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Influence of Processing Sequence on the Tribological Properties of VGCF-X/PA6/SEBS Composites

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Abstract. In order to develop the new tribomaterials for mechanical sliding parts with sufficient balance of mechanical and tribological properties, we investigated the influence of processing sequence on the tribological properties of the ternary nanocomposites: the polymer blends of polyamide 6 (PA6) and styrene-ethylene/butylene-styrene copolymer (SEBS) filled with vapor grown carbon fiber (VGCF-X), which is one of carbon nanofiber (CNF) and has 15nm diameter and 3 μ m length. Five different processing sequences: (1) VGCF-X, PA6 and SEBS were mixed simultaneously (Process A), (2) Re-mixing (Second compounding) of the materials prepared by Process A (Process AR), (3) SEBS was blended with PA6 (PA6/SEBS blends) and then these blends were mixed with VGCF-X (Process B), (4) VGCF-X was mixed with PA6 (VGCF-X/PA6 composites) and then these composites were blended with SEBS (Process C), and (5) VGCF-X were mixed with SEBS (VGCF-X/SEBS composites) and then these composites were blended with PA6 (Process D) were attempted for preparing of the ternary nanocomposites (VGCF-X/PA6/SEBS composites). These ternary polymer nanocomposites were extruded by a twin screw extruder and injection-molded. Their tribological properties were evaluated by using a ring-on-plate type sliding wear tester under dry condition. The tribological properties such as the frictional coefficient and the specific wear rate were influenced by the processing sequence. These results may be attributed to the change of internal structure formation, which is a dispersibility of SEBS particle and VGCF-X in ternary nanocomposites (VGCF-X/PA6/SEBS) by different processing sequences. In particular, the processing sequences of AR, B and D, which are those of re-mixing of VGCF-X, have a good dispersibility of VGCF-X for the improvement of tribological properties.

Keywords: Tribological properties, Processing sequence, Ternary composites, Vapor grown carbon fiber, Polyamide

PACS: 81.05.Qk, 81.40.Pq, 83.50.Xa

INTRODUCTION

Recently, there has been a great discussion on the tribomaterials of polymer nanocomposites^{1),2)} for mechanical sliding parts such as bearings, gear, seals and so on. However, little study has been done to develop these tribomaterials suitable for micro size devices with sufficient balances between mechanical and tribological properties. In our previous works, the effect of the addition of thermoplastic elastomer (TPE) on the mechanical and tribological properties of nano sized filler filled thermoplastic nanocomposites, which are layered silicate (Clay) filled polymer blends of polyamide 6 (PA6) and styrene-ethylene/butylene-styrene copolymer (SEBS) (PA6/Clay/SEBS)^{3), 4)}, vapor grown carbon fiber (VGCF), which is one of carbon nanofiber, filled polymer blends of polybutylene terephthalate (PBT) and TPE (VGCF/PBT/TPE)⁵⁾ and VGCF-X, which is one of CNF and its diameter is smaller than VGCF, filled polymer blends of PA6 and SEBS (VGCF-X/PA6/SEBS)⁶⁾, was investigated. It is necessary for design of tribomaterials with sufficient balances between tribological and mechanical properties to control the morphologies, which are the internal structure such as phase structure and filler dispersion of these ternary nanocomposites. On the other hand, the morphologies of these ternary nanocomposites are influenced by the processing sequences. Several investigations have been conducted on the effect of processing sequences at melt mixing by twin screw extruder on the relationship between the morphology and the physical properties of these ternary nanocomposites such as PA/Clay/SEBS^{7), 8)}, VGCF/PBT/TPE⁵⁾ and VGCF/PA6/SEBS⁹⁾. However, there is

not enough knowledge of reliable relations between the internal microstructure and the tribological properties of these ternary nanocomposites. The purpose of this study is to investigate the effect of processing sequence on the tribological properties of VGCF-X filled polymer blends of PA6 and SEBS (VGCF-X/PA6/SEBS ternary nanocomposites).

