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Research Article

Aragonite Precipitated Calcium Carbonate – Filler for Light Weight Plastics

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Abstract: A new kind of functional filler, aragonite precipitated calcium carbonate (PCC) which has a specific needle shaped morphology and is prepared from natural limestone is of high industrial importance and is an eco-friendly filler for light weight plastics and also recycled plastics. Aragonite precipitated calcium carbonate was synthesized from natural limestone by carbonation process under optimal experimental conditions. Calcium carbonate is synthesized by carbonation method in which gaseous CO_2 is injected to the Ca^{2+} ion solution/slurry to precipitate calcium carbonate. The carbonation process can be proceeded by liquid – liquid – gas, gaseous CO_2 is injected to a mixture of $MgCl_2$ and $Ca(OH)_2$ solutions. The synthesis of aragonite-type precipitated calcium carbonate (PCC) was carried out by varying the reaction temperature and flow rate of gaseous CO_2. Higher temperatures and flow rates were favoured for the synthesis of phase-pure aragonite-type PCC. The aspect ratio of aragonite-type PCC was controlled by the reaction temperature and CO_2 (g) flow rate. In addition, at the same flow rate, the increase in the reaction temperature resulted a higher aspect ratio of the resulting aragonite-type PCC. The average particle size length of aragonite-type PCC was close to 50 µm. We investigated the mechanical properties such as tensile strength, impact resistance, flexural modulus, Young's modulus and thermal properties of polypropylene homopolymer composites with unmodified aragonite-type PCC. The impact resistance and flexural modulus of polypropylene composite with 9 wt% of aragonite-type PCC were 79 J/m and 1300 MPa, respectively.
Keywords: calcium carbonate, gaseous CO_2, $Ca(OH)_2$, flexural modulus.

INTRODUCTION

Calcium carbonate ($CaCO_3$) is an abundant mineral in nature; approximately 5 % of the Earth's crust consists of it, in the form of limestone, chalk and marble. Among the various mineral fillers, calcium carbonate is one of the most important and widely used filler for plastics in term of weight. Addition of calcium carbonate yields a finished product with an excellent balance of stiffness and impact, and can enhance toughness of unfilled resins. Amongst fillers, it provides superior appearance and color consistency. These materials are commonly used in building and construction products and industrial applications where durability is necessary. Specific uses of calcium carbonate are as a filler or coating pigment in paper, plastics, rubbers and adhesives; as filler, extender and pH buffer in paints; as filler and color stabilizers in concrete; for environmental pollution control and remediation in flue gas and water treatment; in fertilizers and in animal feed as a calcium source; among other uses in glass, ceramics, cosmetics and hygienic products. Calcium carbonate appears in nature in three polymorphs. The most common is calcite, as it is the most stable polymorph at ambient temperature and pressure. Its crystal system is trigonal, and appears in a range of morphologies, the most common being rhombohedral and scalenohedral forms [1]. Aragonite is a metastable polymorph; at standard temperature and pressure, it converts into calcite over several million years. Its crystal system is orthorhombic, and crystals are most commonly needle-like (acicular) [2] or spindle-like, although flower-like (flos-ferri), cauliflower- and flake- like crystals are occasionally observed [3-7]. Lastly, vaterite, which has a hexagonal crystal system and spherical morphology, is the rarest polymorph, being unstable and rapidly reverting to one of the more stable forms.

Calcium carbonate that is industrially used as a filler or pigment is most commonly calcite due to the ease of production. Aragonite, however, presents some better physical and mechanical properties. Polyvinyl alcohol or polypropylene composites with aragonite filler show higher tensile strength, impact strength, glass temperature and decomposition temperature, while aragonite-containing paper coatings benefit from increased brightness, opacity, strength and printability compared to those prepared with calcite as the filler. Given that the differences in material physical properties (Table 1) between the polymorphs are small, the improved aragonite performance is attributable to morphological differences (e.g. particle aspect ratio and packing density)[8].

Table-1: Physical properties of calcite and aragonite

Properties	Calcite	Aragonite
Solubility product(K_{sp})	3.36 x 10^{-9}	6 x 10^{-9}
Density(g/cm^3)	2.71	2.93
Hardness(Mohs scale)	3	3.5-4
Refractive index	1.58	1.63
Coordination number	6	9

In the world of functional mineral fillers for plastics - fillers that in some way improve the mechanical properties of the plastic - reinforcement is promoted by several factors: smaller particle size, higher particle aspect ratio, better matrix-filler contact, more uniform filler dispersion and better matrix-filler adhesion. Reinforcement in this context means improving the engineering value of the composite as measured by properties such as tensile and flexural strength, flexural modulus (stiffness), impact resistance and resistance to heat deformation or distortion. The purpose of using mineral fillers is to lower the composite cost by replacing part of the resin while maintaining or even improving the physical properties. Mineral fillers enhanced the mechanical properties of pp composite for plastics such as: stiffness (Tensile& Flexural modulus), Strength (compressive, Flexural), Thermal conductivity, Abrasion resistance, weather resistance, Dielectric strength, surface hardness, Fluid resistance, Heat resistance, Arc resistance, Opacity and Density.

