

# **EFFECT OF POLY(METHYL METHACRYLATE) MOLECULAR WEIGHT ON ITS TERNARY POLYMER BLENDS MICRO-STRUCTURE USING X-RAY COMPUTED TOMOGRAPHY**

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## **ABSTRACT**

A high-contrast X-ray computed tomography (XCT) applied to the ternary polymer blends of poly(methyl methacrylate) (PMMA), polypropylene (PP) and polyamide 12 (PA12), we investigated micro-structure three-dimensional (3D) images of blends with gradually increasing of molecular weight (Mw) of PMMA. The 1:1:1 mixture of PMMA/PP/PA12 were prepared by mixing on an internal mixer at 200 °C, then annealing at 200 °C under compressor of 5 MPa in order to restore the crystalline structure of polymer blends. After that, blends were compressed molding and cooled by water. Finally, they were stored in the vacuum oven at the same annealing temperature before taking XCT and then rendering to 3D images. Changing various methods of annealing time, we could observe vary 3D internal structure clearly of these blends. We also conclude the effect between Mw of PMMA and the morphologies of these ternary polymer blends.

*Keywords:* X-ray computed tomography, three-dimensional micro-structure image, ternary polymer blends.

## **1. INTRODUCTION**

X-ray computed tomography is known as a CT scan, and it is widely used in medicine to reveal internal hard tissue structures. The same technique can be used to reveal the internal three-dimensional structure and component distribution within materials. Three-dimensional imaging data are available by scanning an X-ray beam in two dimensions across a specimen while rotating about a single axis to include three dimensions in the final image. The X-ray image shows components distributed within the specimen, and cross sections or slices made

through any plane give the distribution of components within that plane. Contrast in the images is reliant on a change in electron density about atoms within the material. CT scanning is a nondestructive test to map the volume distribution of components in a material. Images are processed to provide surface rendering, volume rendering, or image segmentation [1]. Until 2010, more than 500 XCT–installations for industrial and scientific applications in Europe. There are two major application areas of XCT in science and industry: non–destructive testing of materials and dimensional measurement (metrology). XCT is able to measure internal or hidden structures completely without destroying the specimen. Determination of the three–dimensional (3D) distribution of heterogeneities and structures is of primary concern in the field of materials characterization and quality control. XCT provides statistically significant estimates of volume fractions of heterogeneities in materials depending on the spatial and contrast resolution [2]. Multiphase blends consisting of two or more incompatible polymers have achieved major economic importance in the plastics industry. The most widespread examples are impact modified thermoplastics where a rubber is micro dispersed in a glassy polymer matrix. Some materials are reported to have co–continuous phases of different thermoplastics. Most commercial materials have two phases and are formed from two main polymers with minor amounts of a third, compatibilizing polymer, typically a graft or block copolymer [3]. Polymer blends with in homogeneities 10 – 0.1 micrometer, the methods that observing morphology is electron microscopy: SEM, TEM [4]. Besides that, various polymer blend systems have been investigated by using high contrast XCT. The contrasts of various polymers were surveyed and found that many kinds of polymers can be distinguished under XCT. Then, the phase separation structures can be clearly visualized in 3D without any staining [5]. X–ray CT for polymer science with advantages: no staining, high contrast and quick operation. Recently, high–contrast X–ray CT has been optimized for use with polymeric materials and several observations of the polymer blends have been reported. Its spatial resolution is  $\sim 3 \mu\text{m}$  at present [6].

Contrasts of the polymer materials under a high contrast X–ray computerized tomography (XCT) are comprehensively investigated. We developed a high contrast XCT, and demonstrated its capabilities to polymer systems, such as polymer blends. Then we got a hypothesis that the pixel values of the cross–sectional image obtained by XCT agree with the X–ray absorption coefficient at 15 KeV. This hypothesis is intensively examined by using various polymers. Consequently, we propose an empirical criterion that  $0.1 \text{ cm}^{-1}$  difference in the X–ray absorption coefficients at 15 KeV is necessary to distinguish the polymers under XCT. This criterion is also confirmed in the polymer blend systems [2]. It is now commercially available from Beamsense Co. Ltd. [2, 4, 7]. In this paper, blends of PMMA/PP/PA12 1/1/1 were prepared to get 3D micro–structure images with various molecular weight of PMMA. As mentioned in previous studies [5, 8], three types of polymers with distinct colors together while being photographed 3D microstructure XCT.