EXPERIMENTAL

The materials used in this study were ternary nanocomposites of Polyamide 6 (PA6), VGCF-X (Vapor Grown Carbon Fiber, Showa Denko K.K, $d=15\text{nm}$, $L=3\mu\text{m}$), which is one of CNF, PA6 (polyamide 6, 1013B, Ube industries, Ltd., Japan) and SEBS (styrene-ethylene/butylene-styrene copolymer, H1052, Asahi Kasei Chemicals Co., Japan). The composition of PA6 and SEBS was fixed as 80/20 by weight fraction, and three kinds of VGCF-X volume fraction were selected as 0, 1 and 5vol.%. Prior to mixing, VGCF-X, PA6 and SEBS were dried in a vacuum oven at 80°C for 12h. Five different processing sequences: (1) VGCF-X, PA6 and SEBS were mixed simultaneously (Process A), (2) Re-mixing (Second compounding) of the materials prepared by Process A (Process AR), (3) SEBS was blended with PA6 (PA6/SEBS blends) and then these blends were mixed with VGCF-X (Process B), (4) VGCF-X was mixed with PA6 (VGCF-X/PA6 composites) and then these composites were blended with SEBS (Process C), and (5) VGCF-X were mixed with SEBS (VGCF-X/SEBS composites) and then these composites were blended with PA6 (Process D) were attempted for preparing of the ternary composites. Fig. 1 shows the schematic diagram of five different processing sequences for VGCF-X/PA6/SEBS ternary composites. These materials were melt mixed at 85rpm and 240°C on a twin screw extruder (TEX-30, Japan Steel Works, Ltd., Japan). After mixing, the extruded strands of these ternary nanocomposites were cut by a pelletizer and were dried again at 80°C for 12h in vacuum oven. Various shaped samples for mechanical and tribological properties testing were injection molded (NS20-A, Nissei Plastic Industrial, Japan). Tribological properties such as frictional coefficient μ and specific wear rate V_s were measured by a ring-on-plate type sliding wear tester (EFM-3-EN, Orientech Co.) under dry condition. A carbon steel (S45C) ring with the surface finished by No.240 and No.800 polishing paper was used as a counterpart. Tribological testing was evaluated by sliding speed of 0.5m/sec, sliding distance 3000m and normal load of 50N. The sliding surfaces on the counterpart and the wear debris after testing were observed using a scanning electron microscope (EDX-WET SEM, JSM-6360LA, JEOL Ltd., Japan). For understanding the internal structure of these ternary nanocomposites such as the dispersion of VGCF-X and SEBS in PA6 matrix polymer, the surface of samples fractured cryogenically in liquid nitrogen was observed using SEM. The cryogenically fractured surface was etched in toluene for 24h to remove the dispersed SEBS particles. A quantitative analysis of dispersed SEBS particle size was made from several SEM microphotographs using two kinds of image processing software (Adobe Photoshop, Adobe and Image J, NIH). The software used identifies each individual dispersed SEBS particle and evaluates its area A . From this, apparent particle size d was calculated as follows:

$$d = \left(\frac{4A}{\pi} \right)^{\frac{1}{2}} \quad (1)$$

The measured particle size was characterized by evaluating number average diameter d_n , weight average diameter d_w and volume average diameter d_v from more than 250 particles defined as⁴⁾:

$$d_n = \frac{\sum n_i d_i}{\sum n_i} \quad (2), \quad d_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (3), \quad d_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (4)$$

where n_i is the number of dispersed particles having diameter d_i . The ratio of d_w/d_n is an indication of polydispersibility, which is the distribution of dispersed particles.

