Microfluidic Mixer for Polymer Melts

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Abstract

We present a novel microfluidic mixer for high temperature polymer melts based on the platform of the Multi-sample Micro-slit Rheometer (MMR). The device is essentially a static mixer with eight consecutive units of splitting and recombination flow formed by stacking three stainless steel shims (50 μm thickness). The mixing results show both multilayer and domain/matrix morphologies depending on the channel configuration and blend pair. This mixer will be particularly useful not only as a polymer melt mixer but as a multilayer processor when a limited material quantity (typical sample size ≈ 20 μL) is available.

Introduction

*Common polymer melt mixers such as kneaders and single/twin screw extruders are able to melt solid polymers and provide high stress for shearing the viscous materials [1]. These mixers are designed to process g/min to kg/min and cannot handle μL samples.

Recently, microfluidic mixers have been developed [2;3]. Various mixing mechanisms have been adapted for the microfluidic static mixer such as flow focusing, flow separation, chaotic advection and splitting/recombination flow (SAR mixer) [2]. Despite the various mixer designs, they are not applicable to polymer melts due to their inability to function at the required temperature and pressure. Static mixers are more promising than active ones due to their simplicity and reliability [4;5]. The SAR mixer is a reliable and effective static mixer under the low Reynolds number (Re < 1) operations that occur in polymer melts flowing through sub-mm dimensions. Further, the SAR mixer can produce submicron multilayer structures simply by mixing units which make the number of layers increase exponentially. C. D. Mueller *et al.* [6] developed a continuous layer-multiplying coextrusion method for polymer melts which can make nanolayer laminates with thousand of layers, but it needs large scale extruders and a complex die structure.

Indeed, to our knowledge, there are no microfluidic mixers applicable to polymer melts. Here we present a microfluidic SAR mixer for polymer melts which requires approximately 20 μL per sample. This mixer offers flow design flexibility by simply changing the multi-shim configuration.

Experiment

Apparatus

†The design principles of the microfluidic mixer are mechanical simplicity, high temperature operation, cleanability and optical access [7]. The mixing channel is formed by stacking three stainless steel shims (50 μm thickness) in which channels are produced by a laser cutting technique (2 μm resolution) as shown in Fig. 1. Three shims are sandwiched between a sample chamber and a sapphire window and sealed by mechanical pressure. The flow is driven by nitrogen gas (max. 2000 kPa) which pushes the sample from the two sample chambers into the flow channels. The flow pattern from the window side can be viewed and recorded by a video camera.

The mixing channel is designed for two components and has a "T" junction as the initial unit in all three shims. The channel shapes of the upper and lower shims are successive half-circles with short-straight channels which are flipped and facing each other – channel cross-section is 500 μm width and 50 μm thick. The middle layer of the channel has partly straight openings, designed to divide the flow in the thickness-wise or lateral directions (Fig. 1). One splitting/rejoining mixing unit makes the number of layers double so that n mixing units will make 2^n layers. In our channel design, eight mixing units can make maximum 256 layers for lateral-wise lamination and 128 layers for thickness-wise lamination in principle. Resultantly, three kinds of shims with different channel designs were used to realize two different kinds of SAR mixers in our study, one for the upper and lower channels, and two for the middle channels.

† Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

For the experiment of lateral-wise lamination, black and white polystyrene (PS) are prepared by a mini-extruder (DACA Instruments, Santa Barbara, CA) because lateral lamination can be viewed directly through the window. The composition of the black sample is PS (PS612, DOW) 98% + Carbon black 2 % by mass and PS 98% + TiO_2 2 % by mass for white PS. The samples were compounded for 10 min. at 20.94 rad/s and 200 °C. We assume the two sample's viscosities are the same because the amount of colorant is small (2 % by mass) and share the same thermal history during compounding. Two pairs of materials were prepared to examine the thickness-wise lamination mixing, in which case, optical examination was not possible due to the submicrometer multilayer lamination. Therefore, a neat PS (PS612, DOW)/PS + low density polyethylene (LDPE) 2 % blend pair and PS/ polypropylene (PP) pair were used as two components for mixing. For the compatiblized blend (CB) pair, PS + LDPE2% can be differentiated from PS in a Scanning Electron Macrograph (SEM) photograph. Blending was carried out at the same operating conditions as the case in the mini-extruder and the neat PS also was extruded at the same condition for the same thermal history, so that two samples have the same viscosity. The uncompatiblized blend (UB) pair is PS (Styron 666D, Dow Chemical) and PP (Exceed 4062, Exxon) whose viscosities closely match each other over the range (0.1 to 200) s^{-1} in shear rate at 200 °C [8]. The PS/PP pair is selected in order to examine the clear interface structure of multilayer.

