

REVIEW PAPER

# A strategy of precipitated calcium carbonate (CaCO<sub>3</sub>) fillers for enhancing the mechanical properties of polypropylene polymers

Thriveni Thenepalli\*, Ahn Young Jun\*\*, Choon Han\*\*, Chilakala Ramakrishna\*\*\*, and Ji Whan Ahn\*,†

\*Mineral Processing Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, Korea

\*\*Chemical Engineering Department, Kwangju University, Nowon-gu, Seoul 139-050, Korea

\*\*\*Hanil Cement, 302, Maepo-ri, Maepo-eup, Danyang-gun, Chungbuk 395-903, Korea

(Received 18 November 2014 • accepted 25 March 2015)

**Abstract**—A wide variety of fillers are currently used in more than twenty types of polymer resins, although four of them alone (polypropylene, polyamides, thermoplastic polyesters, and polyvinyl chloride) account for 90% of the market of mineral fillers in plastics. Polypropylene (PP) and PVC dominate the market for calcium carbonate. PP is a versatile reinforcement material that can meet engineering and structural specifications and is widely used for automotive components, home appliances, and industrial applications. Talc, mica, clay, kaolin, wollastonite, calcium carbonates, feldspar, aluminum hydroxide, glass fibers, and natural fibers are commonly used in fillers. Among these, calcium carbonate (both natural and synthetic) is the most abundant and affords the possibility of improved surface finishing, control over the manufacture of products, and increased electric resistance and impact resistance. Meeting the global challenge to reduce the weight of vehicles by using plastics is a significant issue. The current the global plastic and automobile industry cannot survive without fillers, additives, and reinforcements. Polypropylene is a major component of the modern plastic industry, and currently is used in dashboards, wheel covers, and some engine parts in automobiles. This article reports that the use of calcium carbonate fillers with polypropylene is the best choice to enhance the mechanical properties of plastic parts used in automobiles.

Keywords: Carbonation Mechanism, Calcium Carbonates, PCC, Fillers, Polypropylene Polymers, Mechanical Properties, Plastics

## INTRODUCTION

Limestone (calcium carbonate (CaCO<sub>3</sub>)) is an abundant mineral, occupying 5% of the earth's crust. Used as functional filler and

coating pigments for paper, rubbers and plastics, adhesives, and paints, calcium carbonate forms in three polymorphs: calcite, aragonite, and vaterite. The most thermodynamically stable form at ambient temperatures is calcite. Generally, calcite shows a variety

Table 1. Physical properties of calcium carbonate fillers (calcite and aragonite)

Properties	Calcite		Aragonite (Orthorhombic)	GCC	
	Rhombohedral	Scalenohedral		Fine ground	Ultrafine ground
Solubility product ( $K_{sp}$ )		$3.36 \times 10^{-9}$	$6 \times 10^{-9}$		
Density (g/cm <sup>3</sup> )		2.71	2.93		
Hardness (Mohs scale)	3.0	3.0	3.5-4	3	3
Refractive index	1.58	1.58	1.63	1.58	1.58
Coordination number		6	9		
Specific gravity	2.71	2.71	2.92	2.71	2.71
TAPPI brightness	99	99	99	95	95
Surface area (m <sup>2</sup> /g)	6-8	9-15	9-13	5-7	10-12
Particle size <sup>2</sup>	-	2			
+5 μm (%)	99	45			
-2 μm (%)	0.7	1.0-3.0	0		
Mean (μm)					

†To whom correspondence should be addressed.

E-mail: ahnjlw@kigam.re.kr

Copyright by The Korean Institute of Chemical Engineers.

of morphologies, the most common being trigonal, rhombohedral, colloidal, needle-like [1], and scalenohedral forms [2,3]. Aragonite is a metastable polymorph under ambient temperature and high pressure. The aragonite precipitated calcium carbonate morphology is orthorhombic, needle-like (acicular) [4-10], flower-like, and flake-like. Lastly, vaterite, a less stable form, shows a hexagonal morphology. Control of the crystal shape and morphology of  $\text{CaCO}_3$  is important for industrial applications. The main differences between the polymorphs in terms of their physical properties are provided in Table 1. The superior performance of aragonite is attributed to its morphological differences (e.g., particle aspect ratio and density).