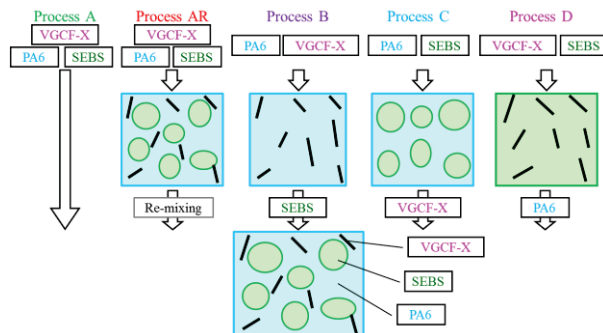


FIGURE1. Schematic diagram of five different of processing sequences for VGCF-X/PA6/SEBS composites

RESULTS AND DISCUSSION

The effect of processing sequences on the tribological properties of VGCF-X/PA6/SEBS ternary nanocomposites are discussed. Fig. 2(a) and Fig. 2(b) show the influence of volume fraction of VGCF-X V_f on the frictional coefficient μ and specific wear rate V_s of VGCF-X/PA6/SEBS composites prepared by five different processing sequences, respectively. μ and V_s show the complex behavior according to the processing sequences. Although the type of processing sequence seems not to affect to μ , the influence of the type of processing sequences on V_s differs. V_s of composites by Process A has a maximum value around 1 vol.%, and decreases with increasing V_f . In contrast, V_s of the composites by other Process (AR, B, C, and D) shows a contrary tendency. The improvement of specific wear rate for VGCF-X/PA6/SEBS ternary nanocomposites decreases in the following order: Process A > Process C > Process D > Process AR > Process B. This tendency has a comparatively close relation with the mechanical properties¹⁰, and it is clear that the influence of the type of processing sequence on V_s is larger than that on frictional coefficient. In particular, the improvement of wear properties is related to the number of mixing of VGCF-X, and the twice mixing methods of VGCF-X which are the re-mixing of VGCF-X such as Process AR, B and D are more effective than uni-mixing methods such as Process A and C. These may be attributed to the change of internal structure formation of ternary nanocomposites (VGCF-X/PA6/SEBS) by different processing sequences.

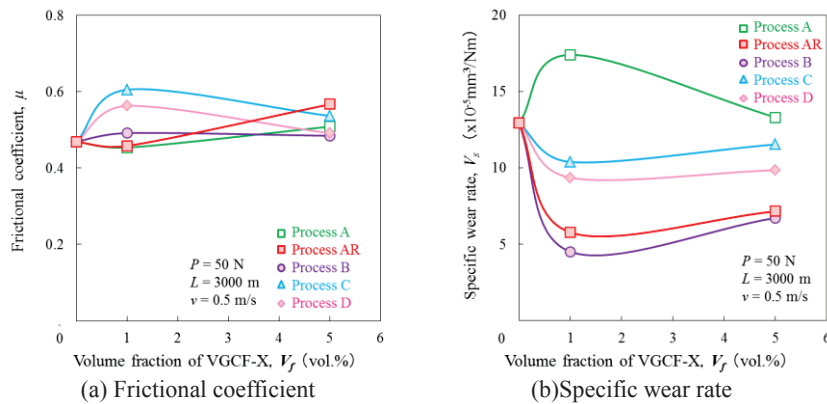


FIGURE 2. Influence of volume fraction of VGCF-X on the various tribological properties of VGCF-X/PA6/SEBS composites.

Because the tribological properties of polymer and polymer composites are strongly influenced by their ability to form a transfer film on the counterpart, it is essential to observe this factor for understanding the mechanisms of tribological behavior^{4), 11)}. Fig. 3 presents SEM photographs on the surface of metallic counterface (S45C) after sliding wear testing against VGCF-X/PA6/SEBS composites ($V_f=1 \text{ vol.}\%$). The morphology of counterface against the composite Process A (Fig. 3(a)) shows thick transfer film surface overall, although that of the composite by Process B (Fig. 3(b)) shows thin ones with shallow grooves in the direction of orthogonal to sliding direction overall. The thickness of transfer film on the counterface differs according to the mechanical properties of VGCF-X/PA6/SEBS ternary nanocomposites. These differences in the formation of transfer films on the counterface are considered to induce the change of the tribological properties of these ternary nanocomposites. The thickness of transfer films on the counterface of the composites by the other processes was formed of an intermediate thickness between Process A and Process B, although the SEM photographs of other processes were omitted due to space limitations.