## 2. MATERIALS AND METHODS

PP used was Novatec ® MA1B M26831 with a weight–average molecular weight ( $M_w$ ) of  $25 \times 10^4$ . Nylon 12 (PA12) is in semi–crystalline state, industrial grade. PMMA is in amorphous state with  $M_w$  in the range of 15,000–70,000, density of  $1.18 \text{ g/cm}^3$ . Both PA12 and PMMA were purchased from JPC – Japan Polychem Corporation. All chemicals were used as received without further purification.

The three polymer components were melt–blended at  $200 \text{ }^\circ\text{C}$  with 1/1/1 weight fraction in a twin screw mixer (IMC-16C, Imoto Industry, Co. Ltd., Japan). Then the mixture was melt–

pressed and annealed at 200 °C for survey hours (0–8 hours) in the vacuum condition or in the air environment in order to develop the phase separation structure. After that, they were stored in vacuum condition at –0.1 MPa, 70 °C.

Table 1. Components of ternary polymer blends PMMA/PP/PA12 1:1:1 in experiments.

	PP	PA-12	PMMA 15k	PMMA 35k	PMMA 70k	PMMA 98k	PMMA 120k	PMMA 540k
<b>Blends 1</b>	x	x	1					
<b>Blends 2</b>	x	x		2				
<b>Blends 5</b>	x	x			5			
<b>Blends 3</b>	x	x				3		
<b>Blends 4</b>	x	x					4	
<b>Blends 6</b>	x	x						6

The sample was cut into the cylindrical round shape of 20 × 2 mm (diameter of 20 mm), and then subjected to X-ray CT (FLEX-M863-CT, Beamsense Co. Ltd., Japan) at Laboratory of Polymer Mechanics – Department of Macromolecular Science and Engineering – Kyoto Institute of Technology. The X-ray generator tube was operated at 40 kV, and the transmission images were acquired using a charge-coupled device (CCD) with a CsI scintillator. To construct a 3D image (at Laboratory of Polymer Mechanics – Department of Macromolecular Science and Engineering – Kyoto Institute of Technology), the sample was rotated over 180° at 0.25° intervals. At each rotation angle, four transmission images were taken with the exposure time of 1 s, and they were averaged to provide a total exposure time of 4 s. The obtained 720 transmission images were reconstructed into a 3D image using a standard filtered back-projection algorithm.



Figure 1. Experimental procedure.

### 3. RESULTS AND DISCUSSION

The use multi planar reformatting (MPR) reconstructs two-dimensional views of a series after creating a three dimensional volume. The MPR mode allows to view the image in three views. Users are able to change the layout, view modes and the viewing angles in MPR view. The cross-sectional image of the PP/PA12/PMMA obtained by X-ray CT is shown in Figure 2 and Figure 3; while MPR mode ones are Figure 2 and Figure 3A. Inside the structure, PMMA rich-phase is white, PA12 rich-phase is light gray, and PP rich-phase is dark gray. As discussed in the introduction, the X-ray absorption of the material corresponds to the pixel intensity in the reconstructed image, they suggest that PMMA has larger X-ray absorbance than PA 12 and PP respectively. By surveying the pixel intensities over various polymers, it is concluded that the amount of the oxygen and nitrogen significantly increase the pixel intensity in our XCT.

When we use the higher Mw of PMMA into 70,000, this trend has not changed though the molecular weight of PMMA again be doubled. However, the increased size of the PMMA and PA 12 phase than PP was evident. PP is now spherical particles no larger in size than the

continuous phases of PMMA and PA 12. This phenomenon is understood as an increase in the density of molecular bonds corresponding to molecular weight increase. Through photographs and images 3D structure Figure 3, prediction was illustrated vividly.

