Structural change of polymethylmethacrylate/poly(vinylidene fluoride) blends

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Introduction

In miscible polymer blends, it has been recently reported that gradient structure is formed by applying temperature gradients or velocity gradients during processing.[1-5] The gradient structure in polymers refers to a structure in which a compositional gradient is formed inside the material, with regions of high and low concentrations of one of the components. By forming a gradient structure, it becomes possible to enhance the concentration of a specific polymer on the surface of the material, leading to a potential to improve surface properties and a reduction in stress during injection molding. Additionally, for amorphous polymers, desirable surface properties can be imparted while maintaining transparency.

The formation of gradient structures in miscible polymer blends under a temperature gradient was reported by Sako et al.[1] It is known that polymethylmethacrylate (PMMA) is miscible with polycarbonate (PC) with low molecular weight. When such blends are exposed to a temperature gradient, the concentration of the low-molecular-weight component becomes higher on the high-temperature side. This is considered to occur because the low-molecular-weight component, which is rich in chain ends, requires a larger free volume and thus tends to segregate toward the high-temperature side. Furthermore, segregation of low-molecular-weight components to the surface under a velocity gradient has also been reported by Sako et al.[4] This phenomenon is considered to occur by stabilizing the flow field. When a low-vis material is rich in the high shear rate region, the whole stress decreases. Products obtained using these methods have been shown to maintain transparency while forming a concentration gradient without phase separation.

However, the formation of concentration gradients in miscible polymer blends by applying a temperature gradient has only been reported for blends of PC and PMMA, where one of the components has a low molecular weight.

Therefore, in this study, I investigated to confirm the formation of gradient structure by applying temperature or velocity gradients using another miscible polymer blend, i.e., PMMA and poly(vinylidene fluoride) (PVDF)[6-8].

Experimental

1) Materials

In this study, commercially available PMMA (ACRYPET™ VH; Mitsubishi Chemical, Tokyo, Japan) was used as the high molecular weight polymer, and PVDF (Kynar 705; Arkema, Colombes, France) was used as the low molecular weight polymer. The number-average molecular weight (M_n) of PMMA is 58,000, and the weight-average molecular weight (M_w) is 120,000. The molecular weights of PVDF are M_n = 42,800 and M_w = 83,100.

2) Sample preparation

PMMA was vacuum-dried at 80°C for 4 hours and then melt-blended using an internal mixer (Labo Plastmill™; Toyo Seiki Seisakusyo, Tokyo, Japan) at 250°C for 3 minutes. The blade rotation speed was 30 rpm. The blend ratios of PMMA to PVDF were 90/10, 80/20, 70/30, and 60/40 in weight ratios. The blend was compression-molded into films using a compression molding machine (SA303IS; Tester Sangyo, Saitama, Japan) at 250°C with spacers of 0.5 mm and 1.0 mm thickness and a 10 cm square frame. The 1 mm-thick films were prepared under a temperature gradient by setting the upper plate of the compression molding machine to 250°C and the lower plate to 200°C. The films were then immediately cooled to 25°C.

PMMA/PVDF (70/30) blends were extruded using a capillary rheometer (RH7, NETZSCH) with the barrel temperature set at 210°C. A rectangular die (length: 16 mm; width: 10 mm (W) gap 0.5 mm (H)) was attached to the extruder's tip, forming film-like strands. The shear rates were set at 4.7 s^{-1}, 12.5 s^{-1}, 33.3 s^{-1}, and 88.6 s^{-1}, respectively.

3) Measurements

The angular frequency dependence of the dynamic shear modulus was assessed using a cone-plate rheometer (MCR301; Anton Paar, Graz, Austria). The cone angle was 2°, and the diameter was 25 mm. Measurements were conducted at temperatures of 200°C and 250°C.

The thermal properties were evaluated using a differential scanning calorimeter (DSC) (DSC8500; PerkinElmer, Waltham, MA, USA). Approximately 7 mg of each sample was sealed in an aluminum pan and subjected to a temperature program under a nitrogen atmosphere. The temperature was first increased from 20°C to 200°C to remove the thermal history at a rate of 10°C/min and then cooled. Subsequently, the temperature was increased again from 20°C to 200°C at 10°C/min for the measurement.

