

# STUDY OF PP/CLAY NANOCOMPOSITES PREPARED BY SUPERCRITICAL FLUID FOAMING

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## 1 General Introduction

Organic/inorganic nanocomposites recently studied by many researchers because of various properties such as mechanical strength, gas permeability, thermal stability and electrical properties. These attractive properties of nanocomposites depend on dispersion and morphology of inorganic fillers in organic matrix. But there are no effective method to perfectly disperse fillers in matrix yet.

Several reviews described various usages of carbon dioxide supercritical fluid. It can exchange many organic toxic solvent because have both liquid-like solubility and gas-like diffusivity. It is very useful in many industrial processes because low critical temperature of carbon dioxide, 31.1°C, and safe for environments. Carbon dioxide supercritical fluid is used also foaming agent of commercial polymers such as PE [1], PC [2], PS [2], and PP [3].

In this study, we achieve good dispersion of intercalated and exfoliated Clay in PP matrix by apply carbon dioxide supercritical fluid foaming process.

## 2 Preparation and Submission

### 2.1 Materials

The polymers used for the preparation of the PP/Clay nanocomposites are commercial polypropylene terpolymer (호남석유화학(주) SEP-740) and maleic anhydride grafted PP, PP-g-MA (호남석유화학(주) PH-200).

Clay, Cloisite 20A, was from Southern Clay Products, Inc Organic modifiers are dimethyl, dehydrogenated tallow, quaternary ammonium.

### 2.2 PP/Clay nanocomposites

Before sample preparation, Clay and PP-g-MA were dried 24h in the vacuum oven to remove moisture. Clay and PP-g-MA powder were mixed in internal mixer (HAAKE Polydrive mixer). Then PP and Mixed Clay/PP-g-MA was grinded to powder. After that powder PP and Clay/PP-g-MA were mixed in twin screw extruder (Thermo PRISM TSE 16 TC) to make PP/Clay nanocomposites. Clay composition in PP/Clay nanocomposites is 0.2, 0.5, 1, 2 and 5wt%

### 2.3 PP/Clay nanocomposite foams

Batch type reactor was used in this study, design was presented in Fig 1.. supercritical fluid gas was carbon dioxide, critical condition is 31.1°C and 75.2kgf/cm<sup>2</sup>. Experimental conditions are summarized in Table 1.

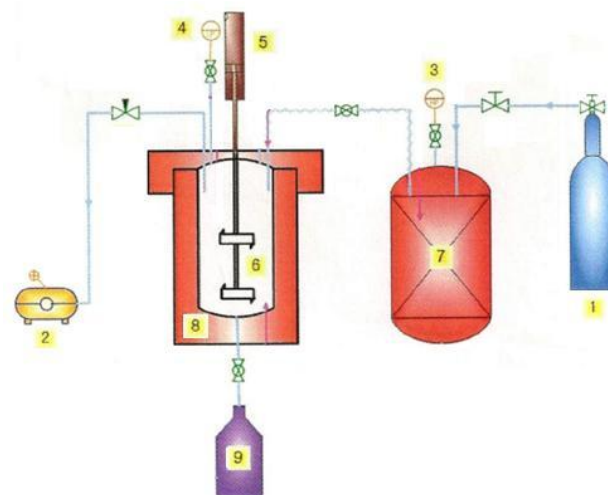


Fig.1. Carbon dioxide supercritical fluid foaming reactor. 1) carbon dioxide cylinder, 2) vacuum pump, 3) pressure gauge, 4) high pressure gauge, 5) agitator, 6) screw, 7) sub-reactor, 8) main-reactor, 9) product receiver

Samples	Clay (wt%)	Temperature (°C)	Pressure (kgf/cm <sup>2</sup> )
1	0.2	135	53
2	0.2	130	86
3	0.2	125	86
4	1	135	53
5	1	130	86
6	1	125	86

Table 1. Samples and foaming process condition

## 2.4 Characterization

The periodic structure of silicate layers in the PP/Clay nanocomposite foam was evaluated by SAXS. The micro structure of PP/Clay nanocomposite foam was analyzed by SEM. The morphology of PP/Clay nanocomposite foam was observed by TEM after cryogenic ultra microtoming [4].

## 3 Results

SAXS pattern of PP/Clay nanocomposites and foamed nanocomposites are shown in Fig 2. Peaks from 12° to 25° is  $\alpha$  and  $\gamma$ -phase of PP [5]. Peaks of unfoamed nanocomposites at 7° is ordered structure of layered silicate of Clay. This peak disappeared in foamed samples and implies exfoliation of silicate clay in PP matrix.

