

비상용성 고분자 브렌드에서의 Nanoclay의 이동

김용경, 홍정숙*, 안경현, 이승종
서울대학교 화학생물공학부, *고려대학교 유변공정연구센터

Migration of nanoclay in immiscible polymer blends

Yong Kyoung Kim, Jung Sook Hong*, Kyung Hyun Ahn,
Seung Jong Lee
School of Chemical and Biological Engineering, Seoul National University
*Applied Rheology Center, Korea University

Introduction

Blending of two immiscible polymers has become increasingly crucial because it provides superior properties than original components. However, immiscible polymer blends system is not thermodynamically stable during post-mixing. The change in morphology can reduce the profits received by blending. Therefore, morphology control is an important way to optimize their properties. Usually, the morphological stability of immiscible polymer blends is improved by either adding pre-made or in-situ formed copolymers. In recent years, clay has been widely used to play the role of compatibilizers instead of block copolymer^{1, 2}. TEM micrographs revealed that clay platelets locate at the interface of two polymers or only their more favourable polymer component. Like compatibilizers, it can lead to more stable morphologies because drop sizes were decreased and the degree of dispersion was improved.

In this study, we investigated the migration of nanoclay in two immiscible polymers (PBT/PS) under well defined shear flow. First of all, we observed the morphology evolution of pure PS/PBT five multi-layered film with same shear rate(1/s) and different time scale which is the same method to prepare the sample as below one. These morphology evolution was investigated by confocal scanning laser microscope. In addition, to understand the mechanism of clay migration between PS and PBT phase, the experimental samples were elaborately prepared such that five layers of films are sandwiched. The morphology was subsequently studied by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). The PBT/PS films were first made by alternately superposing PBT film and PS/clay film with the thickness of 0.2mm. Though the clay used in this study has a slight compatibility with PBT, the thermally induced migration of clay in PS phase into PBT phase was not observed. However under shear flow, the migration of clay across the interface was observed. Also this migration of clay brings about domain size reduction by the compatibilization effect of clay. As the shear rate increases, the clay is migrated even into PBT phase and the domain size is effectively reduced. Furthermore, if we compare the crystallinity of the blend

under shear conditions, DSC analysis shows that the crystallization speed of PBT obtained under high shear rate becomes faster, which means the clay migrates into PBT phase and it play a role as a nucleating agent. Therefore, in immiscible blends system, the organoclay can be migrated into the interface by the strong shear flow and it plays a role as a compatibilizer during morphology evolution.

Experimental

PS (MFI: 17.6g/min at 200°C) under the grade name of GPPS HF2680 was provided from Samsung Cheil industries Inc. Poly(1,4-butylene terephthalate) (PBT, Mw: 53K) was purchased from Sigma-Aldrich Co.. Nanofil 919 was supplied from Sud-Chemie Inc. and used without further treatment. This kind of organoclay based on montmorillonite has been modified with the long chain hydrocarbon (>C10). Prior to compounding, all samples were dried in the vacuum oven at 70°C for 12 hours. Melt compounding was performed using counter-rotating twin crew extruder (L/D=16, D=4/3, Haake) and the weight fraction of clay was 15phr. The PS/clay composites and virgin PBT pellets were molded in a hot press (Carver, CH4386) with 0.2mm thickness/25mm diameter mold at 180°C and 240°C, respectively. Then three PBT films and two PS/clay films were alternatively superposed at 180°C. At this temperature, the melting PS/clay layers could act as an adhesive. The pressure was not applied on the sandwiched films in order to avoid the squeezing flow between the layers. RMS800 was used to give sandwiched multi-layer different strains in the nitrogen atmosphere. The blend morphologies were investigated by SEM using JEOL model JSM-840A apparatus operating at an accelerating voltage of 20K. The samples were fractured in liquid nitrogen and etched for 30min using THF, then sputtered with palladium. The morphology evolution of pure PS/PBT multi-layered were studied by confocal scanning laser microscope LEXT OLS3000 with micro-tomed samples. The localization of clay platelets in polymer blends was investigated by TEM using JEOL model JEM-3010 apparatus operated at an accelerating voltage of 300KV.

Result and Discussion

Figure 1 shows Confocal micrographs of the micro-tomed surfaces of the multi-layered films prepared with RMS at different time. White gray is PBT phase and black gray is PS phase. As time goes by, both PBT and PS films become drop and sizes are getting decreased. Figure 2 exhibits SEM micrographs of the fractured surfaces of the sandwiched films. The influence of strain is obvious that drop sizes become decreased and the size distribution becomes narrowed. To investigate the mechanism of the morphological change, the clay localization and migration in the blend have to be considered. TEM micrographs in Figure 3 reveal that clay platelets are only located in PBT and interface of both immiscible polymers. Even though PS/clay nanocomposites films were originally used, clay platelets are absent inside of PS phase in the sandwiched samples that were applied with strains. Furthermore, the amount of

clay in the interface gradually decreased and clay platelets become more dispersed by increasing the amplitude of strain. To classify which kind of driving force makes this phenomenon, we are considering to compare the sandwiched films of PS/PBT and those of PS/(PBT+clay) and internal mixer (Haake) will be used to observe general views. DSC results showed that the addition of clay has no considerable effects on the T_g of amorphous PS component. On the contrary, the crystallization behaviours of semi-crystalline PBT component are remarkably influenced by the presence of clay, which acts as nucleating agent of PBT phase. As shown in Figure 4, crystallization peak and temperature are shifted by dispersed clay platelets and the more strain is applied, the faster crystallization is occurred. It is the evidence of migration of clay.