The temperature dependence of the dynamic tensile modulus was evaluated using a dynamic mechanical analyzer (Rheogel-E4000; UBM, Muko, Japan). Test specimens, cut from the compression-molded films to dimensions of 10 mm (length) × 5 mm (width) × 0.5

mm (thickness), were used for the measurements over a temperature range from -80°C to 230°C at a heating rate of 2°C/min and a frequency of 10 Hz.

The surface composition of compression-molded and extruded films was analyzed by attenuated total reflection Fourier transform infrared (ATR-IR) spectroscopy using an FT-IR spectrometer (Spectrum 100; FT-IR spectrometer, PerkinElmer). For compression-molded films, KRS-5 (refractive index 2.5) was used as the ATR crystal. For extruded films, both KRS-5 and Ge (refractive index 4.0) were employed.

The cross-sectional composition in the thickness direction of compression-molded films was evaluated using a Fourier transform infrared microscope (Spectrum Spotlight 200 FT-IR Microscope; PerkinElmer) in the mapping mode. Films were prepared by cutting them into 10 μm-thick sections using a microtome, and a 188 μm × 188 μm area in the thickness direction was measured.

The blend composition of compression-molded films was also analyzed using energy-dispersive X-ray spectroscopy (EDS) coupled with field emission scanning electron microscopy (FE-SEM JSM-7100F/EDS JED-2300; Jeol, Akishima, Japan). The carbon, oxygen, and fluorine contents on the film surface and cross-sectional thickness direction were estimated.

The contact angle of the compression-molded films was measured using a contact angle meter (Drop Master DM 501; Kyowa Interface Science, Saitama, Japan). After cleaning the surface with ethanol, liquid droplets were applied to the surface. The test liquids were distilled water and diiodomethane.

Results and discussion

First, the miscibility of PMMA and PVDF used in this study was investigated. The master curves of the angular frequency dependence of G' and G'' for molten PMMA, PVDF, and PMMA/PVDF blends with ratios of 90/10, 80/20, 70/30, and 60/40 are shown in Fig. 1. The dynamic moduli of PVDF were lower than those of PMMA, and the blends exhibited intermediate values. When phase separation occurs, G' and G'' typically show higher values in the low-frequency region; however, such phenomena were not observed for any of the blends.

Additionally, when comparing the zero-shear viscosity (η_0) calculated from the slope of G'' at the same temperature, the viscosity of PVDF was approximately two orders of magnitude lower than that of PMMA at 200°C and about one order of magnitude lower at 250°C. Furthermore, it was confirmed that the η_0 values of the blends decreased as the PVDF content increased.

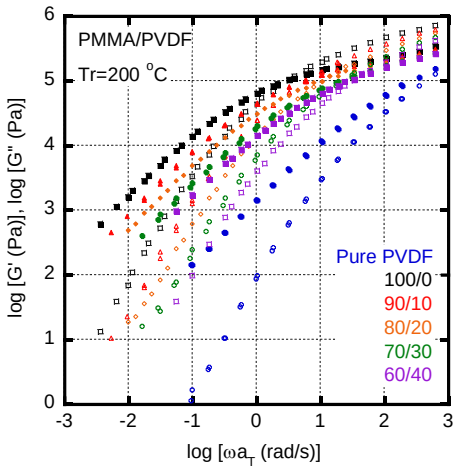

Fig. 1 Angular frequency dependence of (open symbols) shear storage modulus *G'* and (closed symbols) loss modulus *G"* of PMMA, PVDF, and their blends at the reference temperature T_r of 200°C.

The DSC heating curves for PMMA, PVDF, and their blends are shown in Fig. 2. The blends exhibited a single glass transition temperature (T_g), which decreased with increasing the PVDF concentration. Similar results were observed in the temperature dependence of tensile storage modulus (E') and tensile loss modulus (E") shown in Fig. 3, supporting the DSC findings. Additionally, the melting temperature (T_m) of PVDF, observed in pure PVDF, was not detected in either the DSC or the temperature dependence of dynamic tensile modulus for the blends. This is attributed to the inhabitation of the PVDF crystallization by PMMA. These results indicate that the blends used in this study are miscible.

