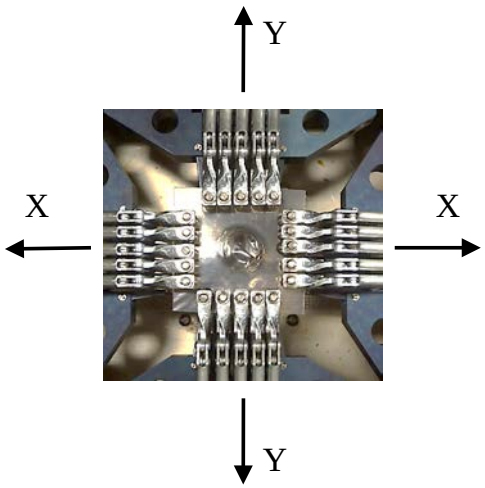

Figure 1. Photograph of clamps in a biaxial stretcher.

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Phase structure of the blends was observed under unpolarized optical microscope and also a polarized optical microscope (Olympus BX53-P) equipped with charge-coupled device (CCD) camera (Olympus DP73). The structure under polarized optical microscope was observed by the optical microscope equipped with a sensitive tint plate having an optical path difference of 530 nm under crossed polarizers P and A. Here, the optical axis of polarizer was rotated at 45° to the stretching directions of X and Y, and that of the sensitive tint plate (ST).

The phase structure of the blend was also observed under a scanning electron microscope (SEM) (Hitachi S2100A) with an accelerating voltage of 20 kV. In order to observe the surface and cross section of the blend specimen, the PMMA component was etched by 2-butanone for 3 h at room temperature, and the PC one was etched by sodium hydroxide (NaOH) solution (30wt% NaOH) for 48 h. For SEM observation, the etched specimen was sputter coated with platinum using a sputter system (JEOL JFC-1300).

The surface hardness of the blend specimen was estimated by pencil hardness test according to ISO 15184. A graphite pencil was drawn on the film specimen with uniform pressure and maintaining the pencil at a constant angle of 45 °. The surface hardness was determined using pencils of various degrees of hardness by judging whether indentation was caused or not; i.e., the specimen was judged as harder than pencil hardness when no indentation was seen.

3. Results and Discussion

Figure 2 shows unpolarized and polarized optical micrographs of 30/70 polycarbonate (PC)/poly(methyl methacrylate) (PMMA) obtained by simultaneous biaxial stretching at draw ratio λ of 1.5 ($\lambda = 1.5$) and the unstretched blend ($\lambda = 1.0$). Spherical PC domains with diameter of several micrometers were dispersed in the PMMA matrix at $\lambda = 1.0$ (Figure 2a). The spherical domain became larger without change of the shape and the domain distance became longer by simultaneous biaxial stretching (Figure 2b), indicating that the two-phase structure of the spherical domain and matrix is enlarged uniformly at all in-plane direction. In spite of the enlargement of the two-phase structure, change of the interference color was small by stretching (Figure 2b'), indicating that the deformed structure was optically isotropic in spite of the stretching. These results suggest that the two-phase structure of the spherical domain and matrix is elongated uniformly at all in-plane direction without preferred orientation by simultaneous biaxial stretching. The results are consistent with those demonstrated in neat polymers such as polypropylene, poly(lactic acid) and poly(ethylene terephthalate) in which the stretched specimen exhibits optically isotropic due to uniform deformation without preferred in-plane orientation by simultaneous biaxial stretching [19,29,31].

Co-continuous two-phase structure was obtained in 50/50 PC/PMMA. The change of the co-continuous two-phase structure by simultaneous biaxial stretching is shown in Figure 3. The size of the co-continuous structure became larger by stretching (Figures 3a and 3b). The interesting result here is that blue and yellow interference color appeared, and crosshatched pattern was seen in the stretched blend under the polarized optical microscopy (Figure 3b'), indicating that the component phase is optically anisotropic and the anisotropic-shaped phase is formed along the crosshatched structure. The change and enlargement of the phase structure might be attributed to the evolution of the liquid-liquid phase separation as discussed later in the results of 70/30 PC/PMMA. Blue and yellow interference colors were seen along the crosshatched structure which was elongated to X and

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Y stretching directions. These results suggest that anisotropic-shaped domain is deformed to X and Y stretching directions by in-plane bimodal orientation to yield crosshatched structure.

