Effect of Ultrasonic Oscillations on Weld Line Strength of PS, PMMA, and Their Blends

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ABSTRACT: The effect of ultrasonic oscillations on the weld line strength of amorphous polystyrene (PS), polymethyl methacrylate (PMMA), and PS/PMMA (20/80, 50/50, 80/20) blends at various temperatures was investigated. By facilitating the molecular diffusion across the weld line, the introduction of ultrasonic oscillations could evidently improve the weld line strength of PS, PMMA, and their blends. The different effects on the weld line strength of PS/PMMA (20/80, 50/50, 80/20) blends were investigated. The ultrasonic oscillations could greatly increase the weld line strength of PS/PMMA (80/20) by $\sim$ 70%, but was less efficient to PS/PMMA (50/50, 20/80) blends, due to the great difference of weld line morphologies of these blends. The dispersed phase of PS/PMMA (80/20) in the weld line was spherical while two different morphologies in the weld line of PS/PMMA (50/50) were observed. And the stripe-like morphology of PS perpendicular to the flow direction in the weld line of PS/PMMA (20/80) is responsible for the little effect of ultrasonic oscillations. The fractured surfaces of PS, PMMA, and PS/PMMA (80/20) with weld line became much rougher due to the introduction of ultrasonic oscillations. The morphology study of PS/PMMA (80/20) showed that the spherical dispersed phase of PS/PMMA at the skin turned smaller under ultrasonic oscillations. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2990–2997, 2006

Key words: weld line; PS/PMMA; ultrasonic oscillations; co-continuous

INTRODUCTION

Weld line, which is generated when two separate polymer melt streams join either in multigated molds or as a consequence of flow around obstacles, is a common defect in the plastic injection molding. For different polymers the weld line strength is different, and generally the brittle amorphous polymers such as polystyrene (PS) and polymethyl methacrylate (PMMA) tend to give a weak weld line,[1,2] while in the ductile-amorphous and the crystalline polymers, their weld line strength is almost as high as their bulk strength.[3,4] The weakness of a weld line can be attributed to three factors: poor bonding at the interface of the two melt fronts, the molecular orientation parallel to the interface, and the V-notches around the weld line surfaces.[5] Tomari et al.[6,7] reported that the weakness of weld line of PS lays in the V-notch of surface and a poor bonded layer. Recently, Debondue et al.[8] proved that PS is sensitive to the surface notch at the weld line, while PC is nearly not affected by it.

Because of the presence of the weld lines, the mechanical strength loss for immiscible polymer blends is usually much more pronounced than that for their corresponding neat polymers owing to much more complicated morphology in the weld line region.[9–14] It was reported that the addition of compatibilizer can vary the weld line morphology of polymer blends and improve the weld line strength.[11,15,16] Osman and Nihan[17] reported that the addition of talc as a filler to PP/PA6 can improve the weld line strength by varying the elongated spherical domains of PA6 to a homogenized plated-like morphology because of its viscosity increase, but is still not effective compared with the addition of compatibilizer PP-*g*-MA (maleic anhydride grafted polypropylene).

The strength of weld lines is influenced by the process parameters, such as melt temperature, mold temperature, injection pressure, and injection velocity.[1,18–21] With the optimization of these process parameters, the weld line strength can be enhanced to a great extent.[22]

Besides the variation of process parameters, some novel process techniques have been developed to improve the weld line strength. Michaeli and Galuschka[23] developed a sequential filling method through an appropriate control of the shut-off system of the two hot runner nozzles. At the start of the melt filling

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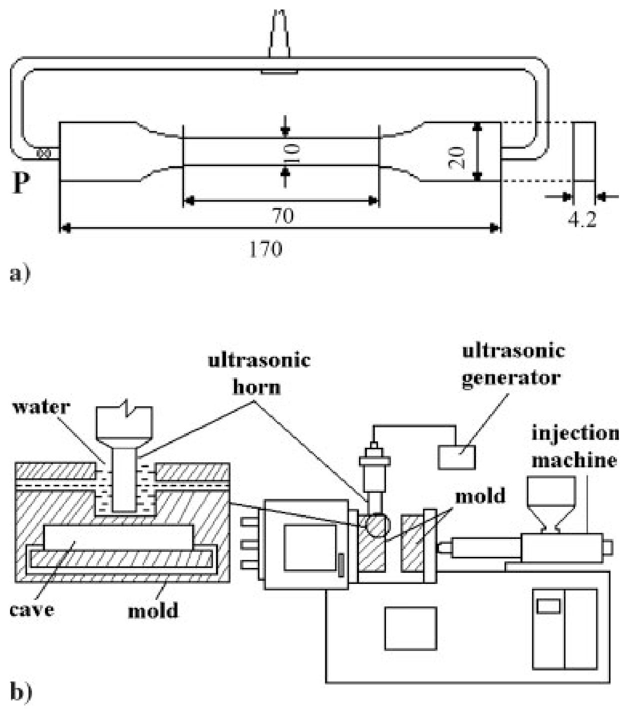