## PRECIPITATED CALCIUM CARBONATES

The controllable synthesis of calcium carbonate ( $\text{CaCO}_3$ ) has received considerable attention owing to the wide variety of applications of  $\text{CaCO}_3$  in industrial fields such as paper, rubber, plastics, and paints [11]. Calcium carbonate also plays an important role in reduction of flue gases and waste water treatment [11]. The applications of  $\text{CaCO}_3$  particles are determined by a number of parameters, including specific surface area, morphology, size, brightness, oil adsorption, and purity. Particle morphology plays an important role in industrial applications. Control of crystal shape and size is therefore a basic requirement from the viewpoint of applications.

Polymers filled with aragonite filler show improved mechanical properties such as impact resistance, tensile strength, glass temperature, and decomposition temperature, while aragonite-containing paper coating shows benefits including improved brightness, opacity, strength, and printability. The morphology of  $\text{CaCO}_3$  particles plays an important role in paper and painting industries, especially cubic shaping. These particles may also lend high electric insulation and a high elasticity modulus to composites [12].

A newly identified source of aragonite calcium carbonates is bivalve shell waste, which is available from marine aquaculture and is currently dumped into landfills. Recently, some value added products (calcium carbonates) have been obtained from bivalve shell waste in efforts to control the disposal problem and in particular the waste has been utilized as a filler for polymers [13].

### 1. Global Consumption of Ground Calcium Carbonates and Precipitated Calcium Carbonates (PCC)

The global demand for calcium carbonates has been rising continuously and is expected to reach 108.5 million tons (Mt) by roughly 2016. Demand for both ground calcium carbonates (GCC) and precipitated calcium carbonates (PCC) continue to increase for paper coating applications as well as mineral fillers for plastics industries (Fig. 1(a)). Recently, precipitated calcium carbonate (PCC) and nano calcium carbonates have been used for polypropylene composites in both the paper and plastic industries (Fig. 1(b)) [14]. Among the global consumers of calcium carbonates, Asia is expected to occupy a major share, particularly in the paper industries, in the near future.

### 2. Synthetic PCC Production by Carbonation Process

Calcium carbonate is synthesized by a carbonation method in which gaseous  $\text{CO}_2$  is injected to a  $\text{Ca}^{2+}$  ion solution/slurry to precipitate calcium carbonate. The carbonation process can be conducted by

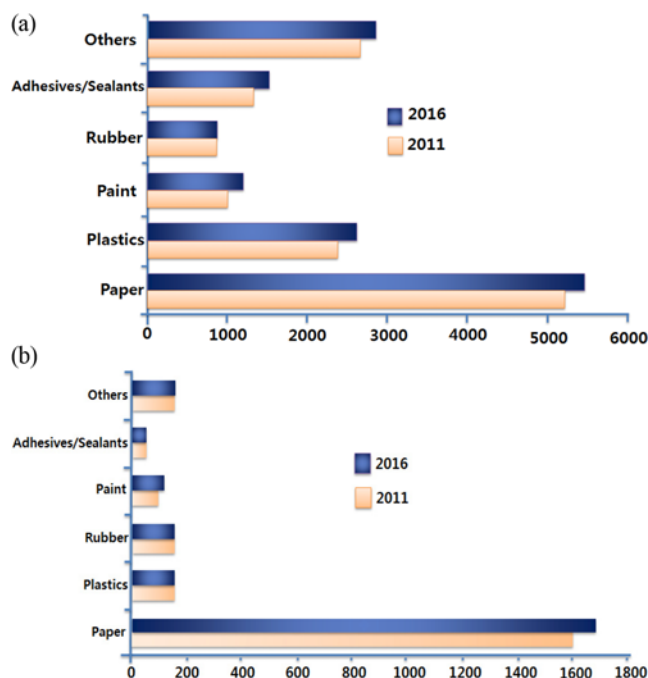
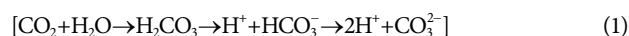