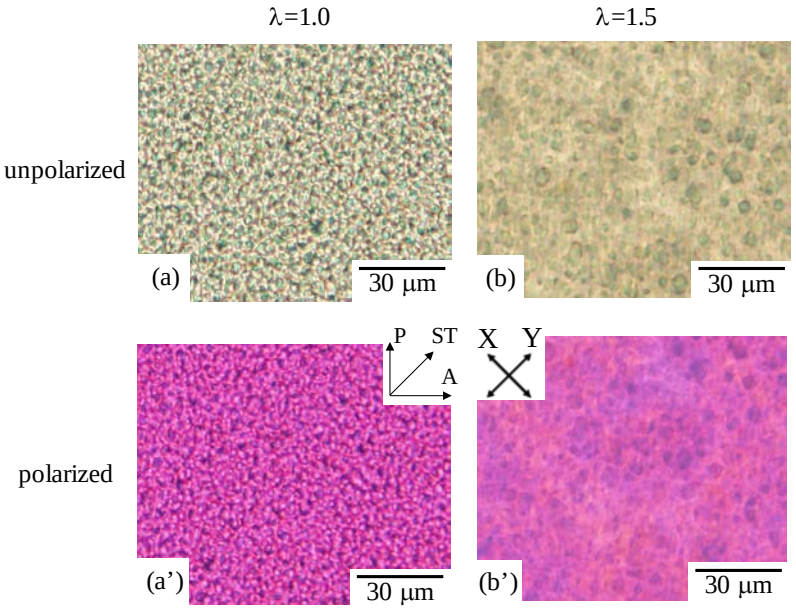

Figure 2. Unpolarized and polarized optical micrographs of 30/70 PC/PMMA obtained by simultaneous biaxial stretching at draw ratios λ of 1.0 and 1.5.

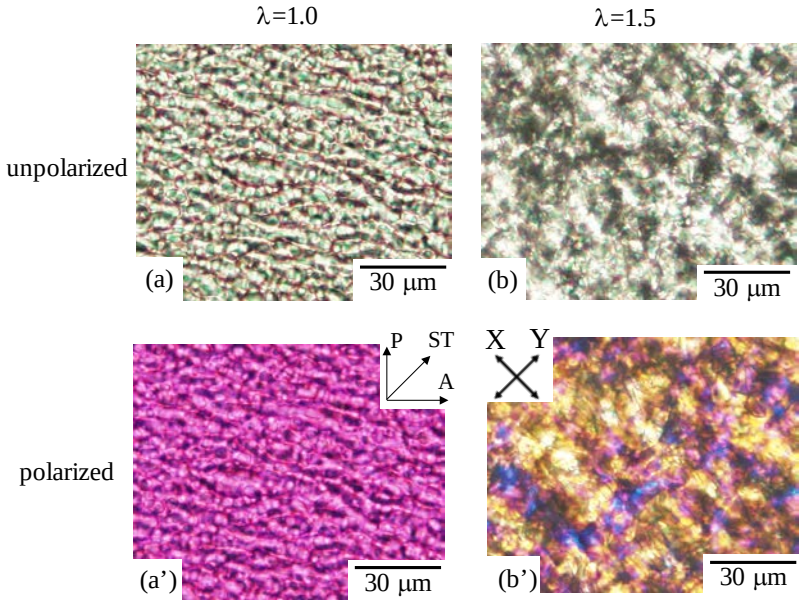

Figure 3. Unpolarized and polarized optical micrographs of 50/50 PC/PMMA obtained by simultaneous biaxial stretching at draw ratios λ of 1.0 and 1.5.

Figure 4 shows the schematic illustration for the deformation of two-phase structure of PC/PMMA blends by simultaneous biaxial stretching. The symmetric spherical domain is deformed uniformly at all in-plane direction without preferred orientation by stretching (Figure 4A). On the other hand, co-continuous two-phase structure consist of unsymmetric anisotropic-shaped domain and long axis of the anisotropic shaped domain is rotated to X and Y stretching directions, and the domains are deformed by in-plane bimodal orientation (Figure 4B).

