Effect of processing conditions on mechanical and barrier properties of PLA/Clay nanocomposites

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Abstract

Elongation, toughness, and barrier properties of PLA are not sufficient to use for many applications such as food packing and films. But, elongation, toughness and gas barrier can be improved by addingnanoclay in the PLA. Now, the most used Melt-Compounding Method is the twin-screw extruder because of productivity and continuity. The processing conditions such as screw configurations and screw speed determine the dispersions state of nanoclay in the matrix: hence affect the mechanical and barrier properties of PLA/clay nanocomposites. We prepared nanocomposites using three types of screw configulations with various screw speed. Dispersion state of nanoclays in the PLA was evaluated by TEM observation and rheology tests. It was found the screw configurations with mixing and blister elements showed the best in dispersion of clay.Furthermore, elongation of PLA nanocomposites increased from 5% to 15% with improving the dispersion state of nanocomposites. We confirmed that the processing consitions of twin-screw extruder was important to enhance the properties of PLA/clay nanocomposites.

1. Introduction

Recently, global warming and depletion of oil resources are a world problem. So practical applications of the biodegradable plastic are expected. In particular, because PLA is made from corn, PLA is expected high transparency and high mechanical property. However PLA is very brittle, and barrier properties of PLA is low. So PLA is not popular. Therefore, in this study, PLA/Clay nanocomposites are prepared using three types of screw configulations with various screw speed in the twin-screw extruder because of productivity and continuity to improve toughness and gas barrier properties of PLA. Dispersion state of nanoclays in the PLA was evaluated by TEM observation and rheology tests. Elongation break and gas barrier properties of PLA/Clay was evaluated by tensile and gas permeability testing.

2. Experimental section

2.1 PLA/Clay nanocomposites production

The materials we used were PLA(polylactide “HISON”) and nanoclay(T(NI)). Table 1 shows the production condition of the PLA/Clay nanocomposites. PLA was added 2.5w% of nano clays by twin-screw extruder. We prepared nanocomposites using three types of screw configulations with various screw speed. Figure 1 shows three types of screw configulations.

Dumb-bell test specimens made from the PLA/Clay nanocomposites by twin-screw extruder were prepared by injection molding machine to do tensile testing. Table 2 shows Injection condition. Figure 2 shows dumb-bell test specimens made by injection molding machine