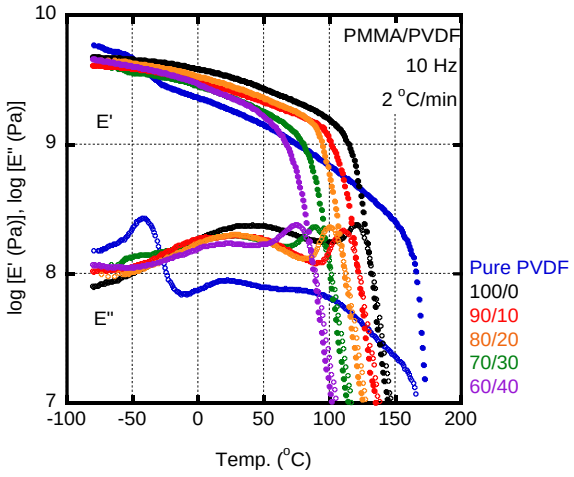

Fig. 2 Temperature dependencies of (closed symbols) tensile storage modulus *E'* and (open symbols) loss modulus *E"* obtained at 10 Hz of PMMA, PVDF, and their blends.

Structure after exposure to temperature gradient

The surface composition of PMMA/PVDF (70/30) subjected to a temperature gradient was analyzed using ATR-IR. Fig. 4 shows the ATR-IR spectra of the film after applying the temperature gradient for 200 minutes, normalized to the PMMA absorbance at 1720 cm^{-1} as unity. The absorbance of PVDF at 880 cm^{-1} was higher on the high-temperature side and lower on the low-temperature side.

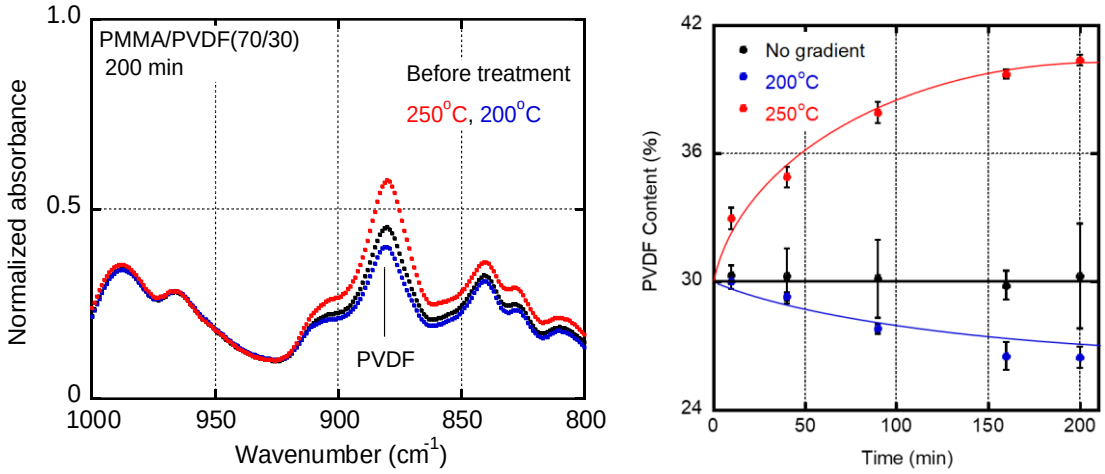

Fig. 4 (left) Normalized ATR-IR spectra of a 1 mm thick PMMA/PVDF (70/30) sample before/after exposure to the temperature gradient between 250 and 200°C.
(right) Growth curves of the PVDF content of the PMMA/PVDF (70/30) sample at both surfaces during exposure to the temperature gradient.

The PVDF concentrations on the high-temperature and low-temperature sides, calculated using a calibration curve, are shown in Fig. 5. When a temperature gradient was applied for 200 minutes, the PVDF concentration increased by approximately 10 % on the high-temperature side and decreased by approximately 3.5% on the low-temperature side. The significant change on the high-temperature side is believed to be due to a large diffusion coefficient.

The micro-FT-IR mapping at the cross-section of the blend, subjected to a temperature gradient for 200 minutes, is shown in Fig. 6. The PVDF concentration is indicated by the color; red for high concentration and blue for low concentration. It was revealed that a gradient structure was formed in the thickness direction of the film.