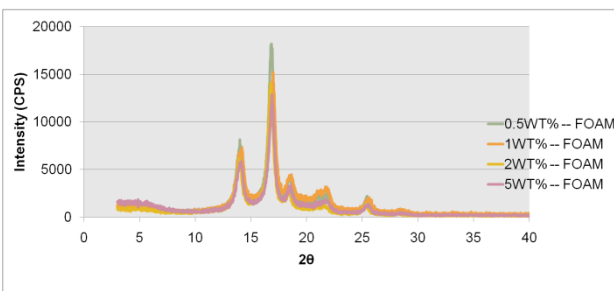
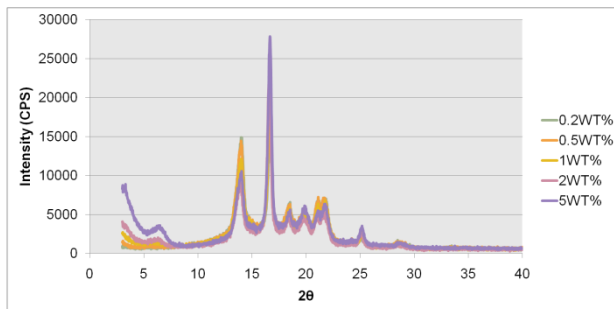


Fig.2. SAXS pattern of nanocomposites. a) unfoamed, b) foamed.

SEM images of PP/Clay nanocomposite foams are shown in Fig 3. Supercritical carbon dioxide acted as foaming agent, so micro pores were generated. Pore size of 1wt% PP/Clay composite is larger than that of 0.2wt% PP/Clay composite. Because more clays dispersed in PP and dispersed clay acted as nuclei of cell growth. Pore size is larger with increasing temperature, both 0.2wt% and 1wt% cases. In high temperature, melt viscosity of PP is decreases and composite expands easily during foaming process. So pore size increases and cell density decreases in high process temperature.

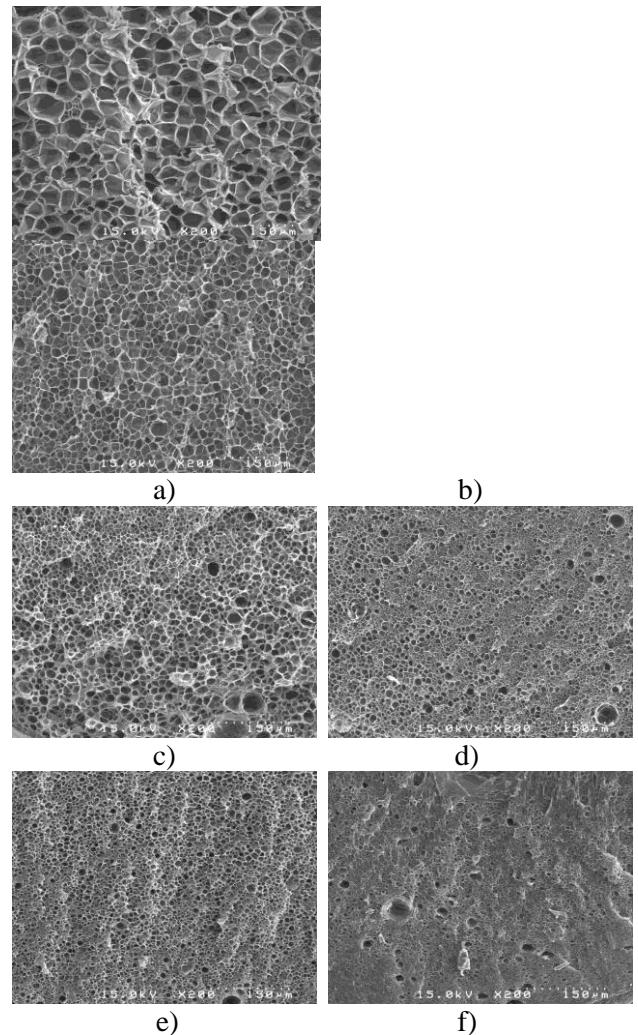


Fig.3. SEM images of nanocomposites. a) 0.2wt% 135°C 53kgf/cm<sup>2</sup>, b) 1wt% 135°C 53kgf/cm<sup>2</sup>, c) 0.2wt%

130°C 86kgf/cm<sup>2</sup>, d) 1wt% 130°C 86kgf/cm<sup>2</sup>, e) 0.2wt% 125°C 86kgf/cm<sup>2</sup>, f) 1wt% 125°C 86kgf/cm<sup>2</sup>

This tendency is supported by pore cell density in Table 2.

