

Effect of Grain Size and Replacement Ratio on the Plastic Properties of Precipitated Calcium Carbonate Using Limestone as Raw Material

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ABSTRACT

Precipitated calcium carbonate(PCC) inorganic fillers for plastic offer a higher replacement ratio with improved mechanical properties than any other inorganic fillers. Due to its secure economic feasibility, its fields of application are expanding. For optimized PCC grain size and polymer replacement ratio, it is good to maintain at least 0.035 μm grains and keep double the grain size of distance between particles, depending on the molecular weight and volume replacement rate of the polymer. PCC has unique characteristics, ie, with smaller grain size, dispersibility decreases, and if grain size is not homogenous, polymer cracking occurs. The maximum replacement ratio of PCC is approximately 30%, but in the range of 10 - 15% it produces the highest mechanical strength. When mixed with a biodegradable plastic like starch, it also improves initial environmental degradability.

Key words : Precipitated calcium carbonate(PCC), Limestone, Polymer, Particle size, Replacement ratio

1. Introduction

Precipitated calcium carbonate(PCC) was first manufactured commercially in England in the 1850s, and since then, these inorganic fillers have been used for nylon in the plastic industry by Monsanto and DuPont Inc., U.S.A. and its use as an inorganic filler for plastic has been expanding. In 2011 the plastics industry was the second largest source of demand for calcium carbonate inorganic filler, following the paper industry, and 15.5 million tons of ground calcium carbonate(GCC) and 3.8 million tons of PCC were used. Calcium carbonate inorganic filler now accounts for over 90% of the inorganic filler consumed for the production of polyvinyl chloride(PVC), polypropylene(PP), and polyethylene(PE). Global consumption of GCC was about 74 million tons in 2011, and PCC was about 14 million tons. PCC has a higher purity and whiteness index than any other GCCs, and is a synthetic mineral with adjustable particle size and shape. Fig. 1 presents the consumption of calcium carbonate by industry in 2011 and its forecasted demand in 2016.

Commercial PCC varies in size: it ranges from 0.05 μm to 5 μm . The shape of the particle is rhombohedral, prismatic, or scalenohedral in the case of calcitic PCC, and acicular in the case of aragonite PCC. Moreover, nano-sized PCC provides excellent performance as an adhesive and its use has been expanding recently. Fig. 2 presents the major inorganic fillers, including PCC, and the major characteristics

by type. This data suggests that it is easier to secure homogeneity in minute particle size and increased brightness for PCC, compared to GCC.

Calcium carbonate, a mineral-derived inorganic filler, is

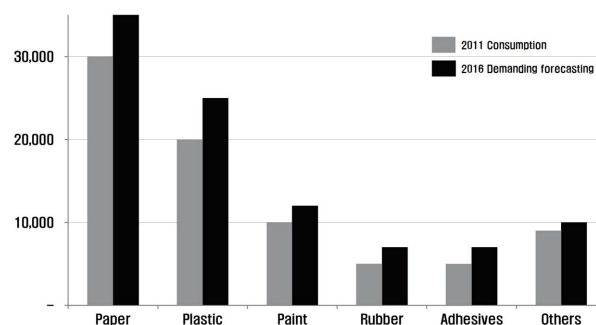


Fig. 1. Consumption of calcium carbonate in 2011 & forecasted demand in 2016.¹⁾

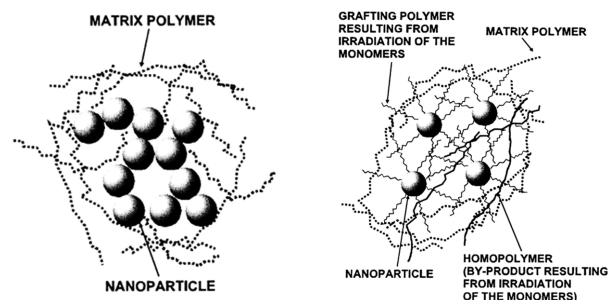


Fig. 2. Changes in contact area with polymer matrix depending on the agglomeration and dispersion of inorganic filler.