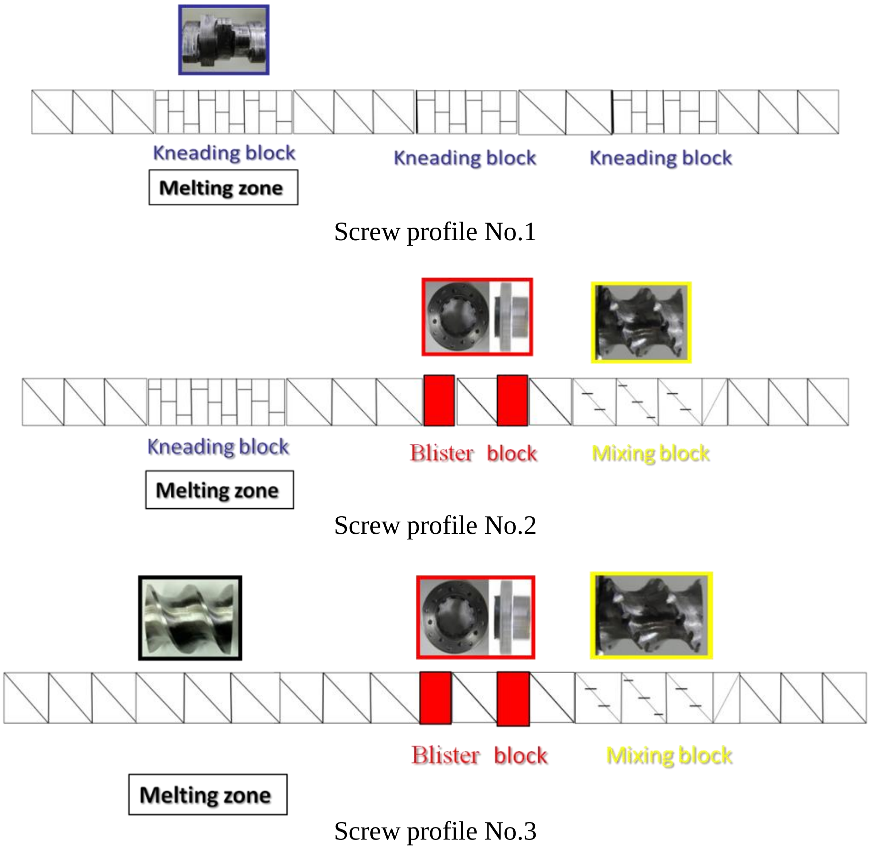


Figure 1 Three types of screw configulations using twin-screw extruder

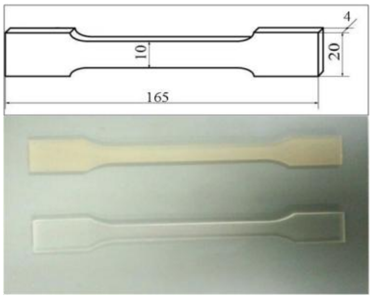


Figure 2 Dumb-bell test specimens made by injection molding machine

Table 1 Mixing condition of the PLA/Clay nanocomposites using twin-screw extruder

sample code	Clay [wt%]	screw rotation speed [rpm]
PLA/Clay	2.5	150 300 420

Table 2 Injection condition

Screw rotation speed [rpm]	100
Back pressure [MPa]	4
Holding pressure [MPa]	60
Cylinder temperature [℃]	180
Injection speed [mm/sec]	100

2.2 Rheology tests

Dispersion state of nanoclays in the PLA was evaluated by rheology tests using rotary rheometer(Bohlin Gemini Ⅱ, MALVERN)[1][2]. Parallel plate of 25[mm] in diameter was used. Rheology tests was conducted in measurement condition that the frequency domain was from 0.1 to 100[rad/s], strain was 0.01, and temperature was 180[℃]. The yield stress was demanded by $\eta^*-\omega$ curve line obtained from rheology tests fitting Carreau-Yasuda model according to (1) to quantitatively evaluate dispersion state of nanoclays in the PLA[3][4][5].

$$\eta^* = \frac{\sigma_0}{\omega} + \eta_0[1+(\lambda\omega)^a]^{(n-1)/a} \tag{1}$$

2.3 TEM observation

The dispersion state of the clay was observed visually by TEM observation. Films of thickness is 100[nm] were made from dumb-bell test specimens by electric microtome. The dispersion state of the clay was observed on acceleration voltage of 200[kV] and magnification of ×10000.

2.4 Gas permeability testing

Gas barrier properties were tested by gas permeability measuring device. Films of 100×100×0.3[mm] for gas permeability testing were prepared. Films were put in the vacuum dryer of 80 degrees for 10 hours. Measurement area was the circle of 70[mm] in diameter, and O_2 gas was used as the measurement gas. Gas permeability(GTR) was measured by testing, and permeability was calculated by using an equation (2).

$$P = \frac{l}{6.566\times10^{14}}\cdot GTR \tag{2}$$

P : permeability [cm^3 · cm/(cm^2 · s · cmHg)], GTR : gas permeability [cm^3/(m^2 · day · atm)], l : thickness [μm]

2.5 Tensile testing

Tensile strength and elongation break were investigated by extensometer(ST50-10-10"SHIMADZU") and autograph(AG-1"SHIMADZU").

3. Results and Discussion

3.1 Rheology tests

Figure 3 shows the yield stress of three types of screw configulations with various screw speed provided by rheology tests. Because No.2 screw of 300[rpm] showed the best yield stress, No.2 screw of 300[rpm] showed the best dispersion state of nanoclays in the PLA. So the screw type of Blister/Mixing disperses the nanoclays in the PLA effectively. From the result of No.2 and No.3 in figure 3, it is important for the dispersion of nanoclay in the PLA to be kneading in the Melting zone.