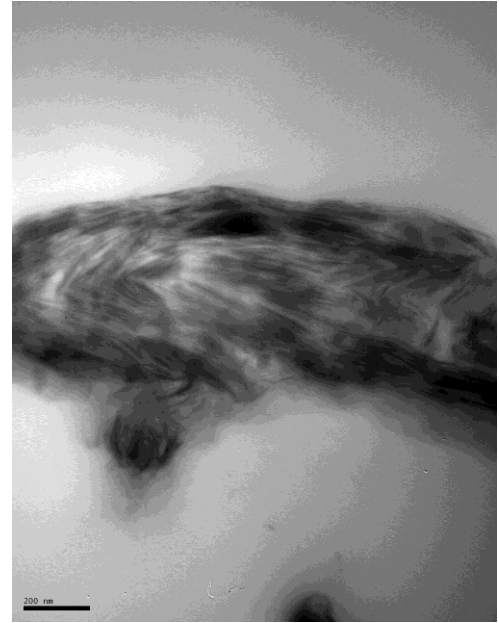
samples	Number of cells per unit volume (#/cm <sup>3</sup> )
1	$9.50 \times 10^6$
2	$1.43 \times 10^8$
3	$3.33 \times 10^8$
4	$1.48 \times 10^8$
5	$4.68 \times 10^8$
6	$8.08 \times 10^8$

Table 2. Pore cell density

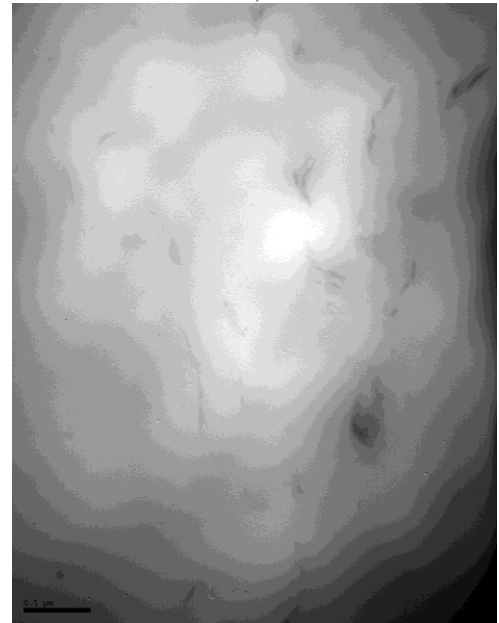
TEM micrograph of PP/Clay nanocomposite foams is shown in Fig 4. We can show that silicates of clay are well dispersed.



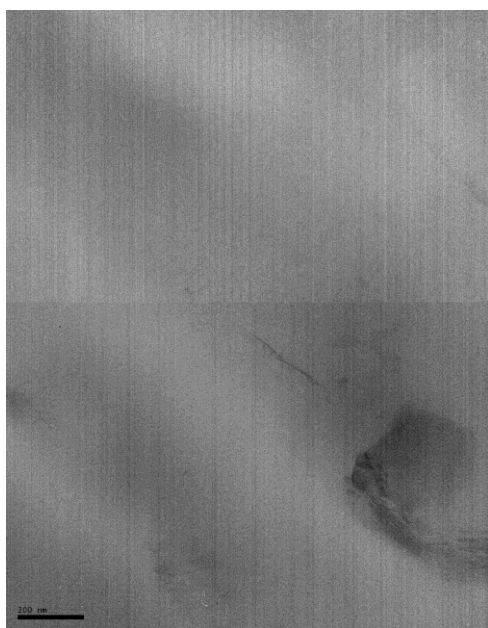
a)



b)



c)



d)

Fig.4. TEM images of nanocomposites. a) unfoamed 1wt% x40000, b) x100000, c) 1wt% 130°C 86kgf/cm<sup>2</sup> x40000, d) x100000

#### 4 Conclusion

We made PP/Clay nano composite foams by CO<sub>2</sub> sub and supercritical fluid foaming. Silicate clays exfoliated and were well dispersed in PP matrix by our process. It is supported by SAXS patterns and TEM images. Dispersed clays also acted as nuclei of pore cell growth. It is confirmed by SEM images and cell density calculation.

#### 5 References

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