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The Synthesis of Vaterite and Physical Properties of PP/CaCO$_3$ Composites

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Abstract–Vaterite was synthesized in the emulsion state at 50 °C. The mixing method was found to have a significant effect on the shape of vaterite. In order to investigate the effect of CaCO$_3$ morphology on mechanical property and thermal property of polypropylene, cubic forms of calcite and needle forms of aragonite were also prepared in the emulsion states. When vaterite was used as a filler in the PP/CaCO$_3$ composites, the crystallization temperature and crystallinity were higher than those with other forms. In addition, the size of spherullite of polypropylene was the finest when vaterite was used. Therefore, the vaterite is considered as a proper nucleating agent for polypropylene.

Key words : Calcium Carbonate, Calcite, Vaterite, Aragonite, Polypropylene

INTRODUCTION

Compounding is often associated with methods for combining polymer with additives, such as fillers, pigments or reinforcements, which may aim to influence its appearance, processibility, or simply to reduce overall cost.

Fillers, which are finely divided solids added to polymer systems to improve properties or reduce cost, can be minerals, metallic powders, organic by-products, or synthetic inorganic compounds. They cover a broad range of particle sizes and shapes and may have undergone surface treatments. Although most fillers are solids, a few silicate types contain air voids to reduce effective filler density.

In plastics, fillers increase stiffness, affect electrical properties, improve chemical resistance and reduce costs. In rubber, reinforcing fillers improve rigidity and tear strength. In liquid systems, such as sealants and adhesives, functional fillers control thixotropy, sag, and shrinkage.

There are several kinds of fillers such as calcium carbonate, talc, kaolin, organic fillers, and other fillers. Among them calcium carbonate is the dominant filler in terms of tonnage in the plastics, paints, and sealant industries.

Calcium carbonate is classified both by polymorphism and by technology. There are three kinds of calcium carbonate on the basis of polymorphism such as calcite, vaterite, and aragonite [Aglaia et al., 1989; Hakanen and Koskikallio, 1982]. Also, calcium carbonate is classified on the basis of technology such as limestone powder, ground calcium carbonate, and precipitated CaCO$_3$.

The two common forms in nature are calcite and aragonite. Because of its instability, vaterite is rare in nature [Andersen and Brecevic, 1991; Kojima et al., 1995; Wray and Daniels, 1957]. But vaterite has some features such as high specific area, high solubility, high dispersion power as compared with calcite and vaterite. Therefore, many researchers have tried to synthesize vaterite [Kojima et al., 1992; Kralj and Brecevic, 1990; Lyu et al., 1998]. We have previously investigated the crystal shape of the precipitated calcium carbonate formed in the emulsion state [Lyu et al., 1997], and the effect of amount of calcium carbonate encapsulated by polystyrene, and the thermal properties of the resulting polystyrene through in-situ emulsion polymerization [Lyu et al., 1996]. We have also investigated thermal and mechanical properties of hydrophobic calcium carbonate/LDPE composites [Lyu et al., 1997], and suspension polymerization of styrene in the presence of precipitated calcium carbonate [Lyu and Sur, 1996].

In this study, we have developed methods to synthesize vaterite and investigated the effects of particle shape and content on mechanical and thermal properties of PP/CaCO$_3$ composites.

EXPERIMENTAL

1. Materials

The starting materials were calcium chloride and potassium carbonate (Junsei Co., First grade). Benzene (Junsei Co., First grade) were used as aromatic solvents, and Span 60 and Tween 80 (Junsei Co., First grade) as non-ionic surfactants. Polypropylene (PP, Korea Petrochemical Industry Co., 5014, MFI = 3.5 g/10 min) was used as polymer matrix.

2. Preparation of Calcium Carbonate

To prepare o/w emulsion, 1 g of span 60 (HLB 4.7) and 2 g of tween 80 (HLB 15.0) were dissolved in 50 g of benzene, and this solution was mixed with calcium chloride solution. Then potassium carbonate solution was poured into this solution. The suspension was filtered, washed with deionized doubly distilled water and dried.