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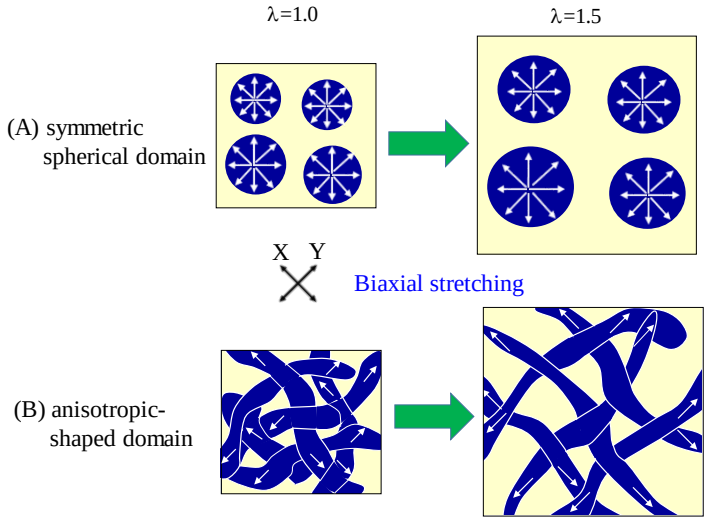

Figure 4. Schematic illustration for the deformation direction of two-phase structure by simultaneous biaxial stretching.

In 70/30 PC/PMMA, characteristic change of the two-phase structure occurred as shown in Figure 5. Two-phase structure of PMMA spherical domains dispersed in the PC matrix was seen in the unstretched blend (Figure 5a). Though the phase structure with spherical domains was similar to that observed in Figure 2 for 30/70 PC/PMMA, the structural evolution by stretching was quite different in 70/30 PC/PMMA. Spherical shape of the PMMA domains changed to the anisotropic-shaped one (Figures 5b and 5c). Blue and yellow interference color appeared, and crosshatched pattern was seen under the polarized optical microscopy (Figures 5b' and 5c'), indicating that the component phase is optically anisotropic and the anisotropic-shaped phase is formed along the crosshatched structure, though deformed structure was optically isotropic and no change of the spherical shape was seen in 30/70 PC/PMMA. The change and enlargement of the phase structure observed in 70/30 PC/PMMA might be attributed to the evolution of the liquid-liquid phase separation. Crosshatched structure consisting of long fibrils with different interference colors was observed at λ = 2.0. Blue and yellow interference color was seen along the crosshatched structure which was elongated to X and Y stretching directions (Figure 5c'), as observed in Figure 3 for 50/50 PC/PMMA. The interference color for the fibrillar structure aligned in Y direction was yellow. Considering that the optical axis of sensitive tint plate (ST) is parallel to Y direction, yellow is a subtractive interference color caused by a component polymer of the blends having a negative birefringence [35]. Since PMMA has negative birefringence by orientation while PC has positive one [36], PMMA domain was deformed uniaxially to X and Y stretching direction with in-plane bimodal deformation to yield crosshatched structure by simultaneous biaxial stretching.

Figure 6 shows SEM micrographs of the surface of 70/30 PC/PMMA obtained by simultaneous biaxial stretching which correspond to the optical micrographs shown in Figure 5. Since SEM observation was carried out after extraction of PMMA phase by etching with 2-butanone, the remaining material was PC. Thus spherical holes with diameter of several micrometers seen in Figure 6a are assigned to PMMA domain while white matrix is assigned to PC matrix. This indicates that PMMA domain is dispersed in PC matrix in the unstretched blend. Spherical domain of PMMA

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changed to ellipsoidal or fibrillar one, and the aspect ratio increased to X and Y direction with increasing draw ratio (Figure 6b). This result supports the result demonstrated in Figure 5 that spherical PMMA domains are elongated to X and Y stretching directions by bimodal in-plane orientation. At $\lambda = 2.0$, crosshatched network structure was formed in PMMA phase (Figure 6c). That is, phase inversion occurred by simultaneous biaxial stretching; i.e., PMMA spherical domain was inverted to the crosshatched network matrix. To our knowledge, this is the first study to observe the phase inversion by two-phase polymer blends. The phase inversion might be caused by the coalescence and aggregation of PMMA domains owing to the Ostwald ripening [37] due to evolution of the liquid-liquid phase separation by stretching, as demonstrated in the following.