Figure 1 (a) Specimen dimension (**P**: valve controlling the specimen with or without weld line) (units: mm) and (b) Schematic diagram of injection and mold, equipped with ultrasonic oscillation system.

operation, the melt first flowed across the two nozzles and then one nozzle was shut as the weld line was formed, the remainder of the cavity was filled via the second nozzle still open. As a result the weld line was displaced. Malloy et al.[24] used ''multi-live'' feed injection molding process (push–pull method) with two injection units controlled independently to improve weld line strength. Firstly, the melts were injected into the cavity by both units via two separate gates, once the weld line is formed the two injection units began to move mutually in reverse direction, pushing the melts across the joint, and the weld line area was enlarged with the strength improved. Briank and Sinner[25] improved the weld line strength of reinforced crystal polymers by locating a relief tab in the mold near the weld line. As the melt was injected into the cavity, the melt flowed past the opening of the relief tab and formed a thin skin over that opening. Once the pressure increased in the mold cavity, the skin was ruptured and the melt was forced to flow into the relief tab, which caused polymer melt to flow across the weld line and the interdiffusion occurred. Dooley[26] placed an alternate flow diverter on the mold to produce a transient flow. The objective of the design of the flow diverter was that at 80% of fill, the weld line was formed. At this point, the remaining material flowing from the runner at the side of the diverter and across the weld line filled the flow diverter and then sufficient transient flow across the weld line occurred. The studies on PP, PE, PS, ABS, and PC showed a good improvement of their weld line strength.

In our lab, a novel method to improve weld line strength was applied by introducing ultrasonic oscillations into mold to promote the diffusion of melt at the weld line. The effect of ultrasonic oscillations on the weld line strength of PS, PMMA, and their blends was studied. And the effect of weld line morphology of the blends on ultrasonic oscillations improvement of their weld line strength was discussed.

EXPERIMENTAL

Material

The materials used were polystyrene, (PS, PG-33, $MI = 8.5$ g/10 min, $d = 1.05$ g/cm^3) and poly(methyl methacrylate), (PMMA, CM-211, $MI = 16$ g/10 min, $d = 1.19$ g/cm^3) from ZhenJiang Chi Mei Chemicals (China).

Preparation of PS/PMMA blends

PMMA and PS were dried prior to blending at 80°C for 3 h. PS/PMMA blends (20/80, 50/50, 80/20 by weight) were prepared in a corotating twin screw extruder (SHJ-20, a screw diameter of 20 mm with $L/D = 40$, manufactured by Nanjing Giant Machinery, Nanjing, China) at a screw speed of 300 rpm and the temperatures from hopper to die are 170, 185, 190, and 185°C respectively. The extrudates were pelletized prior to injection molding.

Injection molding

PS/PMMA blends were dried at 80°C for 24 h before injection molding. Injection and holding pressure were kept at 60 bar. The mold temperature was 40°C, and the injection temperatures were varied from 180 to 240°C by a step of 30°C. Injection time and cooling time were fixed at 15 and 20 s respectively, for all specimens. The injection mold used to generate weld line specimens and nonweld line specimens was shown in Figure 1(a). The improved injection mold used in this work is a special ultrasonic oscillations mold developed in our lab as described in Figure 1(b). The maximum power and

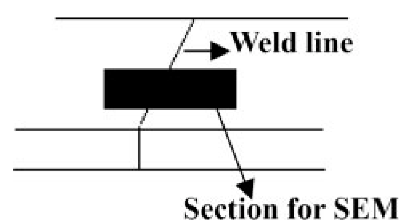

Figure 2 Schematic diagram for SEM section.