3. Mixing and Moulding

In order to investigate the property of PP/CaCO$_3$ composites, PP and CaCO$_3$ particles were mixed with Bench Kneader (Model PBV-03, Trie Shokai Co.) at 200 °C for 8 min and the

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mixture was pressed at 200 °C under a pressure of 500 Kg/cm^2.

4. Analysis

The shape and polymorphs of calcium carbonate were examined by SEM (HITACHI S-4100) and XRD (RIGAKUO D-MAX-3C).

DSC measurements were performed with a DSC-700 (PL Co.) apparatus. In the non-isothermal crystallization experiments, the samples were heated up to the melting point, kept at this temperature for 2 min and then cooled down to 50 °C at a cooling rate of 10 °C/min under nitrogen atmosphere. The mechanical properties of composites were measured by tensile tester (Testometric Micro 350).

RESULTS AND DISCUSSION

1. CaCO$_3$ Preparation

We previously investigated the crystal shape of the calcium carbonate formed in the emulsion state [Lyu et al., 1997]. Also, we have reported that the reaction temperature, type of solvents and the reaction method were found to have significant effects on the shape and crystal structure of calcium carbonate. In this study, to synthesize vaterite, the precipitate was prepared by using different mixing method at 50 °C using benzene as a solvent. Fig. 1 shows the morphology of the precipitates. To prepare o/w emulsion, surfactants were dissolved in benzene, and this solution was mixed with 600 ml of 3 mol/*l* calcium chloride solution, and then 20 ml of 0.2 mol/*l* potassium carbonate solution was poured into this solution for 45 min. As shown in (a), the precipitates were spherical forms of vaterite. And in the case of 600 ml of 3 mol/*l* potassium carbonate solution which was poured into this solution for 45 min, calcium carbonate was another form of vaterite as shown in (b). On the other hand, when o/w emulsion was prepared using 600 ml of 3 mol/*l* potassium carbonate solution instead of calcium chloride solution, and then 20 ml of 0.2 mol/*l* calcium chloride solution was poured into this solution for 45 min, the precipitates were the mixtures of vaterite and aragonite as shown in (c). When 600 ml of 3 mol/*l* calcium chloride solution was poured into this solution for 45 min, calcium carbonate was vaterite as shown in (d). These results indicate that the mixing method has a significant effect on the shape of calcium carbonate. Because vaterite is known to be very unstable in nature, it is difficult to synthesize. But in this study, several shapes of vaterite were found to be synthesized.

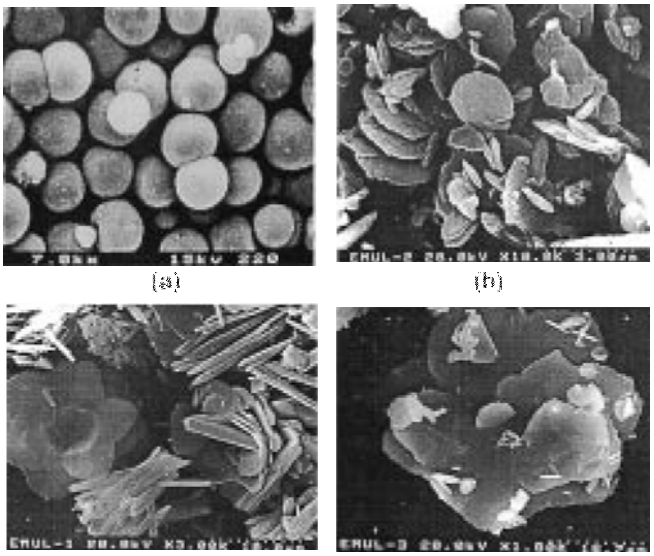
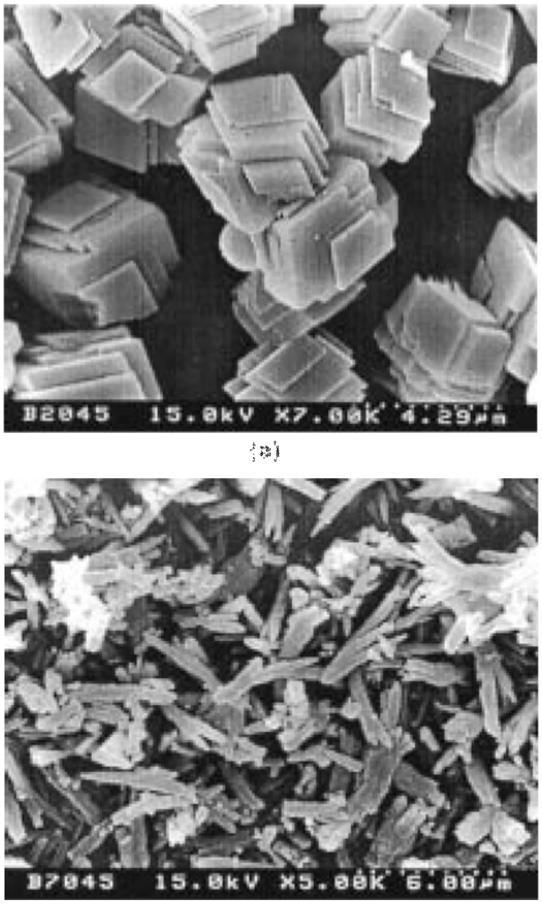