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Table 1. Characteristics of PCC for Inorganic Filler and GCC by Type²⁾

Type	Calcite PCC		Aragonite PCC	GCC	
	Rhombohedral	Scalenohedral	Orthorhombic	Fine	Ultrafine
Refractive index	1.58	1.58	1.63	1.58	1.58
Specific gravity	2.71	2.71	2.92	2.71	2.71
TAPPI brightness (%)	99	99	99	95	95
Surface area (m ² /g)	6 - 8	9 - 15	9 - 13	5 - 7	10 - 12
Einlehner abrasion (mg)	3	3 - 5	4 - 8	8	4
Particle size					
+5 μm (%)		2	3	20	3
-2 μm (%)	99	45	75	70	90
Mean (μm)	0.7	1.0 - 3.0	0.5 - 1.0	2.0	0.8

Table 2. Major Mineral Fillers in the Plastic Industry

Mineral	Plastic resin	Function/things to consider
ATH	ABS, TPES, PVC, PU, Epoxy, Phenolics	bauxite-based / flame resistant and smoke suppressant
Barytes	PEU, PU	white dye / impact resistance/chemical resistance improvement / increase in mass
CaCO ₃	ABS, PP, PS, PVC, TPES, PU, Phenolic Fluoroplastics, Polyolefin, Epoxy	improvement in strength / improvement in bending strength / improvement in surface finish / viscosity control / weight lightening effect with low density
Feldspar	PP, PS, PCV, PEU, Acrylic, Cellulosics, Epoly	Special filler / transparency/translucency properties / increase in chemical resistance
Kaolin	PEU, PVC, TPES, PU, SMC, BMC, Vinyl flooring, Nylon	Liquidity adjustment / hydration/plasticity used for all grades
Mica	ABS, PC, TPES, PP, Nylon, Polyolefins, Epoly	heat conduction quality/mechanical property improvement / reduction in electrical conductivity / creep resistance / relatively cheap price
Silica	ABS, PS, PVC, TPES, PU, Polyolefins, Epoxy	antigloss agent / taxopropize
Talc	PVC, PU, PS, Nylon, Polyolefins, Phenolic, PP	hardness, bending strength improvement / creep resistance
Wollastonie	Nylon, PC, TPES, PS, Polyolefins, Thermosets	intensity increase / reduction in water uptake / increase in heat resistance, dimensional stability / reduction in electrical conductivity

added to plastic for three purposes: physical performance improvement, as an auxiliary material for processing, and for cost reduction. Table 1 and 2 presents the major consumption of mineral fillers in the plastic industry. Particularly in the case of PCC, particle size and shape can be controlled and are used for amending the physical characteristics of polymer. Aragonite PCC with its high height-to-width ratio can provide a relatively high flexural modulus improvement, compared to the existing hexahedral calcite.²⁾ As an auxiliary material for processing, PCC is used for improving the formability of final products. In general, the smaller the grain size of the inorganic filler, the higher the viscosity increases.³⁾ Finally, in terms of cost reduction, calcium carbonate inorganic filler is less expensive than polymer, unlike Talc, Whisker, Nano Clay, etc, which are not produced in Korea. As it has a high replacement ratio, the cost reduction effect is excellent. It is also used for improving the blockage phenomenon of extruders, the final production process of plastic products. Recently, it has also been

used for improving the functionality of general-purpose plastic, and applied in biodegradable plastics as a nano PCC composite.

With that perspective, this study investigates the boundaries and features of PCC as an inorganic filler for plastic, its effect on improving polymer physical properties, then analyzes the effect of nano-PCC composite on polymer physical properties, and presents methods of optimizing PCC as an inorganic filler for plastic.

2. Experimental Procedure

2.1. Utilization of PCC in Plastic Industry

PCC, an inorganic filler derived from natural mineral, can lessen the environmental occurrence of hormones like bisphenol A which are eluted from plastic produced with organic additives like phthalate plasticizers, and of hazardous substances released during incineration. There is an increasing interest in eco-friendly additives and fillers suit-

able for bio-plastics in advanced countries. The demand for plastic for flexible packaging and for packaging industry bio-plastics continues to increase.⁴⁾ PCC manufacturing technology has 'balloon effect' like the emission of 750 kgco₂/ton limestone in the process of plasticizing limestone as natural mineral. The recent trend of the plastic industry is focus on the carbon reduction effort with biodegradable technology. PCC manufacturing which utilizes industrial by-products such as slag, incineration ash, lime kiln dust, etc, may also reduce the occurrence of greenhouse gas emissions from the processing of raw materials, manufacturing products, and their decomposition.⁵⁾

The automotive plastics market increases the application of general-purpose plastics for reducing environment load. And, the use of inorganic filler has been increased to improve the mechanical properties of general-purpose plastics like polypropylene and polyethylene having the weak points about the impact strength.

