

Migration of Nanoclay in Immiscible Polymer Blends

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Introduction

Blending of two immiscible polymers has become increasingly crucial because it provides superior properties to 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} because clay can act like both the compatibilizer and reinforcing filler in the polymer blends. TEM micrographs revealed that clay platelets locate at the interface of two polymers and only their more favorable polymer component. Like compatibilizers³, it can lead to more stable morphologies because drop sizes were decreased due to the lower interfacial tension and the degree of dispersion was improved. In addition, clay exhibits remarkable improvement in material properties as reinforcing filler. Even though, many research groups studied the effects of clay in the polymer blends and the properties of polymer nanocomposites, they have not considered the development of clay in the polymer blends system and the reason of the selective localization of clay.

Experimental

Polystyrene (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 which has good affinity for PBT was supplied from Sud-Chemie Inc.. 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, Bautek) 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 as Figure 1. 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 sputtered with palladium. 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.



Figure 1. Sandwiched sample (left). Illustration of TEM sampling location and SEM observed position (right).

Results and discussion

Figure 2 (above) shows SEM micrographs of the fractured surfaces of the sandwiched films as two PS/clay and three PBT films were used prepared using RMS applied fixed shear rate at 1/s and different time. The influence of strain (shear × time) is obvious that the morphology of minor phase (PS/clay) is gradually changed from sheet

formation to stable drops in process of time. To investigate the mechanism of the morphological changes, the clay localization and migration in the blend have to be considered. TEM micrographs in Figure 2 (below) reveal that clay tactoids which is originally located at PS phase are migrated into PBT phase and the interface of both immiscible polymers. TEM micrographs show that clay tactoids did not exist inside of PS phase after 1200seconds. Even though PS/clay nanocomposites films were originally prepared to do test, clay platelets are absent inside of PS phase in the sandwiched samples that were applied with strains. It means that the migration of clay is possible in the conditions of low shear and enough time. However, clay tactoids are still observed in both PBT (much more favourable phase) and interface due to not sufficient force to separate into individual layers. To understand the effect of shear, higher shears were introduced as shear rate at 10/s and 50/s in Figure 3. Applied time was fixed at 700seconds. In the case of shear rate at 10/s, many clay tactoids are observed in the interface. On the other hand, shear rate at 50/s shows that the interface is covered by clay platelets and the dispersion of minor phase is improved as increasing shear rate in Figure 3 (b). It indicates that higher shear provides good ability to compound and enough force to separate clay tactoids into individual layers. However, the highest shear rate at 50/s in Figure 3 (c) also presents small clay tactoids in the interface and PBT phase. We can conclude that applied shear with RMS800 can not make completely exfoliated system. 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) which can give mechanical force will be used to observe general views. In order to observe the migration of clay by the thermal diffusion in this multi-layer system, time sweep test (dynamic oscillatory mode) with low strain using RMS800 will be conducted.

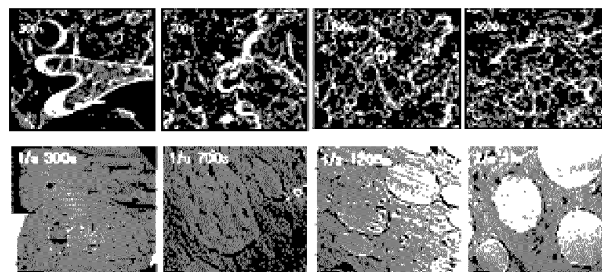


Figure 2. Morphology evolution shear rate at 1/s.

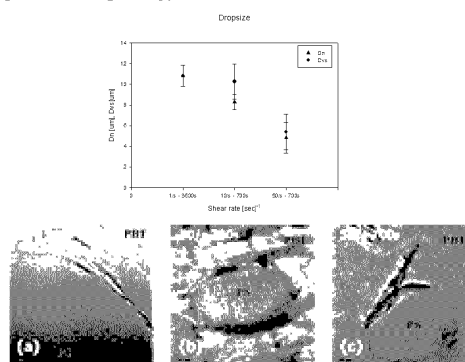


Figure 3. Drop sizes of test samples and TEM micrographs.

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