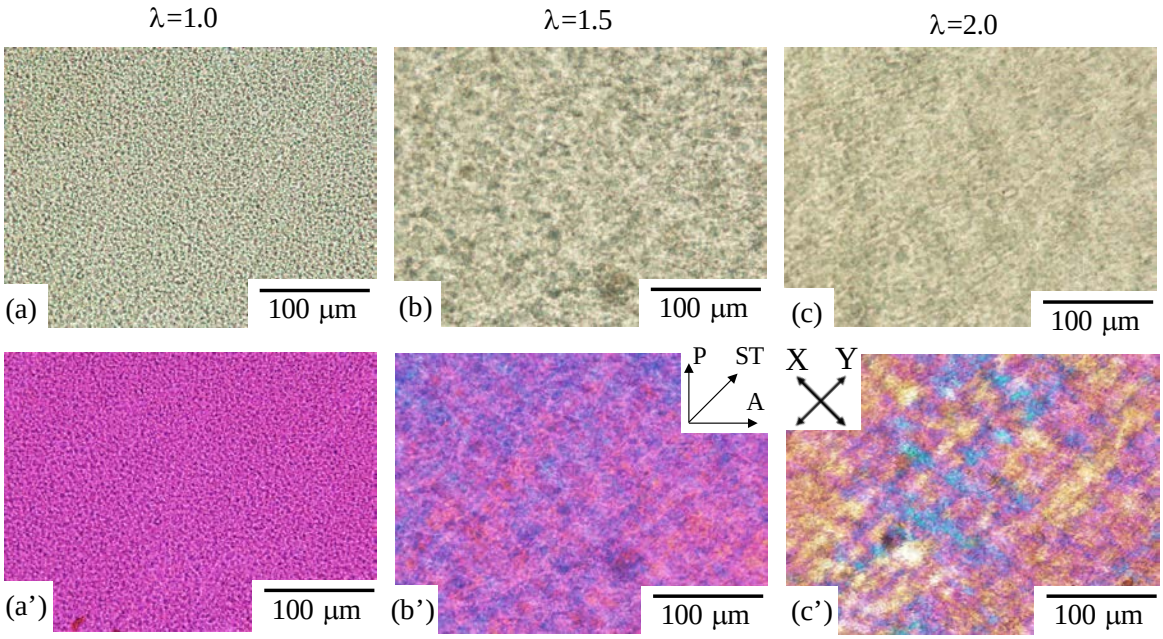

Figure 5. Unpolarized and polarized optical micrographs of 70/30 PC/PMMA obtained by simultaneous biaxial stretching at various draw ratios λ. Uppers are optical micrographs and lowers are polarized optical micrographs.

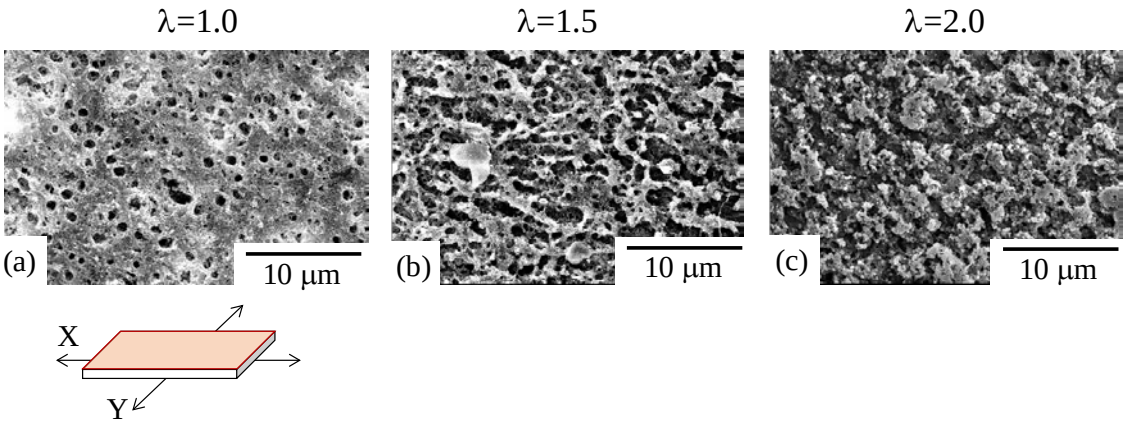

Figure 6. SEM micrographs of the surface of 70/30 PC/PMMA obtained by simultaneous biaxial stretching at various draw ratios λ.