And the use of polyolefin plastic as a light weight automobile material is increasing. In general, 100 pounds of plastic material can replace 200 - 300 pounds of other materials. The use of PCC supports this high replacement ratio and also has the effect of reducing the cost of raw materials for plastic. The use of PCC fillers and inorganic adhesives in general-purpose plastic and highly functional plastic parts for vehicles, can reduce vehicle weight by about 20%, or 10 - 12 g/km. That is about 5% of the average vehicle carbon dioxide emissions, amounting to 150 - 200 g/km.

To increase the rate of direct waste plastic recycling, single raw material-type polymers and single adhesive-contained shapes are the most useful. To accomplish their adoption, a generalized innovation of vehicle and home appliances industries that use plastic packaging and large amounts of plastics is required. Recycled plastic is difficult to use in the packaging industry because its physical properties are reduced when its molecular weight decreases as a result of the recycling process. Further, recycled plastic's turbidity increases due to the mixing of pigments in the plastic, however, if it's being used as a material for parts in the automotive industry, or in industrial products and agricultural products, or in terms of environmental safety, it's likely to be sufficient.

3. Results & Discussion

3.1. Particle size of PCC filler

When used in plastic, the smaller the grain size of PCC is, the higher the strength improvement effect. However, if the grain is smaller than a particular size, its strength decreases. In the case of relatively homogeneous sized PCC, the smaller the grain size is, the higher the viscosity becomes. This is attributable to the fact a smaller size PCC grain has higher specific surface area, and as this increases chemical bonding with the polymer, the viscosity increases, thus providing a resulting increase in strength and improved durability.⁶⁾ As determinants of the impact

strength of plastic polymer, the size and binding power of the inorganic filler are important.⁷⁾ The distance between inorganic filler particle surfaces is an important variable. If it is assumed that the particles are arranged in a cubic structure, shear yield lines cross at $D=0.035 \mu\text{m}$ or less and strength decreases, in theory. Furthermore, if mixed with irregular sized filler particles, cracks between the polymer and PCC are likely to occur. The agglomeration effect should be avoided despite the similar sized particles shown in Fig. 2⁸⁾ but if fatty acid-coated PCC is used to improve dispersion, the viscosity-increasing effect is reduced.

3.2. Substitution Ratio of PCC Filler

The amount of improvement in impact strength, flexural modulus, and tensile strength in PCC-mixed polymer depends on reduction in particle size. If the polymer is replaced by up to 30% (of the polymer weight) 0.44 - 3.5 μm -sized calcium carbonate inorganic filler, the material's modulus of elasticity (Young's modulus) increases, yield stress decreases, and yield strain decreases, but if such effects are over 30%, the other physical property improvements decrease. This suggests that the optimum replacement ratio depends on the molecular weight of the polymer and the particle size of the PCC. However, a maximum replacement ratio exists, and the smaller the grain size is and the smaller the stress-strain ratio is, the higher the strength becomes. In other words, the polymer strength is improved by the addition of PCC, but ductility and toughness decrease.

If 0.044 μm -class PCC is mixed with polypropylene at 15 wt%, 30 wt%, impact strength increases by 2 - 2.2 times and yield strength decreases by 5 - 8%, respectively.⁹⁾ In contrast, if PCC particles ranging from 1 μm to 50 μm is mixed with polypropylene, impact strength increases linearly.¹⁰⁾ Moreover, Qiang demonstrated that in an experiment of impact strength using 6.6 - 15.9 μm sized calcium carbonate-mixed high-density polyethylene, the strength improvement effect for the 6.6 μm -class inorganic filler, mixed at the same rate, was higher by four times than 15.9 μm .¹¹⁾ This suggests that strength improvement increases linearly depending on grain size, and the strength improvement effect as a function of replacement ratio increases linearly up to 15%, but over 15%, the range of increase declines, or mechanical property decreases.¹²⁾ However, a particles-maller than 0.1 μm produces problems to decrease the dispersibility. Fig. 3 represents the variation in impact strength and yield strength depending on grain size and addition of PCC. The smaller the PCC particle size is, the higher the physical property improvement effect is, but if replacement is above 10 - 15%, strength decreases.