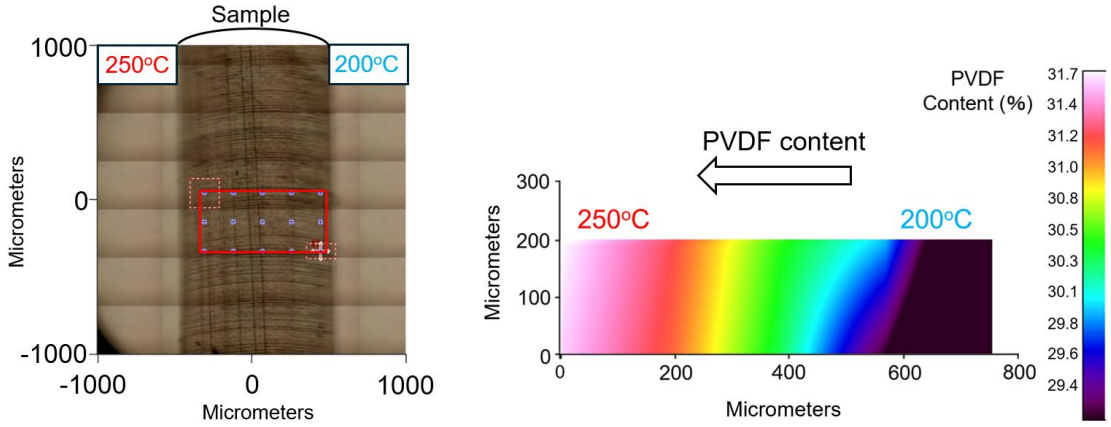

Fig. 6 (left) Measurement area, denoted as a red square, of the cross-section for micro-IR. The sheet was exposed to the temperature gradient for 200 min, and (right) distribution of the PVDF content in the thickness direction.

The PVDF content of the surface and cross-section of the blend subjected to a temperature gradient for 200 minutes, calculated using ATR-IR, micro-FT-IR, and EDS, is shown in Fig. 7. It was found that the PVDF concentration formed a gradient structure from the high-temperature side to the low-temperature side. The segregation on the surface was clearly observed.

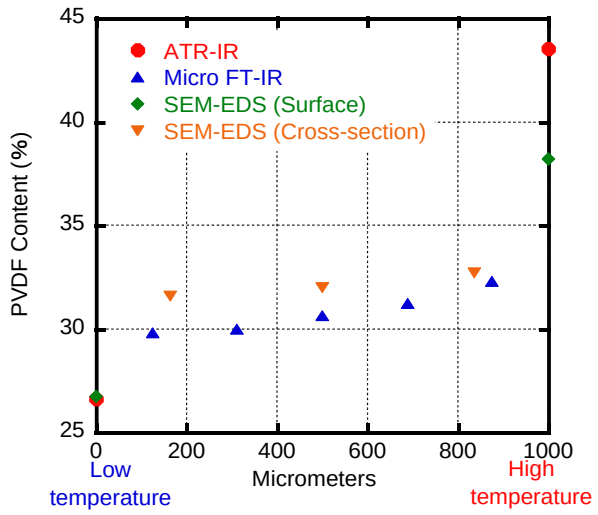

Fig. 7 Distribution of PVDF contents in the thickness direction: (circles) ATR-IR on the surface, (triangles) micro-IR, (diamonds) SEM-EDS on the surface and (inverted triangles) SEM EDS at the cross-section.

Surface properties

The contact angle measurements were performed to investigate the surface property modification by the temperature gradient. The results are shown in Fig. 8. The contact angle of PVDF was higher than that of PMMA, and the blend showed an intermediate value. The contact angle of the blend subjected to a temperature gradient for 200 minutes was larger on the high-temperature side and smaller on the low-temperature side, corresponding to the PVDF concentration.