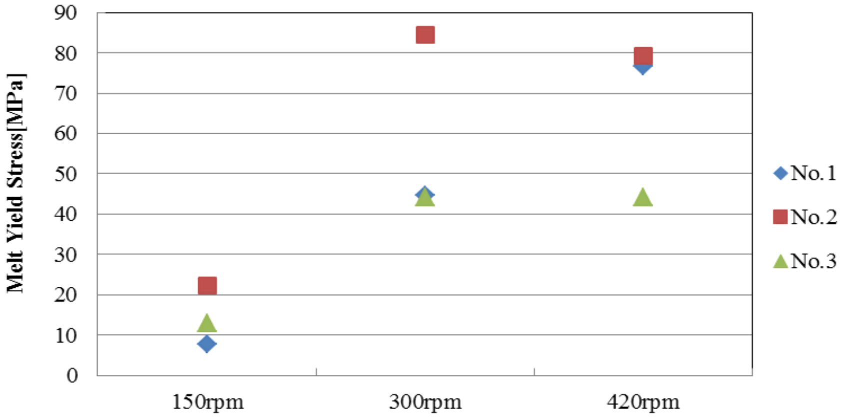
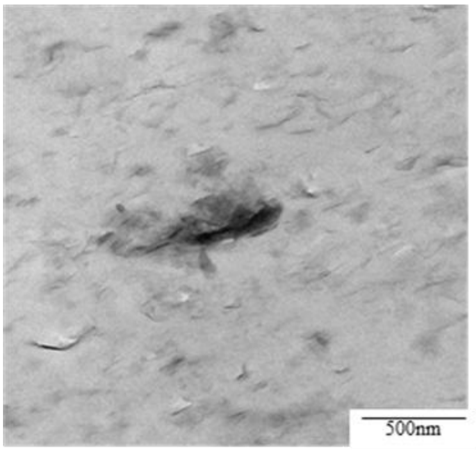


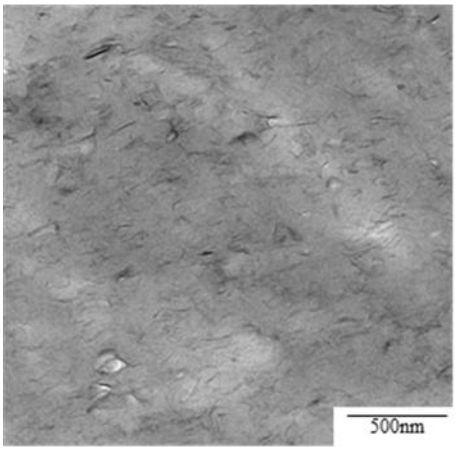
Figure 3 yield stress of PLA/Clay composites prepared at three types of screw configulations with various screw speed using twin-screw extruder

3.2 TEM observation

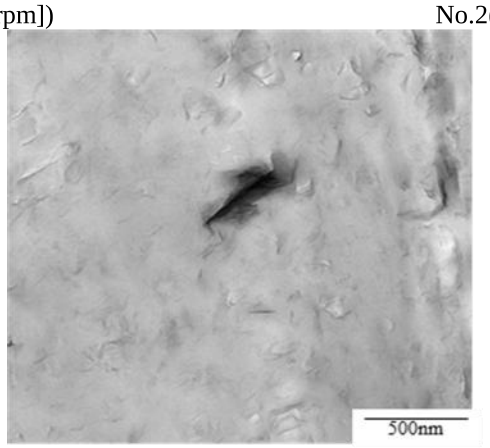
Figure 4 shows TEM images of No.1(150[rpm]), No.2(300[rpm]) and No.3(420[rpm]). Nanoclay in the PLA on TEM image of No.2(300[rpm]) becomes single layered. But, Nanoclay in the PLA on TEM image of No.1(150[rpm]) and No.3(420[rpm]) becomes layered structure. So TEM observation shows the tendency like the yield stress of rheology tests.