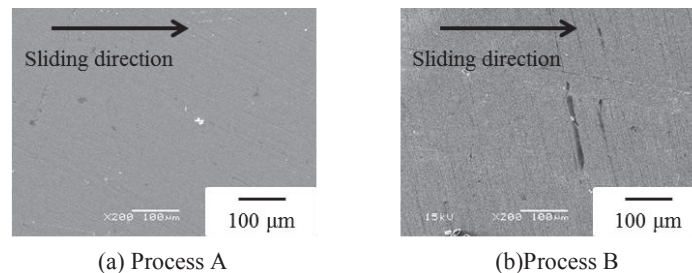


FIGURE 3. SEM photographs of counterface against VGCF-X/PA6/SEBS composites ($V_f=1 \text{ vol.}\%$)

For better understanding the relationship between processing sequences and tribological properties of VGCF-X/PA6/SEBS ternary nanocomposites, we observed the internal structure formation, which is a dispersibility of SEBS particle and VGCF-X in these ternary nanocomposites. Fig. 4 shows the SEM photographs of cryogenically fractured surfaces, which were etched by toluene in order to remove the dispersed SEBS particles, of various VGCF-X/PA6/SEBS ternary nanocomposites ($V_f=1\text{vol.}\%$) at the same magnification rate ($\times 20,000$). Each ternary nanocomposite indicates the typical separate spherical phases (dispersed SEBS particles) in continuous matrix domains (PA6) and the size of dispersed SEBS particles changes according to the processing sequences. Table 1 summarizes the various data of the dispersed SEBS particles in each composite, which are calculated by image processing from SEM photographs such as number average particle size d_n , the weight average particle size d_w , the volume average diameter d_v , and polydispersity d_w/d_n . The sizes of dispersed SEBS particles change with the types of processing sequence, and these sizes decrease in the following order: Process A > Process AR > Process B > Process C > Process D. This behavior may be due to factors such as the number of mixing of SEBS, the physical interaction between PA6 and SEBS, and also the dispersion and location of VGCF-X, however it is difficult to establish the reasons exactly.

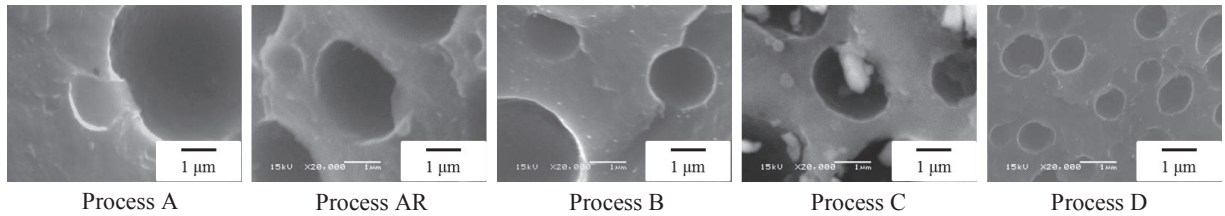


FIGURE4. SEM photographs of fracture surface of VGCF-X/PA6/SEBS composites ($V_f=1\text{vol.}\%$)

TABLE1. Dispersed SEBS particle size of VGCF-X/PA6/SEBS composites ($V_f=1\text{vol.}\%$)

Processing Sequence	d_n (μm)	d_w (μm)	d_v (μm)	d_w/d_n
Process A	2.31	2.49	2.81	1.08
Process AR	1.83	2.16	2.73	1.18
Process B	1.00	1.33	1.88	1.33
Process C	1.00	1.15	1.48	1.15
Process D	0.81	0.88	0.97	1.08