The present objetive of this study was to synthesize of single phase aragnote precitated calcium carbonate by carbonation process and measured mechanical properties of polypropylene composite with aragonite pcc.

METHODOLOGY

Calcium carbonate was synthesized by a carbonation method in which gaseous CO_2 was injected into a Ca^{2+} ion solution/slurry to precipitate calcium carbonate. The carbonation process can be proceeded by liquid – liquid – gas, gaseous CO_2 is injected to a mixture of MgCl2 and $Ca(OH)_2$ solutions. 0.2M $Ca(OH)_2$ (Calcium hydroxide, 95% purity, Junsei Co.) slurry was prepared in a glass reactor using commercial calcium hydroxide and 500mL of high-purity water with electrical resistivity of 18.2 MΩ. 0.6M $MgCl_2$ (Magnesium chloride, 97% purity, Junsei Co.) slurry was prepared in a glass reactor using commercial magnesium chloride and 500mL of high-purity water. Both prepared slurries were transferred into a double jacket glass reactor and heated to 80°C with a heating system attached to the reactor. CO_2 was then bubbled into the reactor at a flow rate of 25mL/min and the precipitation (or production) rate evaluated. The homogenization of the system was fixed at a stirring rate of 400 rpm. The experiments were also carried out at various temperatures from 25°C to 80°C and reaction time durations of 3 hr. Figure 1 shows the flow chart of aragonite-type PCC synthesis.

The obtained solid product was thoroughly characterized through scanning electron microscopy (SEM, JSM-6380 LA, Jeol), a powder X-ray analysis (XRD, Xpert MPD equipped with Cu Kα radiation, Rigaku).

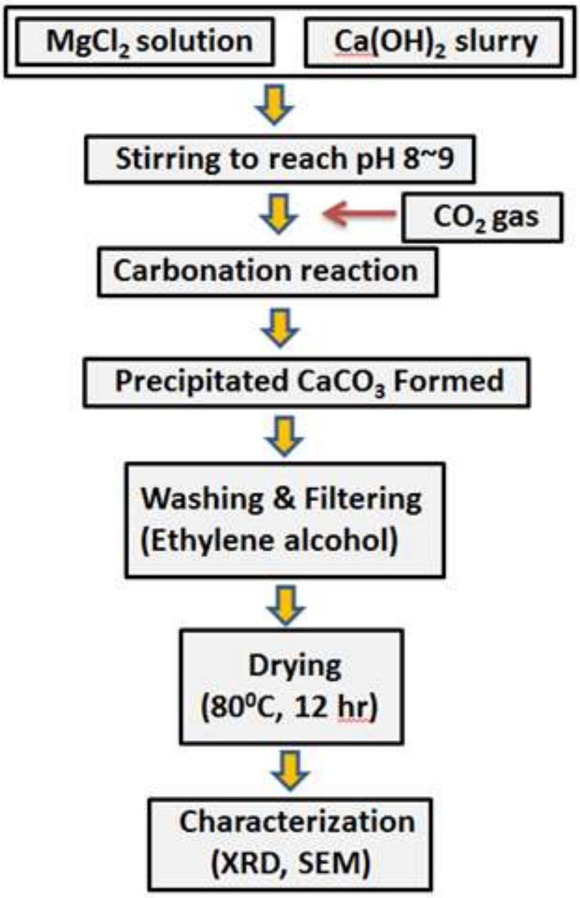

Fig 1: Flow chart of Liquid-liquid-gas(carbonation) process

RESULTS AND DISCUSSION

Effect of temperature for aragonite PCC

Temperature is one of the key determining factors on the formation of aragonite. The first experimental measurement of this temperature coefficient was found on basis of inorganic precipitation of aragonite or an aragonite-calcite mixture from sea water in a temperature range 0°C -80°C[9]. To analyse temperature effects, the liquid-liquid and gas states were more intensively studied. The syntheses of aragonite-type precipitated calcium carbonate were carried out by varying the reaction temperature and flow rate of gaseous CO_2. Higher temperatures and flow rates were favoured for the synthesis of phase-pure aragonite-type PCC. The aspect ratio of aragonite-type PCC was controlled by the reaction temperature and CO_2 (g) flow rate. In addition, at the same flow rate, the increase in the reaction temperature resulted the higher aspect ratio of the resulting aragonite-type PCC. We have synthesized aragonite-type PCC at different temperatures, 25°C, 30°C, 40°C, 60°C, and 80°C. The optimum temperature was determined to be 80°C, at which the average particle size length was close to 50 µm. Figure 2 shows the XRD analysis results of aragonite-type PCC at different temperature and figure 3 shows the SEM images of aragonite-type PCC morphology at 80°C.