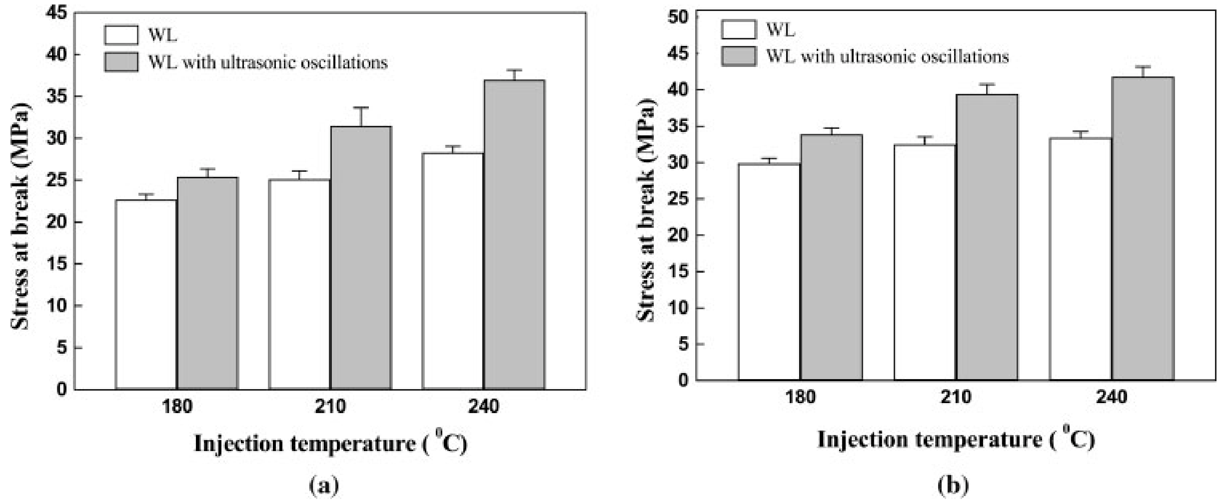

Figure 3 Effect of ultrasonic oscillations on the weld line strength at different temperatures.

frequency of the ultrasonic oscillations are 300 W and 15 KHz, respectively. During injection molding, the oscillations were brought to the melt at the weld line once injection filling was completed.

Measurements and characterization

The tensile properties of injection-molded specimens were conducted according to GB/T 1040-1992 using an Instron tensile machine 4302 with a crosshead speed of 5 mm/min at 23°C. A HITACHI-S520 scanning electron microscope (SEM) machine was used to investigate the morphology of the weld line. Before the observation, the tensile fractured surfaces were covered with a gold–palladium alloy. For PS/PMMA blends, the samples were cut open (shown in Fig. 2) with a method suggested by Guo and Ait-Kadi[12] for microstructure analysis, and then were polished. For PS/PMMA (80/20, 50/50) blends, the polished samples were immersed in acetic acid for a period of 10 h at room temperature to dissolve PMMA (dispersed phase). The polished samples for PS/PMMA (80/20) were immersed in carbon tetrachloride for 10 h at room temperature to dissolve the PS (dispersed phase).

RESULTS AND DISCUSSION

PS and PMMA

Figure 3 showed the influence of ultrasonic oscillations on the tensile properties of injection-molded PS and PMMA with weld line at various temperatures. In the tensile tests, the fractured site appeared at the weld line showing the weak point of the specimens. It is seen that the weld line strength of PS and PMMA was improved with the increase of temperature especially for PS, as confirmed recently by Debondue et al.[8] that the diffusion mobility of polymer melts was enhanced with the increase of melt temperature. It is observed that with oscillations the weld line strength was greatly increased by 6–8 MPa compared with that without oscillations, moreover, the increased temperature was beneficial to this increase trend. To verify the tensile results, the fractured surfaces of PS and PMMA injection molded parts with weld line were investigated. As shown in Figures 4 and 5, the fractured surfaces of specimens with oscillations were obviously much rougher than that without ultrasonic oscillations for both PS and PMMA, indicating ultrasonic oscillations improvement of molecular welding at the weld line.

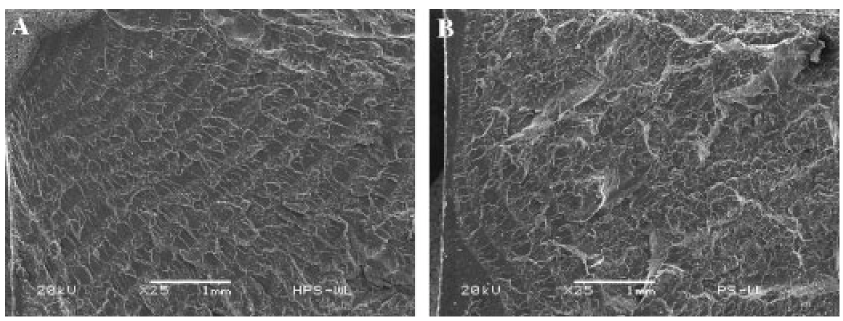

Figure 4 The fractured surface of PS specimens with wed line (a) without oscillations and (b) with oscillations (at 210°C).

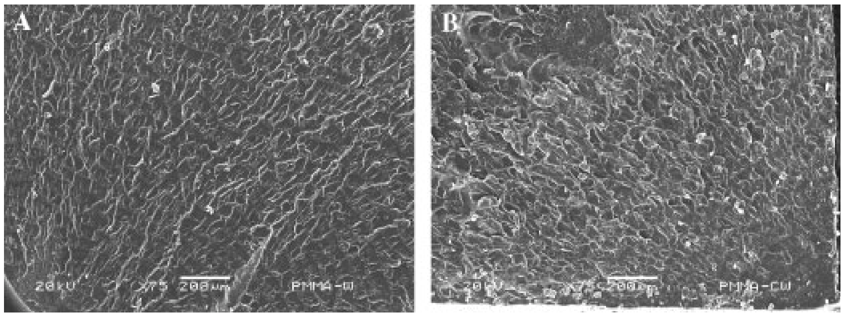

Figure 5 The fractured surface of PMMA specimens with weld line (a) without oscillations and (b) with oscillations (at 210°C).