(a) (b) (c) (d)

Fig. 1. Scanning electron microscopy for several foams of vaterite.
(a) 20 ml of 0.2 mol/*l* K$_2$CO$_3$ solution was poured into 600 ml of 3 mol/*l* CaCl$_2$ solution for 45 min, (b) 600 ml of 3 mol/*l* K$_2$CO$_3$ solution was poured into 600 ml of 3 mol/*l* CaCl$_2$ solution for 45 min, (c) 20 ml of 0.2 mol/*l* CaCl$_2$ solution was poured into 600 ml of 3 mol/*l* K$_2$CO$_3$ solution for 45 min, and (d) 600 ml of 3 mol/*l* CaCl$_2$ solution was poured into 600 ml of 3 mol/*l* K$_2$CO$_3$ solution for 45 min.

Generally, the shapes of calcite, vaterite, and aragonite are cubic, spherical, and needle, respectively. And in order to investigate the effect CaCO$_3$ morphology, on the mechanical property of polypropylene, cubic forms of calcite and needle forms of aragonite were also prepared in the emulsion states. Fig. 2 shows the morphology of the precipitates which were used in this study [Lyu et al., 1997]. When benzene was used as a solvent and reaction temperature was 20 °C and reaction method was bulk-mixing-reaction, cubic forms of calcite were formed as



(a) (b)

Fig. 2. Scanning electron microscopy for calcium carbonate.
(a) cubic forms of calcite, (b) needle forms of aragonite.

shown in Fig. 2(a). As shown in (b), needle forms of aragonite were prepared using benzene as a solvent of the bulk-mixing-reaction at 70 °C. And spherical forms of vaterite which were shown in Fig. 1(a) were used in this study for the purpose of comparison.

Crystal structures of these powders were examined by the X-ray diffraction method, and the results are shown in the Fig. 3. Typical spectra of calcite, vaterite and aragonite, which were prepared in this study, are shown in the Fig. 3(a), (b) and (c), respectively.

2. PP/CaCO$_3$ Composites

2-1. Thermal Properties

The variation of measured crystallization temperature with increased CaCO$_3$ volume fraction is shown in Fig. 4. Generally, the crystallization temperature increased as the volume fraction of all three different polymorphs of CaCO$_3$ increased. It is noteworthy that the crystallization temperature of polypropylene with vaterite was significantly increased as volume fraction was increased to 10 %.