Fig. 1. (a) Estimated consumption and forecast demand for GCC and PCC by market, 2011 and 2016 (000t), USA ((source: Adapted from reference 14). (b) Estimated consumption and forecast demand for PCC by market, 2011 and 2016 (000t), USA (source: Adapted from reference 14).

two methods: i) solid-liquid-gas; solid  $\text{Ca}(\text{OH})_2$  is added to a  $\text{MgCl}_2$  solution and gaseous  $\text{CO}_2$  is injected into a suspension of  $\text{MgCl}_2$ - $\text{Ca}(\text{OH})_2$  or ii) liquid-liquid-gas (Fig. 2(a)); gaseous  $\text{CO}_2$  is injected to a mixture of  $\text{MgCl}_2$  and  $\text{Ca}(\text{OH})_2$  solutions. The general mechanism involved in the carbonation process can be expressed as follows:

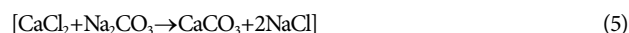


The overall reaction is given as



The carbonation reaction starts from the hydration of carbon dioxide and ionization of calcium hydroxide, as shown in Eqs. (1) and (2). The calcium and carbonate ions react together to form a calcium carbonate precipitate. Calcium carbonate also can be synthesized by a solution process in which an aqueous solution of carbonate salts instead of gaseous  $\text{CO}_2$  is added to the reactants. In the solution process,

( $\text{CaCl}_2$ - $\text{Na}_2\text{CO}_3$ ,  $\text{CaCl}_2$ -( $\text{NH}_4$ ) $_2\text{CO}_3$ ,  $\text{CaCl}_2$ - $\text{K}_2\text{CO}_3$  system),  $\text{CaCO}_3$  can be formed through the following reactions:



Aragonite can be synthesized either by a carbonation process [15] or by a solution process [16]. However, carbonation is prefer-

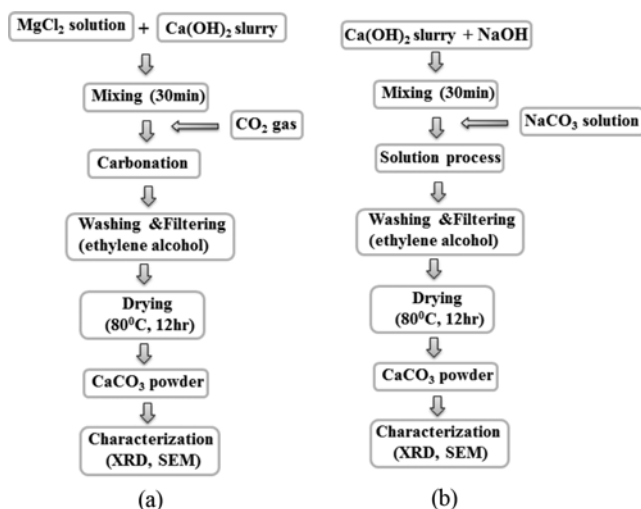
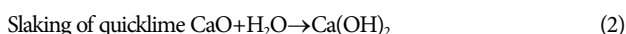
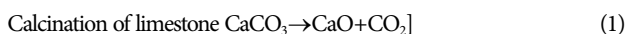


Fig. 2. (a) Flow chart for the synthesis of PCC by carbonation process (b) synthesis of PCC by solution process (source: Adapted from references 15 & 16).

able because precipitated calcium carbonate is produced through a carbonation process in industrial settings. Na<sup>+</sup> ions also promote the formation of aragonite in a solution process in which an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> is added to a slurry of Ca(OH)<sub>2</sub> at 75 °C [17]. Single phase aragonite PCC also can be synthesized by a solution process by the addition of an Na<sub>2</sub>CO<sub>3</sub> solution at a rate of 3 ml/min to a slurry of Ca(OH)<sub>2</sub> and NaOH at 75 °C [17] (Fig. 2(b)).

### 3. From Limestone

The precipitation of calcium carbonate (CaCO<sub>3</sub>) by a carbonation process is one of the most economically efficient processes existing today. Calcium oxide and carbon dioxide are formed from limestone by means of calcination between 900 °C-1,000 °C. After the calcified lime has been treated with water, the resulting milk of lime is purified and carbonated with the carbon dioxide obtained from the calcination process.