To identify the oscillations' promotion of the molecular diffusion, an experiment was designed. Two kinds of specimens, which were injection molded neat PS and PS blended with a few amount of black pigment parts apart, were cut into half of parts equally and then polished. Then half of the polished specimens of PS and half of PS blended with a few pigments were placed into the cavity of mold together. The mold temperature was raised to 180°C and then kept at the mold temperature for a period of 10 min, during this period ultrasonic oscillations were induced or not induced. Finally, the mold temperature was cold down to 60°C and the specimens were taken out.

As shown in Figure 6, for the sample without ultrasonic oscillations the length of the black segment was almost kept unchanged. But, under the ultrasonic oscillations the black segment diffused across most part of the sample. It is obvious that the presence of ultrasonic oscillations promoted the molecular diffusion, resulting in the diffusion of the black segment, which confirmed the foregoing results.

PS/PMMA blends

The effects of ultrasonic oscillations on the weld line strength of PS/PMMA blends at various temperatures were shown in Figure 7. All the specimens with weld line broke at the weld line. The weld line strength of PS/PMMA blends was much lower than those of PS and PMMA. The increase of injection temperature was beneficial to the improvement of weld line strength, as investigated by Guo and Ait-Kadi.[12] It is clear that ultrasonic oscillations could evidently improve the weld line strength, especially for PS/PMMA (80/20) blend by ~ 70%. It is noted that the effects of ultrasonic oscillations depend on the composition of PS/PMMA blends. The weld line strength of PS/PMMA (20/80, 50/50) blends was less sensitive to the ultrasonic oscillations.

To confirm the different effects of ultrasonic oscillations on PS/PMMA blends, the weld line morphologies of PS/PMMA blends were investigated. The specimens were cut open and etched out of dispersed phase in the blends for the observation of the morphology through SEM. As shown in Figure 8, the weld lines of PS/PMMA blends were quite distinct from their bulk morphology showing the oxbow shape. With different composition of PS/PMMA blends, the morphologies of these weld lines were quite different. The weld lines of PS/PMMA (20/80, 50/50) showed more obvious than that of PS/PMMA (80/20) blend.

For PS/PMMA (80/20) shown in Figure 9, the dispersed PMMA phase in the weld line region was spherical, of which the size in the skin [Fig. 9(a)] was smaller than that in the core [Fig. 9(b)], due to the stronger shear-deformation in the skin for the characteristic fountain flow during injection molding. After introducing the ultrasonic oscillations, the dispersed phase was changed. Figures 9(c) and 9(d) were the SEM micrographs at skin and core of weld line with the ultrasonic oscillations. The comparison of Figures 9(a) and 9(b) with Figures 9(c) and 9(d) was found that ultrasonic oscillations greatly decreased the dispersed phase size at the skin, but hardly changed the dispersed phase size at the core of weld line. This can be explained that at the skin of weld line, the intensity of ultrasonic oscillations is so strong to pulverize the dispersed phase. As the distance from the skin rises, the ultrasonic oscillations intensity comes down, and its intensity at the

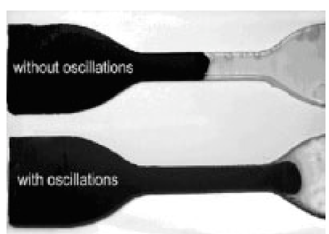

Figure 6 Effect of ultrasonic oscillations on interdiffusion of PS.