And to observe the effect of particle shape on the crystallinity, the heat of fusion of composite was measured. The variation of the heat of fusion with CaCO$_3$ volume fraction is shown in Fig. 5. In the case of calcite and aragonite additions, heat of fusion slightly decreased as volume fraction was increased. However, when vaterite was added, heat of fusion was significantly increased as volume fraction was increased to 10 percent. These results indicate that the crystallinity of polypro-

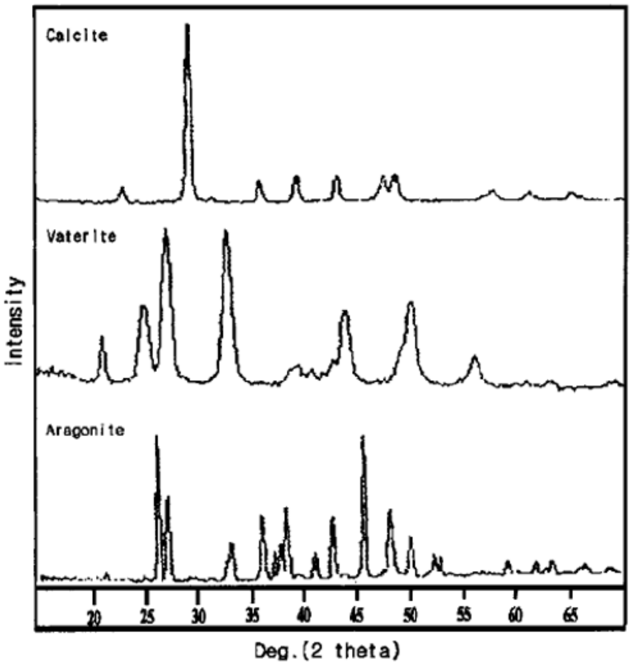


Fig. 3. X-ray diffraction of various shapes of calcium carbonate.
(a) calcite, (b) vaterite, (c) aragonite.

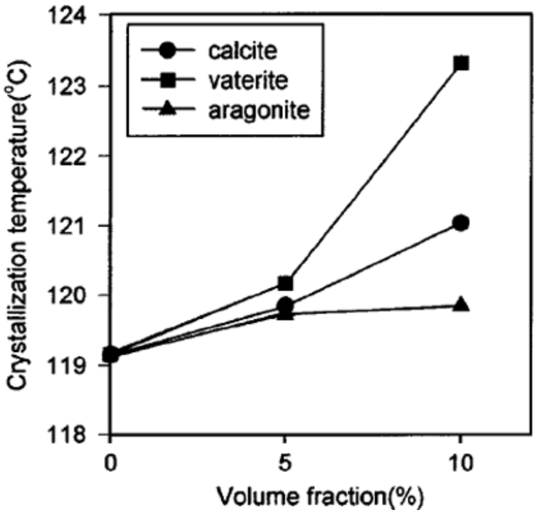


Fig. 4. Crystallization temperature of composites as a function of the CaCO$_3$ volume fraction.

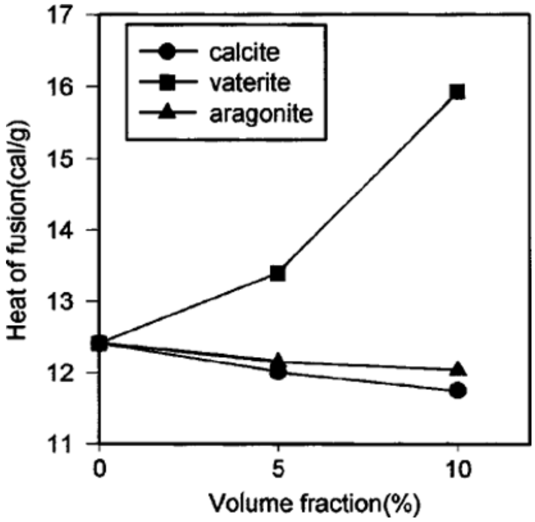


Fig. 5. Heat fusion of composites as a function of the CaCO$_3$ volume fraction.