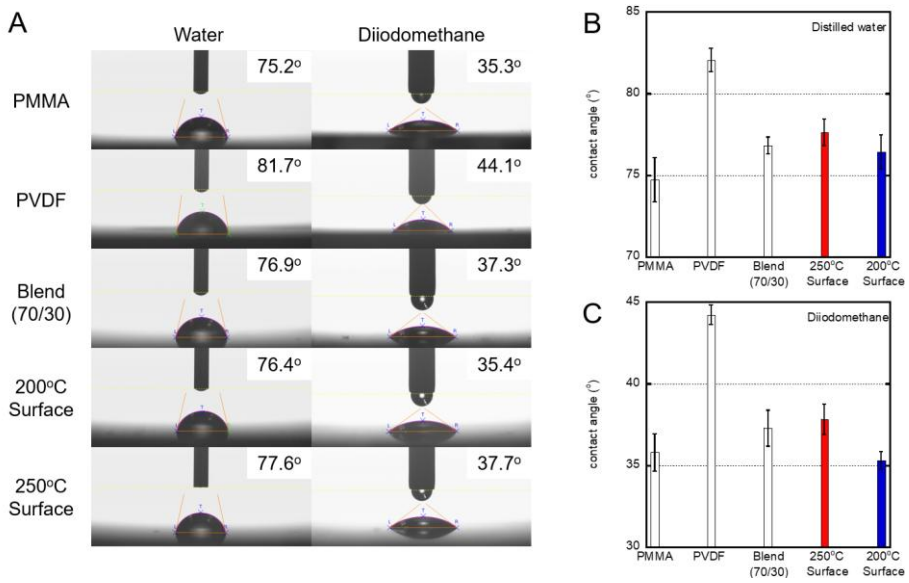

Fig. 9 (A) Contact angles of water and diiodomethane on the high- (250°C) and low-(200°C) temperature surfaces of the blend sheet after exposure to the temperature gradient for 200 min. As references, PMMA, PVDF, and PMMA/PVDF (70/30) prepared by compression-molding at 250°C are also shown.
(B) Contact angles with distilled water and (C) those with diiodomethane.

The surface free energy calculated from the obtained contact angles is shown in Fig. 9. By applying the temperature gradient, the surface free energy was lower on the high-temperature side and higher on the low-temperature side.

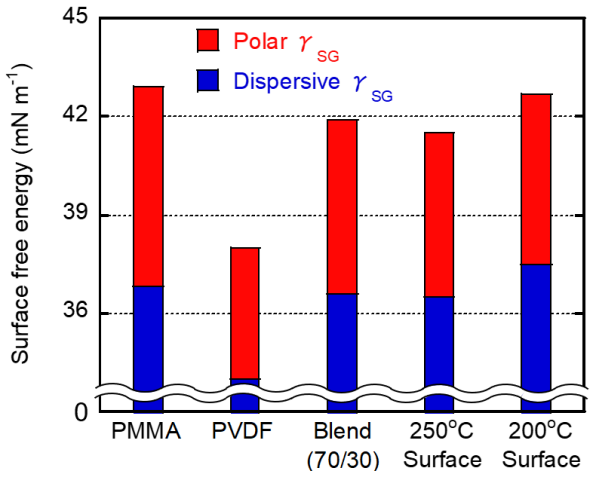

Fig. 10 Surface free energy values of the high- (250°C) and low- (200°C) temperature surfaces of the blend sheet after exposure to the temperature gradient for 200 min. As references, PMMA, PVDF, and PMMA/PVDF (70/30) prepared by compression-molding at 250 °C are also shown. (Blue) dispersive component and (red) polar component.

Structure after exposure to shear rate gradient

ATR-IR measurements were performed to evaluate the surface composition of the extruded specimens. Similar to the samples subjected to the temperature gradient, the PVDF concentration was calculated using a calibration curve. However, no segregation was observed at any shear rate in the experimental range.

Conclusion

In this study, a miscible blend system composed of PMMA and low molecular weight PVDF was used to evaluate the structural changes quantitatively under temperature and shear rate gradients. By applying a temperature gradient, it was confirmed that the low molecular weight component formed a gradient structure. This result is consistent with previous reports on PC/PMMA miscible blend systems. Furthermore, it was found that the surface properties change when a temperature gradient is applied, indicating that surface modification is possible. However, no segregation was observed when a shear rate gradient was applied.

References

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