No.1(150[rpm])



No.2(300[rpm])



No.3(420[rpm])

Figure 4 TEM images of PLA/Clay composites prepared at three types of screw configulations

3.3 Gas permeability testing

Figure 5 shows Oxygen permeability of PLA and PLA/Clay nanocomposites prepared by No.2(300[rpm]) which showed the best dispersion state of nanoclay in the PLA. The permeation of PLA is significantly reduced by incorporating nanoclay platelets; for instance, in nanocomposites containing 2.5[wt%], permeability is reduced 31%. The gas permeability of polymers is believed to be enhanced by the incorporation of nanoclay platelets. Figure 6 shows that nanoclay platelets, which are considered as an impermeable phase, reduce the permeation by forcing the gas molecules to diffuse along a longer tortuous path a cross the polymer film[6].

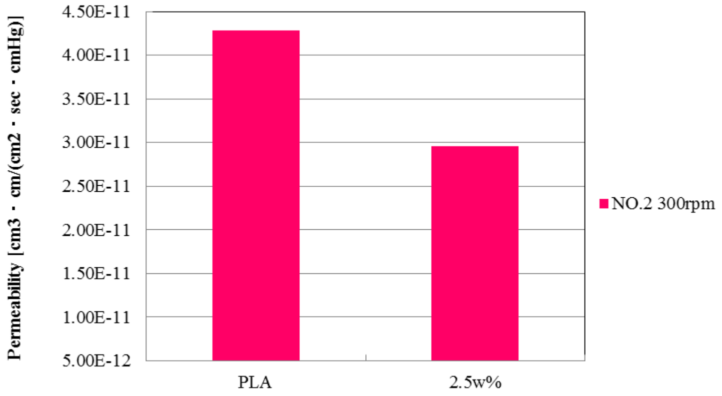


Figure 5 Oxygen permeability of near PLA and PLA/Clay nanocomposites

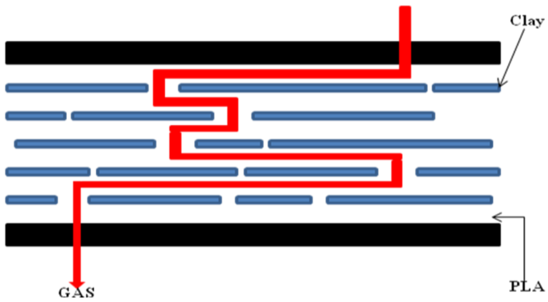
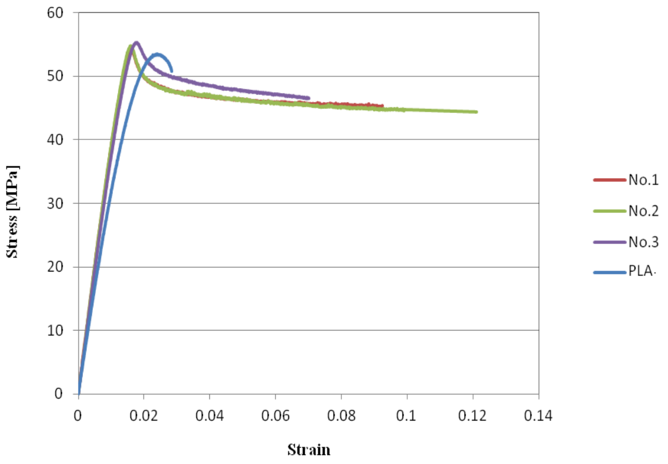


Figure 6 Model of gas molecules through the polymer film

3.4 Elongation break

Figure 7 shows Stress-Strain carves of three types of screw configulations with various screw speed provided by tensile testing. No.2(300[rpm]) of the best yield stress of rheology tests showed the best elongation break. No.2(300[rpm]) showed approximately 3.28 times elongation break in comparison with PLA. Figure 8 shows dumb-bell test specimens after tensile testing. PLA/Clay nanocomposites elongate very well, but PLA break immediately without becoming thinner. Dumb-bell test specimens of PLA are broken by being united with voids made by injection molding machine and causing to collapses before dumb-bell test specimens of PLA are becoming thinner. But, PLA/Clay nanocomposites increase elongation break in comparison with PLA because of Clays between the void prevent to be united with voids made by injection molding machine and cause to collapses[7]. So elongation break depends on the dispersion of nanoclay in the PLA.