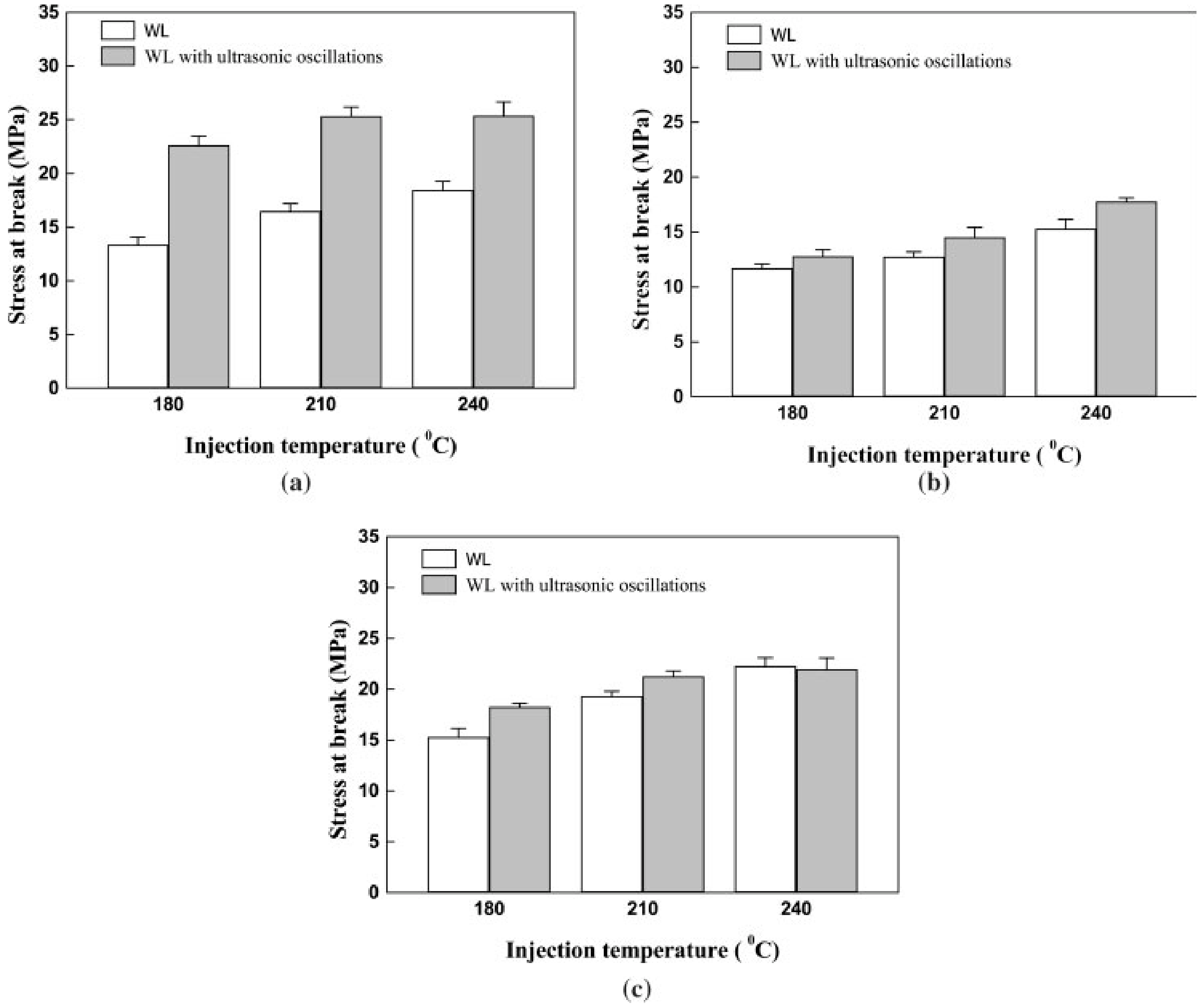

Figure 7 Effect of ultrasonic oscillations on the tensile properties of PS/PMMA blends with weld line at different temperatures.

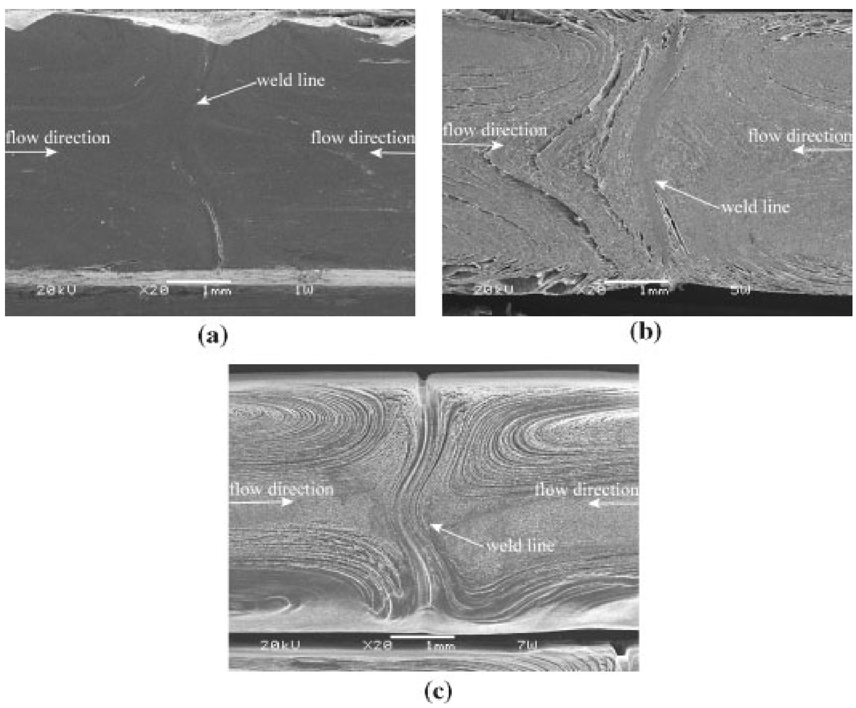

Figure 8 SEM micrographs of weld line for PS/PMMA blends (at 210°C).