3.3. Biodegradability of PCC filler

PCC inorganic adhesives provide improved biodegradability in addition to improving physical properties including bio-plastic strength. This combination is difficult to find in other inorganic and organic additives. A light-sensitive period exists between a biodegradable polymer like starch

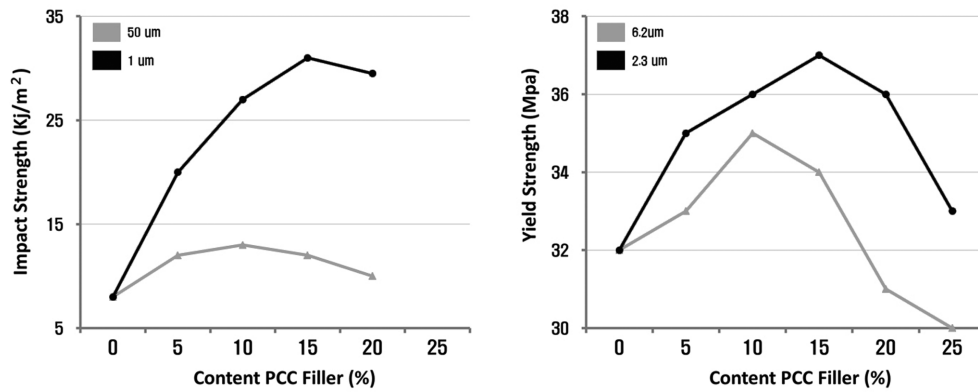


Fig. 3. Changes in impact strength and yield strength depending on PCC replacement.¹²⁾

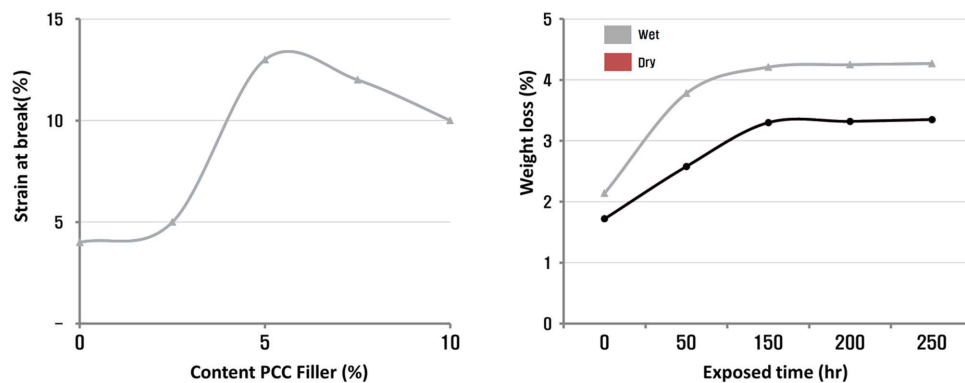


Fig. 4. Changes in yield strength and biodegradability in biodegradable plastics depending on addition of nano PCC.¹⁴⁾

and the calcium carbonate surface. The biodegradable plastic decomposition process is divided into two or three stages.¹³⁾ Ultraviolet rays initially form holes by decomposition of the light-sensitive period and through this, moisture infiltrates and dissolves the PCC; this process repeats. As a result, plastic cracking is expedited and microorganism infiltration becomes easy.^{14,15)} Fig. 4 shows that when PCC with a grain size of 0.04 μm is added into poly lactic acid; a biodegradable plastic, the strain at break is improved by stress. And, decomposition rate of biodegradable plastics is increased in case of the blends with polypropylene 10 wt%, starch 30 wt%, and calcium carbonate 60 wt%.

4. Summary

This study investigated the characteristics of polymer-filler composites using precipitated calcium carbonate as a function of particle size and replacement ratio. The results of the study areas follows:

- The optimum grain size of PCC for improving the characteristics of plastic is determined by the volume fraction of polymer. The minimum effective size of PCC particle is 0.035 μm, and when the distance between particles is twice the size of the PCC grain, it favorably influences plastic viscosity and mechanical characteristics.

- Uncoated PCC produces a higher mechanical physical property improvement than fatty acid-coated PCC for simi-

lar particle size, but the optimal particle size is larger than coated PCC, due to its low dispersibility.

- Maintaining a homogeneous grain size of PCC filler may improve durability by preventing cracking.

- The maximum polymer replacement ratio by PCC is 30% in general, and so higher replacement levels are possible compared to other inorganic fillers. Polymer mechanical characteristics are excellent in the replacement ratio range of 10 - 15%.

- When mixed with biodegradable plastic PCC increases the polymer's environmental disintegration rate, as well as improving its immediate mechanical physical properties.

These results will contribute to establishing a quantitative database of PCC grain size and optimal filling rates for plastics, based on polymer characteristics, to help secure a single inorganic filler technology for plastic that can replace the existing inorganic fillers such as talc, clay, etc in the future.

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