All mixing experiments were carried out at a maximum inlet pressure of 2000 kPa and 200 °C. Samples were melted in a vacuum oven in the sample holder to eliminate air bubbles before the mixing experiment. A video camera was used for the direct examination of lateral mixing and SEM was used to view a cryo-broken cross section of a sample strip for the thickness-wise mixing.

Results and Discussion

Figure 2 shows direct optical observation for the case of a lateral-wise mixing. As shown in Fig.2, the number of black and white stripes increases as the flow goes through more mixing units. At the eighth mixing unit, the average width of one stripe should in principal be ≈ 2 μm (500 μm /2^8). Therefore, the detailed stripe pattern is not visible.

In the case of thickness-wise mixing (Fig. 3), the layered cross-sectional pattern can be found through the first six mixing units (32 layers are expected) for both CB and UB but it is unclear whether the CB has a layer structure in the seventh and eighth mixing unit. In fact,

the LDPE domains have a size larger than 1 μm in diameter; it was not possible to observe the layer structure beyond the seventh mixing unit (64 layer, 0.78 μm layer width is expected).

Figure 3b shows the cross-sectional SEM photographs for the UB pair. A layered (LY) morphology can be found through six mixing units although there is an uneven layer-thickness distribution and domain/matrix (DM) morphology in patches. The DM morphology becomes dominant in the seventh and eighth mixing units. Whitening (degree of opacity) of the sample along the channel also reveals that the LY morphology becomes a DM morphology as the number of mixing unit increases. From this observation, one can conclude that the UB (PP/PS) layer becomes DM in the submicrometer layer thickness in order to reduce the total interfacial energy of the system. From the results, we can conclude that this microfluidic mixer can be an effective mixer for two component polymer melts.

Conclusions

A novel microfluidic SAR mixer can be successfully constructed by stacking 3 different channel shims (50 μm in thickness, stainless steel) based on the MMR platform which works well for two component polymer melts.

This mixer can be a good choice for applications with limited sample quantity and for cases where ease of use is desirable. Moreover, this would be a good platform for a microfluidic device for polymer melts because of its design flexibility of 3D flow.

References

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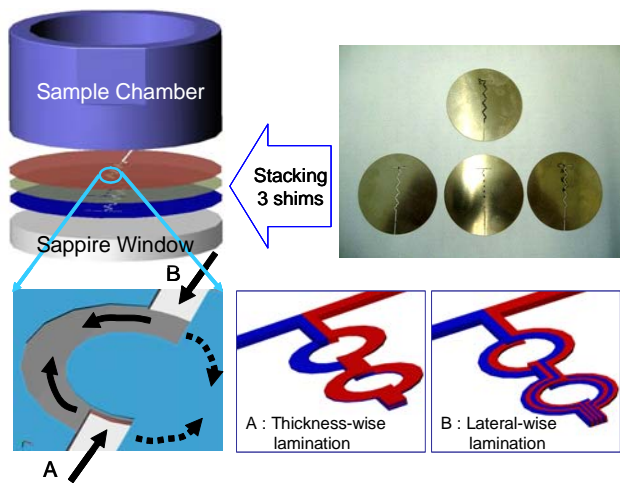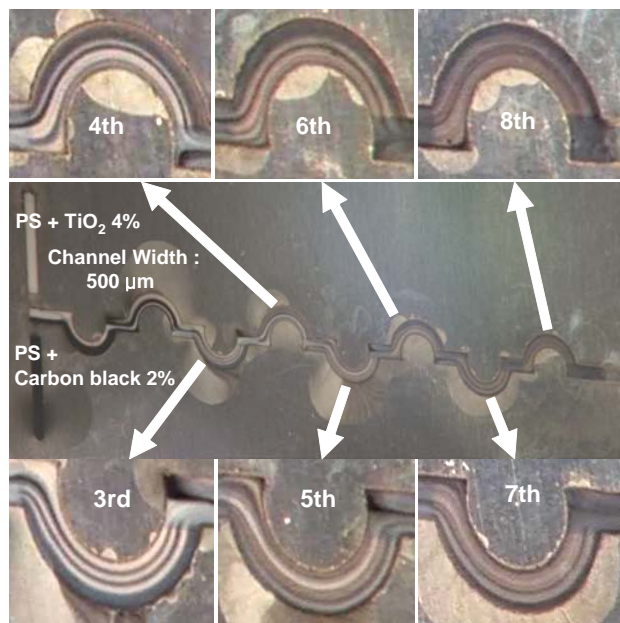
Figure 1. Schematic diagram of microfluidic mixer.