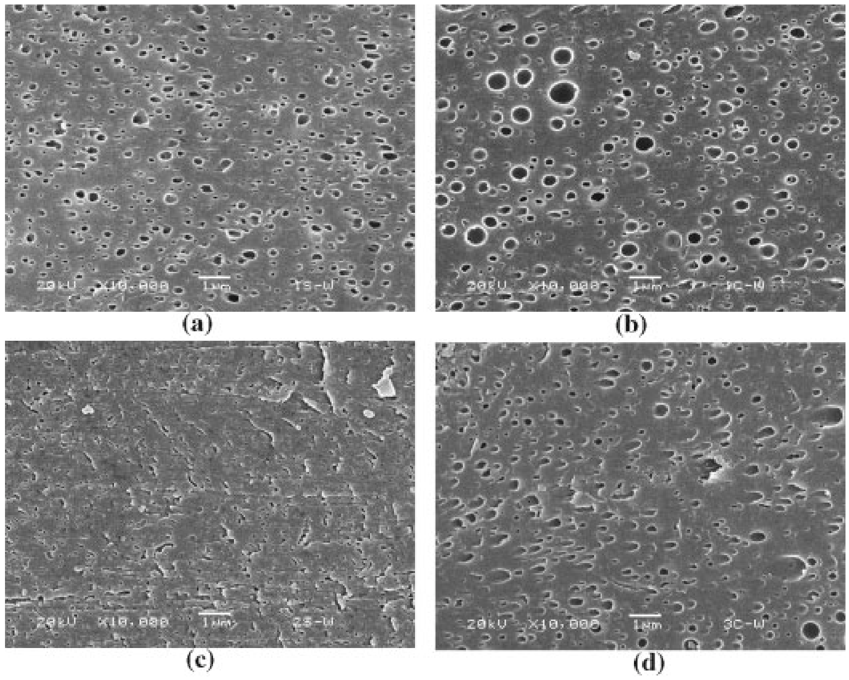

Figure 9 SEM micrographs of weld line for PS/PMMA (80/20) with or without weld line (at 210°C).

core is not enough to deform the dispersed phase. The decreased dispersed phase in the weld line region is beneficial to the improvement of weld line strength.

Figure 10 was the fractured surfaces of injection molded PS/PMMA (80/20). A visible ''sandwich'' structure was observed in the weld line with a poor bond at the skin. Before discussion, the poor bonded

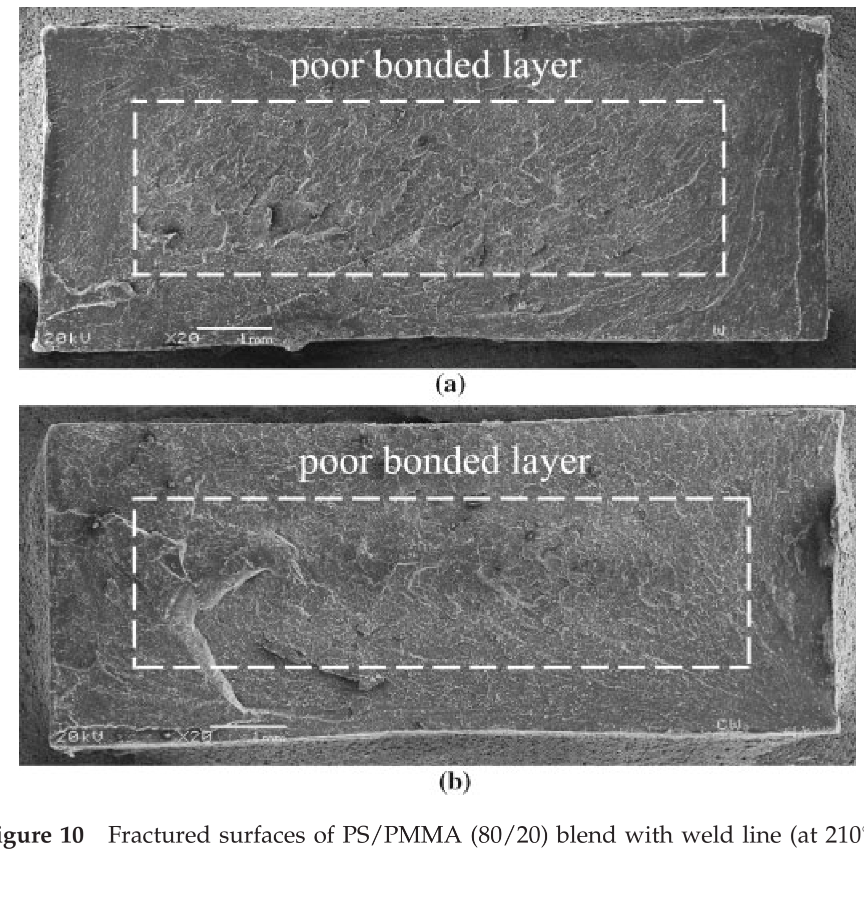

Figure 10 Fractured surfaces of PS/PMMA (80/20) blend with weld line (at 210°C).