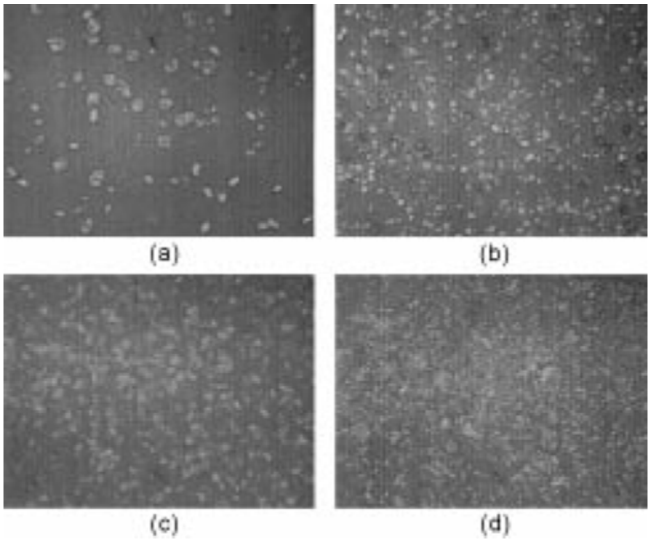


Fig. 6. Spherulite of composites with 10 % CaCO$_3$ at 130 °C (×256).
(a) PP, (b) calcite, (c) vaterite, (d) aragonite.

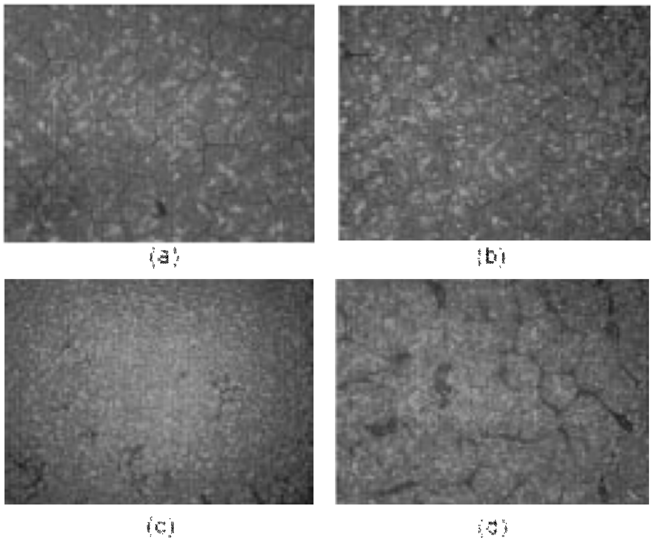


Fig. 7. Spherulite of composites with 10 % $CaCO_3$ at 127 °C (×256).
(a) PP, (b) calcite, (c) vaterite, (d) aragonite.

pylene is influenced by the shape of the $CaCO_3$.

The optical photomicrographs taken at 130 °C showing the spherulite of PP with 10 % $CaCO_3$ are shown in Fig. 6. When vaterite was used, the crystallization rate of composites was faster than that of other crystal forms. These results were consistent with the former results of measured heat of fusion.

The optical photomicrographs taken at 127 °C showing the spherulite of PP with 10 % $CaCO_3$ are shown in Fig. 7. The size of the spherulite of polypropylene with vaterite was the finest.

This difference in crystallization behavior is thought to be caused by surface topography of the filler. Kowalewski et al., using chalk as a crystal nucleating agent, investigated the relationships of crystallization behavior with the structure, surface topography, and state of coagulation of the filler. The size and the surface topography of the filler particle relate to the filler dispersion in the polymer, and the surface topography of the filler was a significant factor influencing the crystallization [Kowalewski and Galeski, 1986]. On the other hand, vaterite has some features such as high specific area, high solubility, high dispersion compared with the other two crystal forms [Nakamae et al., 1986]. From these results, because vaterite is dispersed very well in the PP matrix, the crystallization temperature and crystallinity of composite with vaterite was higher than those with other crystal forms.

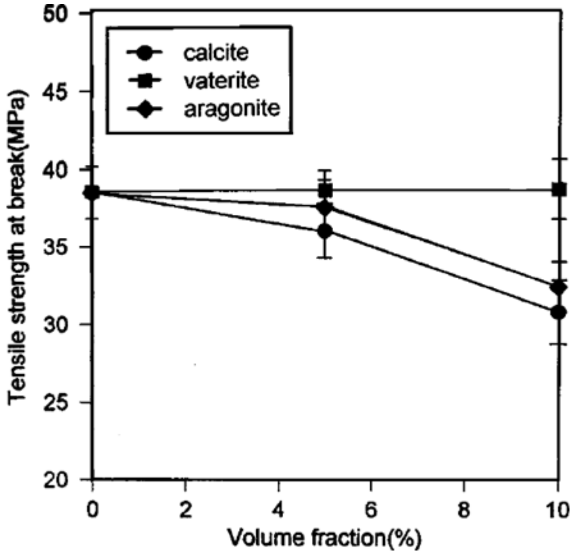


Fig. 8. Tensile strength of composites as a function of the $CaCO_3$ volume fraction at break.