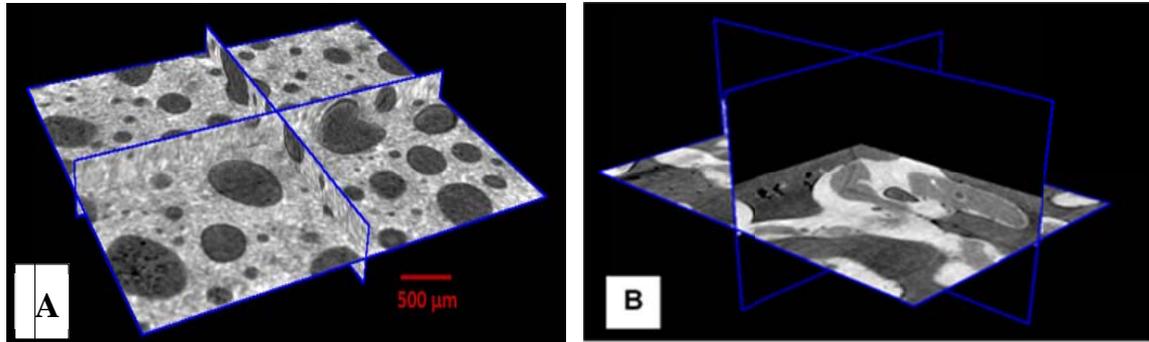


Figure 2. Cross-sectional image of PP/PA12/PMMA blends , Mw of PMMA = 35,000 (A); 15,000 (B).

With low  $M_w$  of PMMA (15,000) in Figure 2B, after heating treatment the PP phases and PA12 phases can separate more clearly into a big phase each other. PMMA has low  $M_w$  and also low viscosity so it trends to be a continuous phase. The suitable annealing time for better observation of morphology is from 4 hours to 6 hours, therefore we can see big phase clearly. After 8 hours, the micro structure of polymer blends is absolutely fixed. It could be when we increase annealing time, PP phase is more stable that it could disperse inside the micro-structure. Any of phases are not continuous and the interfaces tend to be flat, or straight in two-dimensional cross-sections. This kind of ternary phase structures was predicted only in computer simulations [3]. In Figure 2A with Mw of PMMA = 35,000, PP phases become spherical shape forward and there are many different particle sizes. While PA 12 and PMMA distributed together into continuous phases with smaller size than PP sphere. This can be explained by the increasing of the melt viscosity of the PMMA in the mixture. Then it cannot constitute the major challenge of continuity which will be diffused by phase of PA 12. As a result, they form many mixed block unclearly. Along with that, the surface tension of this mixed block phase (PMMA and PA 12) with PP component will cause phase PP spherical particles form.

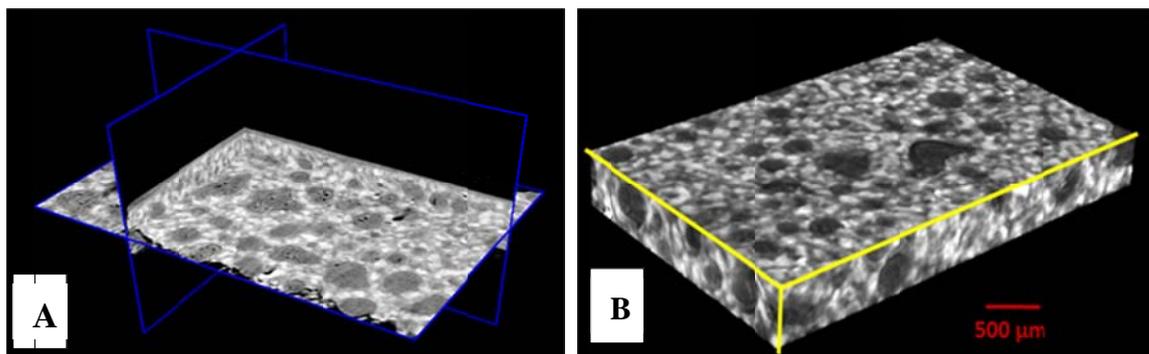


Figure 3. Cross-sectional image and 3D X-CT image of PP/PA12/PMMA blends, Mw of PMMA = 70,000.

Through changing patterns molecular weight, the annealing time allows most clearly observed structures blends are from 4–8 hours. This result coincides with the statement at the beginning of this discussion. Thereby we could realize the role of the annealing process parameters through time and environmental conditions affect the steady recovery of micro-structures of polymer blends. In volume segmentation, components from the image are separated based on a threshold so that the remainder of the image is omitted [1].

#### 4. CONCLUSIONS

Research about the molecular-weight dependance on blends polymer X-CT images, we have demonstrated visually the dependance of PMMA molecular-weight (3 types of Mw) in blends PMMA/PA12/PP 1/1/1 using 3D X-CT microstructure analyzing system; and how about the phase structure of a ternary blends with 3D images. Learn how about the preparation of sample affect to XCT 3D images: mixing, compressing annealing and cooling, vacuum storage, 3D image reconstruct and analysis procedures. We demonstrated the advantage of the high-contrast X-ray CT by applying it to the ternary polymer blends. Since XCT gives the three-dimensional images of the object including its internal structure, XCT is a powerful research tool in polymer science.

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