Figure 7 shows SEM micrographs of the cross section of 70/30 PC/PMMA. Since SEM observation was carried out after extraction of PC phase by etching with NaOH, the remaining material was PMMA. Spherical domain of PMMA changed to ellipsoidal or fibrillar one in which the

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major axis of domain is parallel to the plane of films by stretching (Figure 7a). This is consistent with the in-plane orientation and stretch-thinning in the normal thickness direction suggested in the simultaneously biaxial stretched films [19,29,31]. PMMA domains were then aggregated in the thickness direction and the elongated domains became thicker in the thickness direction by the biaxial stretching (Figure 7b). These results suggest that coalescence and aggregation of PMMA domains occurred by simultaneously biaxial stretching. Thus phase inversion from PMMA domain to PMMA matrix by simultaneous biaxial stretching demonstrated in Figurer 6 is attributed to the coalescence and aggregation of PMMA domains. Such coalescence and aggregation of PMMA domains might be caused by the Ostwald ripening [37] due to evolution of the liquid-liquid phase separation by stretching.

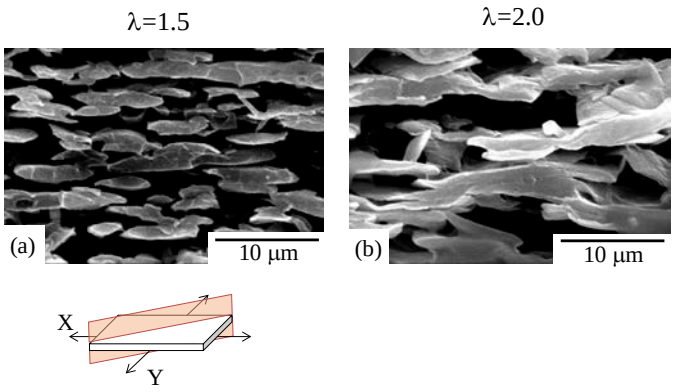

Figure 7. SEM micrographs of the cross section of 70/30 PC/PMMA obtained by simultaneous biaxial stretching at draw ratios λ of 1.5 and 2.0.

Figure 8 shows the schematic illustration for the structural evolution of 70/30 PC/PMMA during simultaneously biaxial stretching. Spherical PMMA domains dispersed in the PC matrix are deformed to ellipsoidal one in X and Y stretching directions. The ellipsoidal domains are coalesced and aggregated by the Ostwald ripening due to the evolution of the liquid-liquid phase separation. Owing to the aggregation of the ellipsoidal PMMA domains, long fibrillar PMMA domains are formed in the X and Y stretching directions by bimodal in-plane orientation. Simultaneously, PMMA domain is rotated in the in-plane projection and is squashed in the thickness direction by stretch-thinning. Due to the aggregation of the biaxially deformed PMMA domains, PMMA domains are inverted to crosshatched matrix.

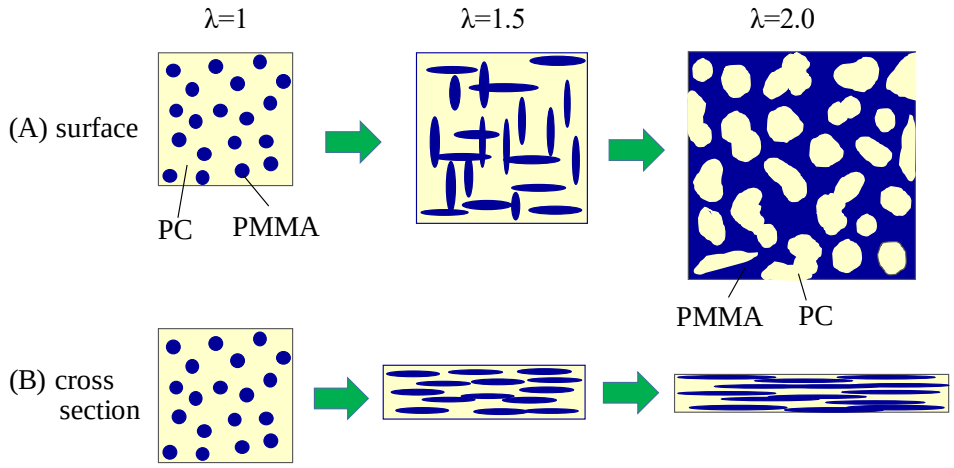

Figure 8. Schematic illustration for the structure change of 70/30 PC/PMMA by simultaneous biaxial stretching.