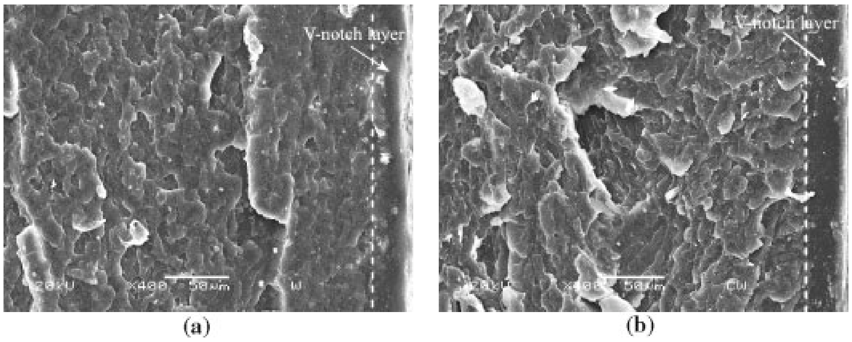

Figure 11 Fractured surfaces micrographs of poor bonded layer for PS/PMMA (80/20) blend with weld line (at 210°C).

area was defined as poor bonded layer marked in Figure 10. Compared with that without ultrasonic oscillations, the fractured surface with ultrasonic oscillations was much rougher especially at the poor bonded layer. This layer was magnified as shown in Figure 11. The shiny smooth surface in the fractured surface designated the V-notch of weld line. Although the V-notch was more obvious, the fractured surface [Fig. 11(b)] was much rougher compared with that without oscillations [Fig. 11(a)], indicating that the oscillations are less beneficial to the melt diffusion at the V-notch layer of weld line due to its fast cooling, but they facilitate the melt diffusion at other layers except the V-notch layer at the weld line, which leads to the increase of weld line strength of PS/PMMA (80/20) blend.

From the SEM (Fig. 12) of the weld line region of PS/PMMA (50/50), a multiple stripe-like morphol-