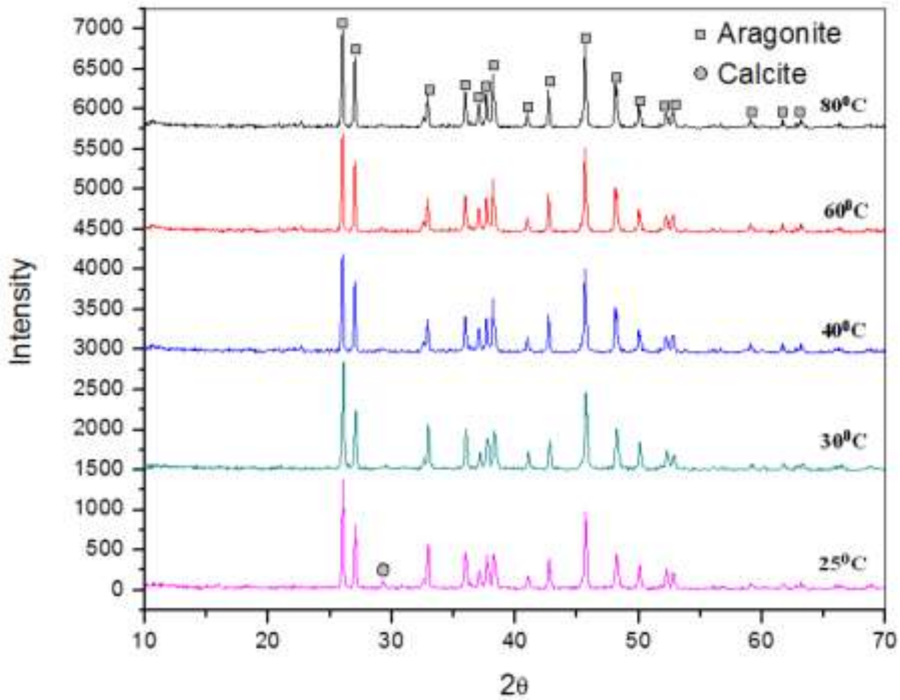

Fig 2: XRD pattern of aragonite-type PCC at different temperature (a) 25°C (b) 30°C (c) 40°C (d) 60°C and (e) 80°C

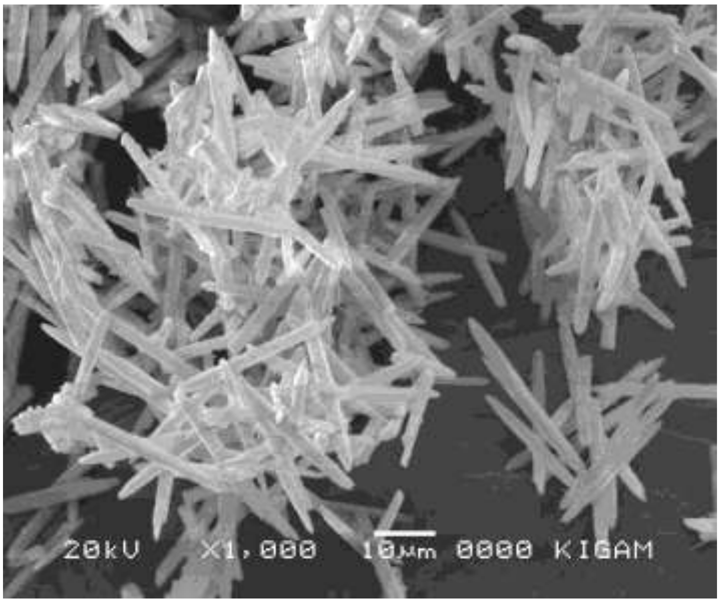

Fig 3: The morphology of aragonite-type PCC at 80°C

Evaluation to aragonite PCC as reinforcement agent for polypropylene

We investigated the mechanical properties such as tensile strength, impact resistance, flexural modulus, young's modulus and thermal properties of polypropylene homopolymer composites with unmodified aragonite-type PCC. Testing was done in our small scale apparatus, which fitted well with the amount of samples available. We tested them against the best aragonite-type PCC. Our goal was to find aragonite-type PCC which would be superior to the reference samples by a significant amount either in stiffness or in impact resistance, or both. A medium impact copolymer was selected as the base which contains a common nucleator used in the automotive industry. All aragonite samples were added to the formulation so that the final loading was 9%. It was melt compounded and then molded into flex bars for testing of modulus and impact resistance.