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Figure 9 shows the surface hardness of the unstretched PC/PMMA films at various blend compositions. Here the surface hardness was estimated by the pencil hardness test. The surface hardness of neat PC and neat PMMA was 4B and 4H, respectively. As shown in Figures 2 and 5, the matrix in 30/70 PC/PMMA and 70/30 PC/PMMA was PMMA and PC, respectively. Hence, the surface hardness of the blends became harder by increasing the amount of PMMA at the surface with the increase of the composition of PMMA.

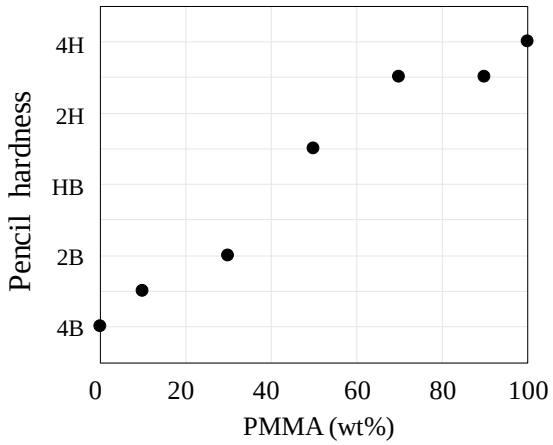

Figure 9. Surface hardness of unstretched PC/PMMA blends at various compositions.

Figure 10 shows the surface hardness of 70/30 PC/PMMA film obtained by simultaneous biaxial stretching at various draw ratios. The surface hardness became harder with increasing draw ratio, e.g., the pencil hardness was 2B at λ = 1.0, HB at λ = 1.5 and 2H at λ = 2.0. By combining the results of Figure 9, the surface hardness of the blend at λ = 1.5 and λ = 2.0 was close to that of 50/50 PC/PMMA and 30/70 PC/PMMA, respectively. The change of the surface hardness in 70/30 PC/PMMA by biaxial stretching is attributed to the increase of the amount of PMMA at the surface by structure change from the PMMA domain dispersed in the PC matrix to the PC domain dispersed in the PMMA matrix during the stretching. This result confirms the phase inversion of the blend by simultaneous biaxial stretching demonstrated in Figures 5-8.

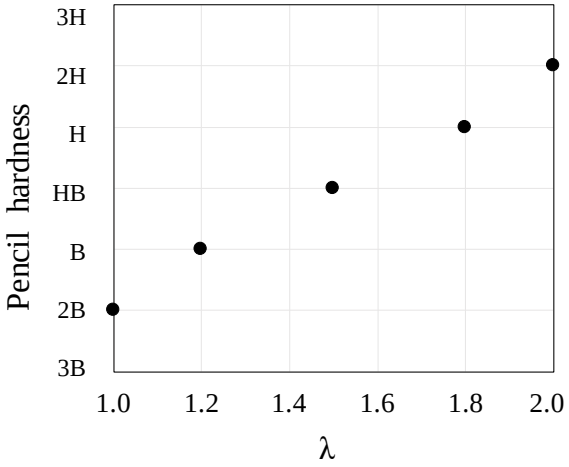

Figure 10. Surface hardness of 70/30 PC/PMMA obtained by simultaneous biaxial stretching at various draw ratios λ.

5. Conclusions

We found characteristic structural evolution in the two-phase blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) by simultaneous biaxial stretching. The phase structure was enlarged at all directions without preferred deformation when the symmetric spherical PC domains were dispersed in the PMMA matrix in 30/70 PC/PMMA, while anisotropic-shaped co-continuous structure was deformed to yield crosshatched one in 50/50 PC/PMMA. On the other hand, in 70/30 PC/PMMA, the phase inversion occurred from the spherical PMMA domains to the crosshatched PMMA network matrix by in-plane bimodal orientation due to coalescence and aggregation of the PMMA domains during the biaxial stretching. Owing to the phase inversion, the pencil hardness became harder from 2B to 2H due to the increase of the amount of PMMA at the film surface by the simultaneous biaxial stretching.

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Conflicts of Interest: The authors declare no conflict of interest.

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