

## Shear effect on crystallization of ethyl-POSS polyethylene / linear low density polyethylene blend

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### Introduction

The addition of inorganic molecules to polymers as fillers gives rise to new physical properties of the composite. In order to obtain better physical properties, it is important to control the shape and dispersion state of fillers and their interaction with polymers. From these viewpoints, polyhedral oligomeric silsesquioxane (POSS) copolymerized polymer system has attracted attention because POSS bound on polymer chain can form nano-sized crystalline aggregates with a plate-like shape in matrix polymer [1]. Furthermore, it was found that the modification of apex region of POSS can control the degree of aggregation [2]. In POSS copolymerized polyethylene (POSS-PE), the introduction of ethyl group to apex region of POSS strongly prevents the aggregation of POSS, resulting in homogeneously dispersed ethyl-POSS-PE in PE matrix. In this study, we observed the effect of the addition of ethyl-POSS-PE on crystallization behaviour of linear low density polyethylene (LLDPE) under shear field.

### Experiment

The sample used was ethyl-POSS-PE/LLDPE blend and the blend ratios were 3/97, 1/99 and 0.1/99.9. The blend samples were mixed by xylene solution and the mixed polymers were precipitated by ethanol. Disk shaped samples with thickness of 0.3mm were prepared by press molding. SAXS measurements during shear-induced crystallization were performed at BL-15A. As a shear apparatus, Linkam CSS 450 (JAPAN HIGH TECH CO. LTD.) was used. SAXS images were measured with an X-ray CCD detector coupled with an X-ray Image Intensifier. The distance between the sample and the detector was around 2000 mm. The X-ray wavelength was 1.5 Å.

### Results and Discussion

Figure 1 shows a typical shear and temperature history in this study. Pulsed-shear ( $35\text{ s}^{-1}$ , 2 sec) was applied to disk samples at 130-150 °C, which was higher than melting point of polymer blend. Thus, no crystallization occurred at the temperature. After a 5-minute annealing at the temperature of shear, the sample was cooled at a rate of 30 °C/min. The structural change during cooling was observed by SAXS. In ethyl-POSS-PE/LLDPE blend, oriented lamella structure grew during cooling, while

isotropic lamella structure was observed in LLDPE. Furthermore, the temperature where crystallization started was 3-4 °C higher than that of LLDPE. The result indicates that the partially stretched structure of ethyl-POSS-PE, which was formed by pulsed-shear, survived the 5 min annealing and that it worked as nucleation agent during cooling. It may be originated from the long relaxation time of ethyl-POSS-PE due to the interaction between ethyl-POSS parts.

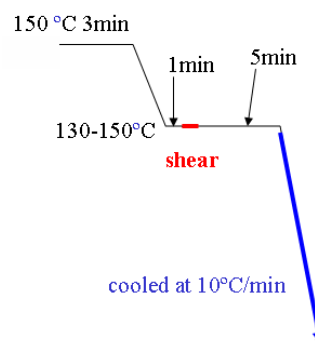


Figure 1. Thermal and shear history in this experiment.

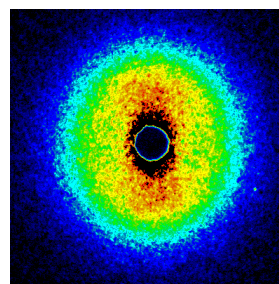


Figure 2. Oriented SAXS pattern of cooled ethyl-POSS-PE/LLDPE=1/99 blend. Shear (35s-1) was applied during 2 seconds at 150 °C.

### References

- [1]. L. Zheng, A. J. Waddon, R. J. Farris and E. B. Coughlin *Macromolecules* **2002**, 35, 2375.
- [2] B. Seurer, E. B. Coughlin, *Macromol. Chem. Phys.*, **2008**, 209, 1198.

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