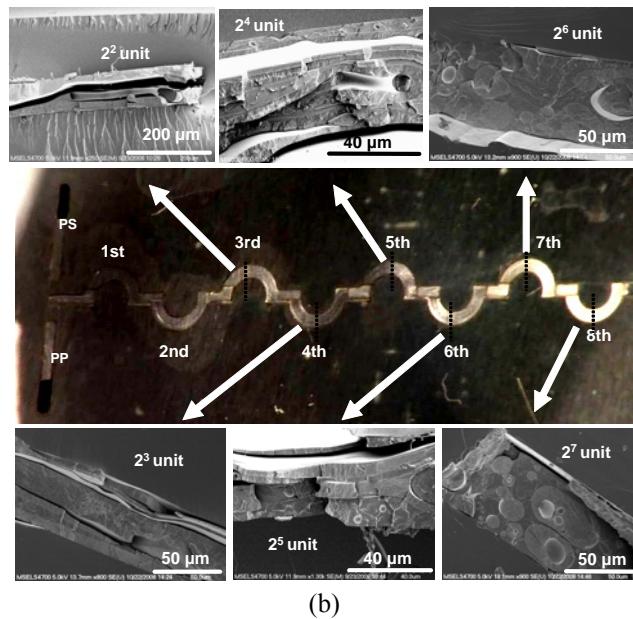Figure 2. Flow pattern of lateral-wise lamination mixing along mixing units.
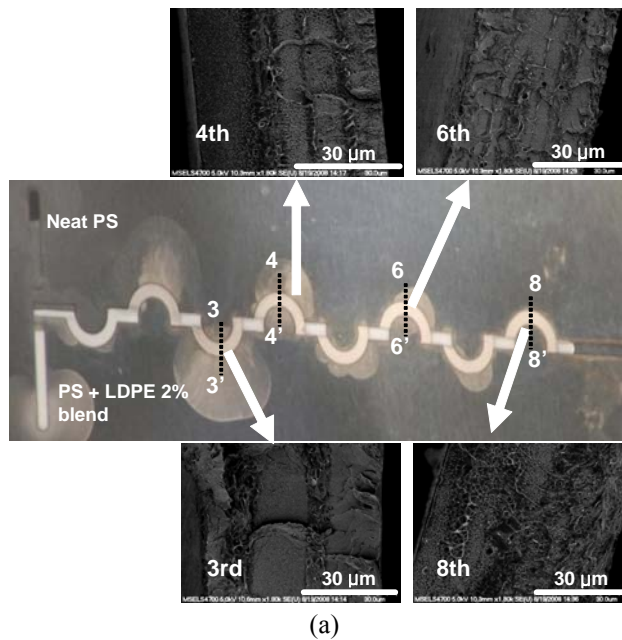

(a)

(b)

Figure 3. Cross-sectional mixing pattern at each mixing unit. Samples were viewed after cryo-broken under epoxy impregnation. (a) compatibilized pair (PS+PS/LDPE2%) (b) uncompatiblized pair (PS + PP).

Key Words: Mixer, Microfluidic, Multilayer, Morphology Polymer melts