It is well known that the morphology of multicomponent composites has a close relationship with the physical properties of ones. To clarify whether these relationships vary or not in this study, it is necessary to investigate the influence of the morphology of ternary nanocomposites on the tribological properties in detail. Tribological properties such as μ and V_s is replotted as a function of the volume average diameter of dispersed SEBS particles d_v in Fig. 5. In the figure, the number after each processing sequence code show the content of VGCF-X in the composites. Although the d_v dependence of μ (Fig. 5(a)) is not clearly recognized, that of V_s (Fig. 5(b)) is slightly observed the correlation between V_s and d_v , which is V_s decreases with decreasing d_v . This tendency is similar to other mechanical properties such as impact strength observed for usual polymer blends and ternary composites^{4), 12)}. However, this relation is weaker than the processing sequence of re-mixing of VGCF-X (Process AR, B and D).

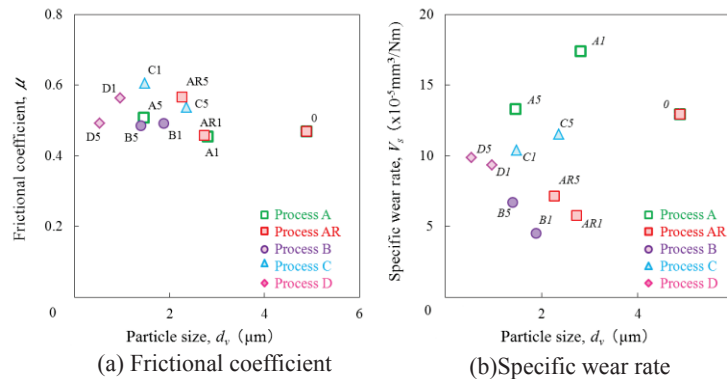


FIGURE5. Influence of particle size of SEBS on the various tribological properties of VGCF-X/PA6/SEBS composites

For further understanding of the dispersion of VGCF-X in VGCF-X/PA6/SEBS ternary nanocomposites, Fig. 6 shows the SEM photographs of fracture surface of these ternary nanocomposites ($V_f=1\text{vol.}\%$). While we can see a few agglomeration of VGCF-X in Process A (Fig. 6(a)), there are no obvious agglomerations of VGCF-X in Process B (Fig. 6(b)), which shows a good dispersion of VGCF-X. In addition, the dispersibility of the other re-mixing of VGCF-X (Process AR and D) has the same tendency. In short, the processing sequences of AR, B and D, which are those of re-mixing of VGCF-X, have a good dispersibility of VGCF-X for the improvement of tribological properties.

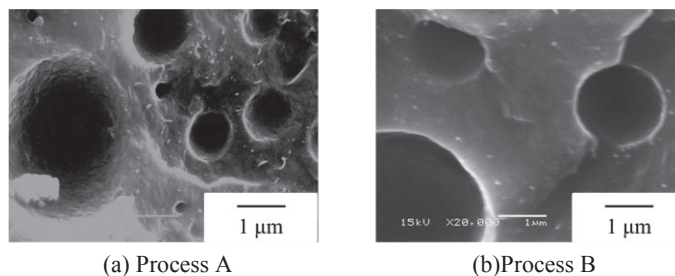


FIGURE 6. SEM photographs of fracture surface of VGCF-X/PA6/SEBS composites ($V_f=1\text{vol.}\%$)

CONCLUSION

The purpose of this study was to investigate the effect of processing sequences on the tribological properties of VGCF-X filled polymer blends of PA6 and SEBS (VGCF-X/PA6/SEBS ternary nanocomposites). It was found that the tribological properties such as the frictional coefficient and the specific wear rate are influenced by the processing sequence. These results may be attributed to the change of internal structure formation, which is a dispersibility of SEBS particle and VGCF-X in ternary nanocomposites (VGCF-X/PA6/SEBS) by different processing sequences. In particular, the processing sequences of AR, B and D, which are those of re-mixing of VGCF-X, have a good dispersibility of VGCF-X for the improvement of tribological properties.

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