Acknowledgment

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Reference

1. Yong Wang, Qin Zhang, Qiang Fu, *Compatibilization of immiscible Poly(propylene)/ Polystyrene Blends Using Clay*, *Macromol. Rapid Commun*, **24(3)**, pp.231-235 (2003)
2. Hong JS, Namkung H, Ahn KH, Lee SJ, and Kim C, *The role of organically modified layered silicate in the breakup and coalescence of droplets in PBT/PE blends*. *Polymer*, accepted for publication (2006)

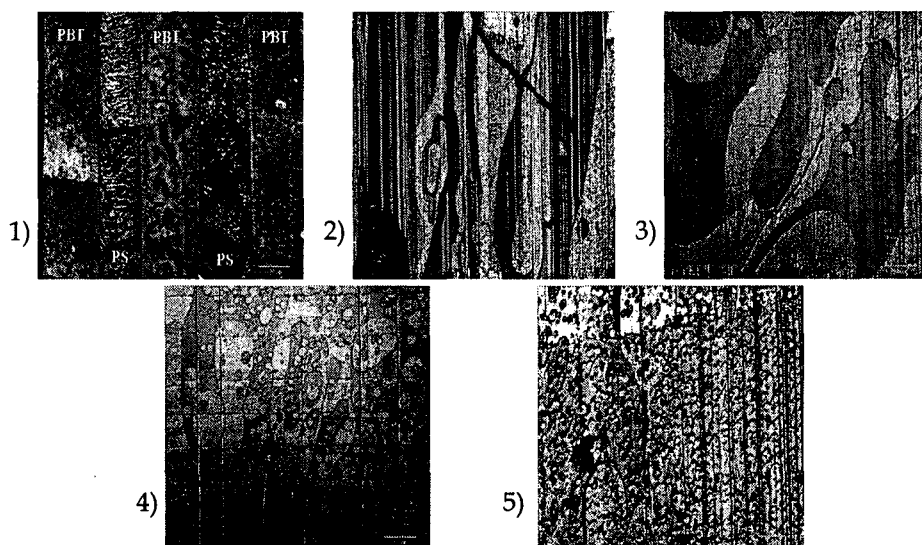


Fig 1. Morphology evolution of pure PS/PBT five multi-layered samples with same shear rate as 1/s and different time scale

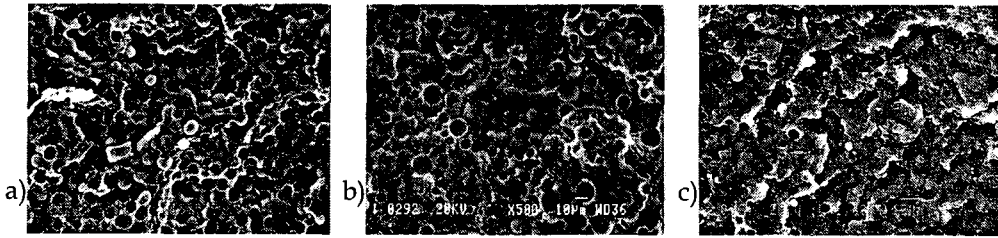


Fig 2. SEM micrographs for (a) strain 3600, (b) strain 7000, and (c) strain 25000

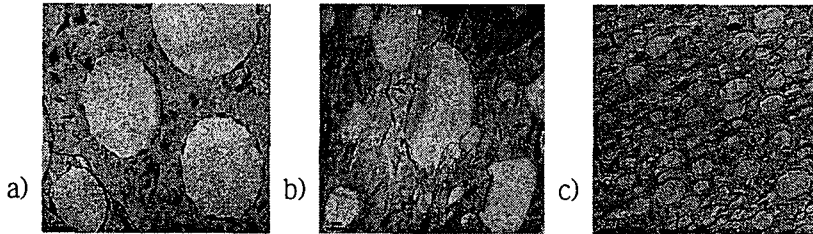


Fig 3. TEM micrographs for (a) strain 3600, (b) strain 7000 (c) strain 5000

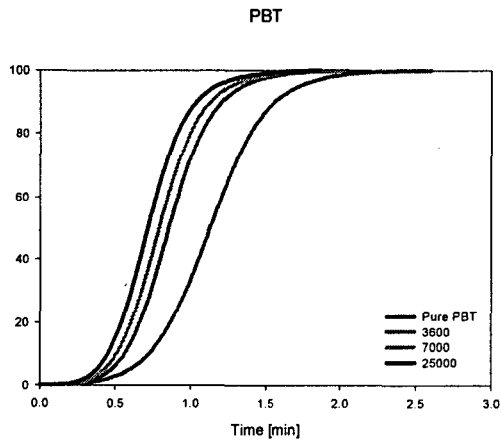


Fig 4. Plots of relative crystallization degree versus time