The best aragonite reference simple registered about 1500MPa flexural modulus, while the synthesized aragonite-type PCC give about 1000MPa flexural modulus. This number is similar to the control's flexural modulus (control is the neat polymer without a reinforcement agent). The best aragonite-type PCC give about 1300MPa modulus, but still lower than the reference aragonite (Figure 4). Room temperature IZOD impact test gives about 79 J/m (Figure 5).

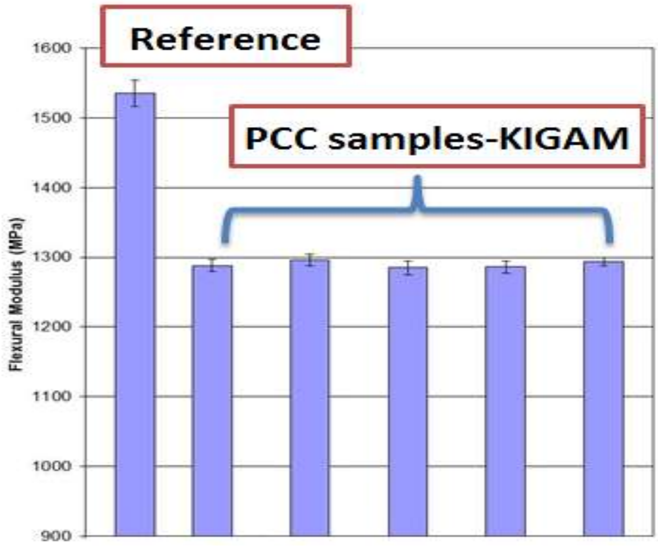

Fig 4: Flexural modulus of ISO bars of 9% aragonite-type PCC in nucleated ICP from screening method

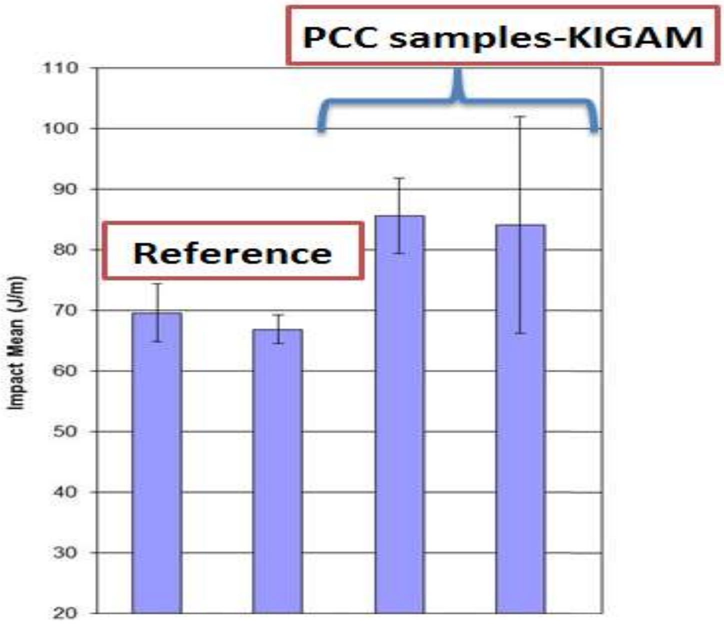

Fig 5: Room temperature IZOD impact of ISO bars of 9% aragonite-type PCC in nucleated ICP from screening method

CONCLUSION

In this study, we have tried synthesis of aragonite-type PCC by carbonation process in which gaseous CO_2 is injected to the reactants. The effects of reaction temperature on the phase purity and aspect ratio of aragonite-type PCC were investigated. The results obtained in this research can be summarized as follows.

1. The reaction temperature is important role for the synthesis of aragonite-type PCC. Higher temperature are favoured for the synthesis phase pure aragonite-type PCC. The aspect ratio of aragonite-type PCC was improved at the high reaction temperature.
2. The impact strength and flexural modulus of polypropylene composite with 9 wt% of aragonite-type PCC were 79 J/m and 1300 MPa, respectively.

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