2-2. Mechanical Properties

The variation of tensile strength of composite with $CaCO_3$ volume fraction is shown in Fig. 8. Usually as the volume fraction of $CaCO_3$ increases, the tensile strength decreases. Tensile strength was the lowest when calcite was added as a filler and

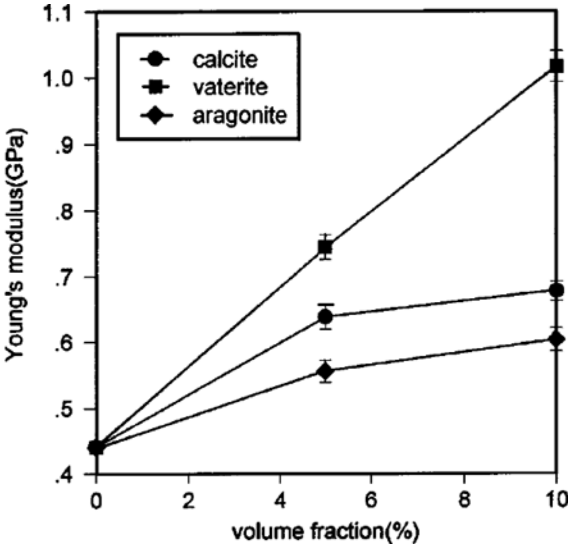


Fig. 9. Young's modulus of composites as a function of the $CaCO_3$ volume fraction.

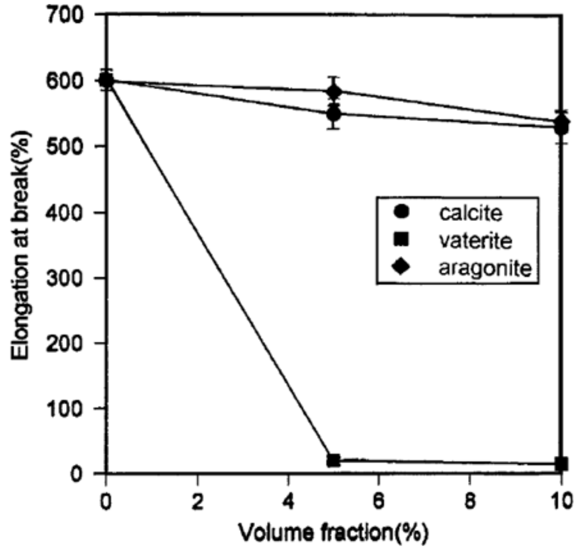


Fig. 10. Elongation of composites as a function of the $CaCO_3$ volume fraction at break.

the next was aragonite addition. However, in the case of vaterite addition, the tensile strength of composite was the highest and the strength was not changed. These phenomena are considered to be due to the different shape of the particles.

The variation of Young's modulus of composite with $CaCO_3$ volume fraction is shown in Fig. 9. Young's modulus of composites with calcite and aragonite was very low and not changed. However, in the case of vaterite addition, the Young's modulus of the composite was significantly increased, indicating stiffness was increased dramatically. The variation of elongation of composite with $CaCO_3$ volume fraction is shown in Fig. 10. In the case of vaterite addition, the elongation was decreased drastically as $CaCO_3$ volume fraction was increased.

CONCLUSION

The shape and crystal structure were significantly affected by mixing method in the emulsion state. When vaterite was used as a filler in the PP/$CaCO_3$ composites, the crystallization temperature and crystallinity were higher than those with other forms. And the size of spherulite of polypropylene with vaterite was the finest. Therefore, the vaterite will be able to be used as nucleating agent for polypropylene. Tensile strength of composite with vaterite was higher than that with other crystal forms.

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