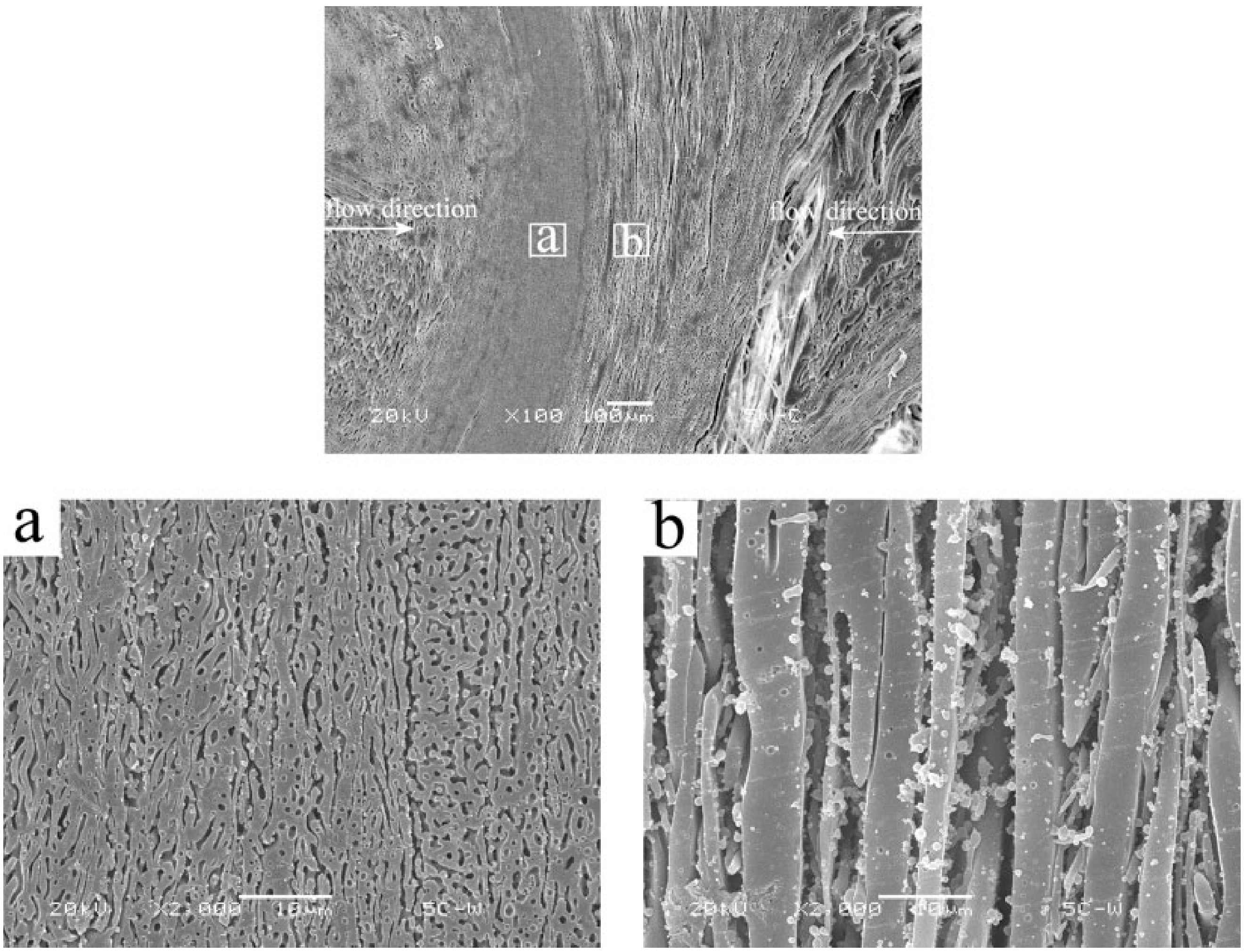

Figure 12 SEM micrographs of weld line for PS/PMMA (50/50) without ultrasonic oscillations (at 210°C).

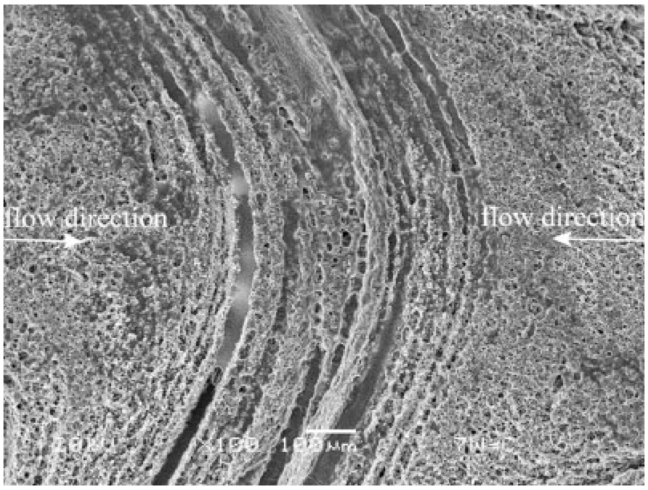

Figure 13 SEM micrograph of weld line for PS/PMMA (20/80) without ultrasonic oscillations (at 210°C).

ogy was observed at the center of weld line which was the contact surfaces of the two flow fronts generated at the time of weld line formation. The size of the two phases, which showed the cocontinuous structure [Fig. 12(a)] in the contacting layer, was much smaller than that observed away from the layer. Away from the layer a much larger fibrous morphology [Fig. 12(b)] was perpendicular to the flow direction. It was concluded that the morphologies difference between the two regions causes poor weld line strength. The orientation of the two phases perpendicular to the flow direction holds up the molecular diffusion across the weld line plane even with the ultrasonic oscillations, and therefore, ultrasonic oscillations have little contribution to the increase of weld line strength for PS/PMMA (50/50) blend.

For PS/PMMA (20/80) blend, the weld line morphology was quite different from that of PS/PMMA (80/20) as shown in Figure 13, due to the change of the viscosity of dispersed PS phase over that of the matrix. The grooves appeared in the SEM was the etched PS phase showing clearly flowing traces. Peculiarly, PS phase accumulated in the weld line region showing stripe shape morphology oriented perpendicular to the flow direction, which was quite different from the bulk away from the weld line. The ultrasonic oscillations was unable to change the orientation of the stripe-shaped dispersed phase in the weld line which is responsible for the poor weld line strength, and so they have little effect on the increase of weld line strength for PS/PMMA (80/20) blend.

CONCLUSIONS

The introduction of ultrasonic oscillations can evidently improve the weld line strength of PS, PMMA by promoting the molecular diffusion across the weld line. While for PS/PMMA blends the effect of oscillations on the weld line strength depends greatly on weld line morphology of blends. Ultrasonic oscillations are more beneficial to PS/PMMA (80/20) whose dispersed phase is spherical in the weld line region. While for PS/PMMA (50/50) the multiple stripe-like morphologies perpendicular to the weld line plane lead to the poor effect of ultrasonic oscillations on the weld line strength. For PS/PMMA (20/80) the ultrasonic oscillations would not change the stripe morphology of PS perpendicular to the flow direction, so the ultrasonic oscillations contribution to the increase of the weld line strength of the blend was not larger compared with that of PS/PMMA (80/20) blend.

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