300[rpm]

Figure 7 Stress-Strain carves

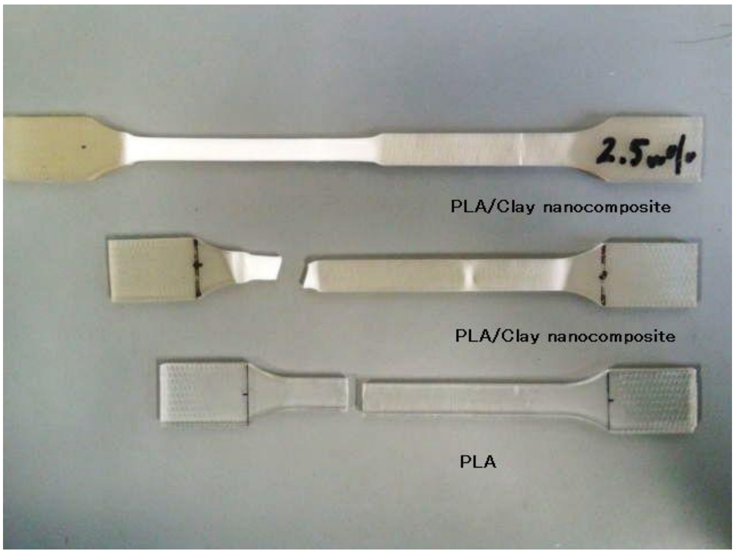


Figure 8 dumb-bell test specimens after tensile testing

4. Conclusion

In this study, we prepared nanocomposites using three types of screw configulations with various screw speed, and we evaluated the characteristic of PLA/Clay nanocomposites affected by the dispersion state of nanoclay in the PLA. As a result, the following things were shown.

(1) The screw type of Blister/Mixing disperses the nanoclays in the PLA effectively.
(2) It is important for the dispersion of nanoclay in the PLA to be kneading in the Melting zone.
(3) The gas permeability of polymers is believed to be enhanced by the incorporation of nanoclay platelets.
(4) Elongation break depends on the dispersion of nanoclay in the PLA.

References

[1] Jiang, G., and Huang, H., "Melt-Compounding of PP/Clay Nanocomposite and Relationship between Its Microstructure and Shear Strain in the Flow Field Based on Rheological Analysis", Polymer Engineering And Science, Vol. 51, No. 11 (2011), pp. 2345-2352.
[2] Vermogen, A., Masenelli-Varlot, K., and Se´gue´la, R., "Evaluation of the Structure and Dispersion in Polymer-Layered Silicate Nanocomposites", Macromolecules, Vol. 38, No. 23 (2005), pp. 9661-9669.
[3] Lertwimolnun, W., Vergnes, B., "Influence of Screw Profile and Extrusion Conditions on the Microstructure of Polypropylene/Organoclay Nanocomposites", Polymer Engineering And Science, Vol. 47, No. 12 (2007), pp. 2100-2109.
[4] Lertwimolnun, W., Vergnes, B., "Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix", Polymer, Vol. 46, No. 10 (2005), pp. 3462-3471.
[5] Lertwimolnun, W., Vergnes, B., "Effect of Processing Conditions on the Formation of Polypropylene/Organoclay Nanocomposites in a Twin Screw Extruder", Polymer Engineering And Science, Vol. 46, No. 3 (2006), pp. 314-323.
[6] Mostafa,Y.,Tahereh,M.,Nathalie,C.,Pascal,H., "Thermal,oxygen barrier and mechanical properties of polylactide-organoclay nanocomposites", Composites Science and Technology,Vol.82,(2013),47-53,pp.50-51.
[7] Long Jiang, Jinwen Zhang*, Michael P. Wolcott "Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms" Polymer ,Vol.48 (2007) pp.7632-7644