### CO<sub>2</sub> EMISSIONS FROM CARS-GLOBAL SCENARIO

CO<sub>2</sub> gas emissions are the main source of global warming (Fig. 3) [18], and 10% of total global CO<sub>2</sub> emissions come from cars, trucks, and motorbikes. As long as CO<sub>2</sub> concentrations continue to rise, we can expect severe global warming and faster climate change. The European Commission has proposed forcing carmakers to increase the fuel efficiency of new cars by 20% (Fig. 4(a)) [19]. Between 2000 and 2050 the fuel consumption and CO<sub>2</sub> emissions by cars is expected to double, as estimated by the International Energy Agency (IEA). In non-OECD countries, transportation is the major source of the overall greenhouse gas (GHG) emissions and CO<sub>2</sub> emissions. To control the CO<sub>2</sub> emissions from the transport sector, new policies and new eco-friendly sustainable innova-

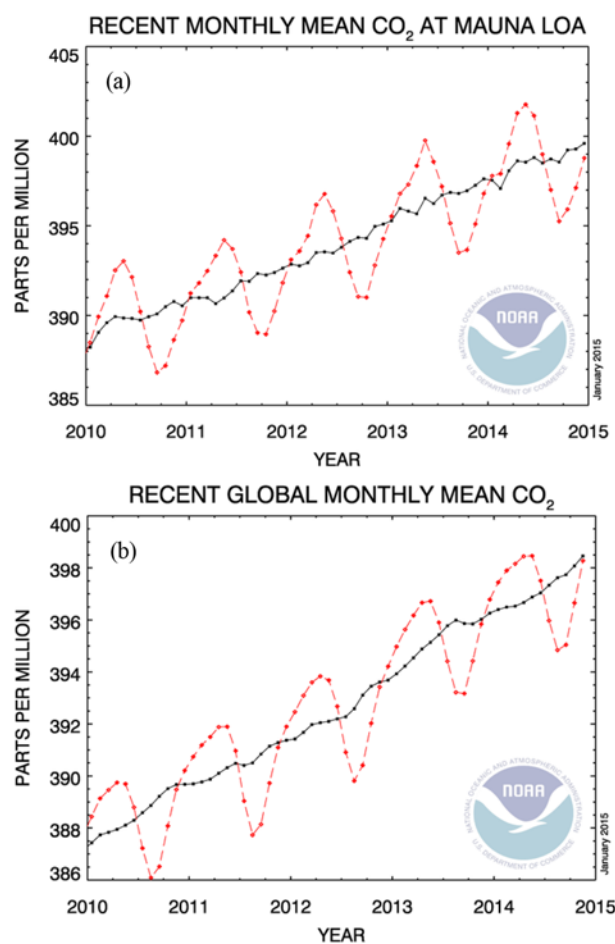


Fig. 3. (a) Instrument record for atmospheric carbon dioxide (CO<sub>2</sub>) at the Mauna Loa Observatory, (b) seasonal fluctuations of atmospheric carbon dioxide (CO<sub>2</sub>) at the Mauna Loa Observatory (source: Adapted from reference 18).

tion technologies are required.

In recent decades, numerous studies have been carried out to reduce vehicle weight, displacement, engine power, and CO<sub>2</sub>. At the same time, global manufacturers have been designing new engines for less fuel consumption. These developments reflect that lower CO<sub>2</sub> emissions are possible if vehicle weight and engine size are reduced. In Europe, in 2013, for the first time the average vehicle weight decreased, falling by nearly 10 kg (Fig. 4(b)) [20].

### PLASTICS IN AUTOMOBILE INDUSTRY

Plastics are highly demanded in almost every industry, including automotive, medical, electrical, and packaging, as well as in construction, consumer goods, and electronics. They show good mechanical properties when combined with polymers and polymer composites. Nowadays, on this basis, plastics are widely used to make cars more energy efficient by reducing weight, together with providing design flexibility, elasticity, toughness, corrosion resistance, breaking strength hardness, and durability.

During the enormous growth of plastic components use in the automotive industry, the advantages of using plastics have changed.

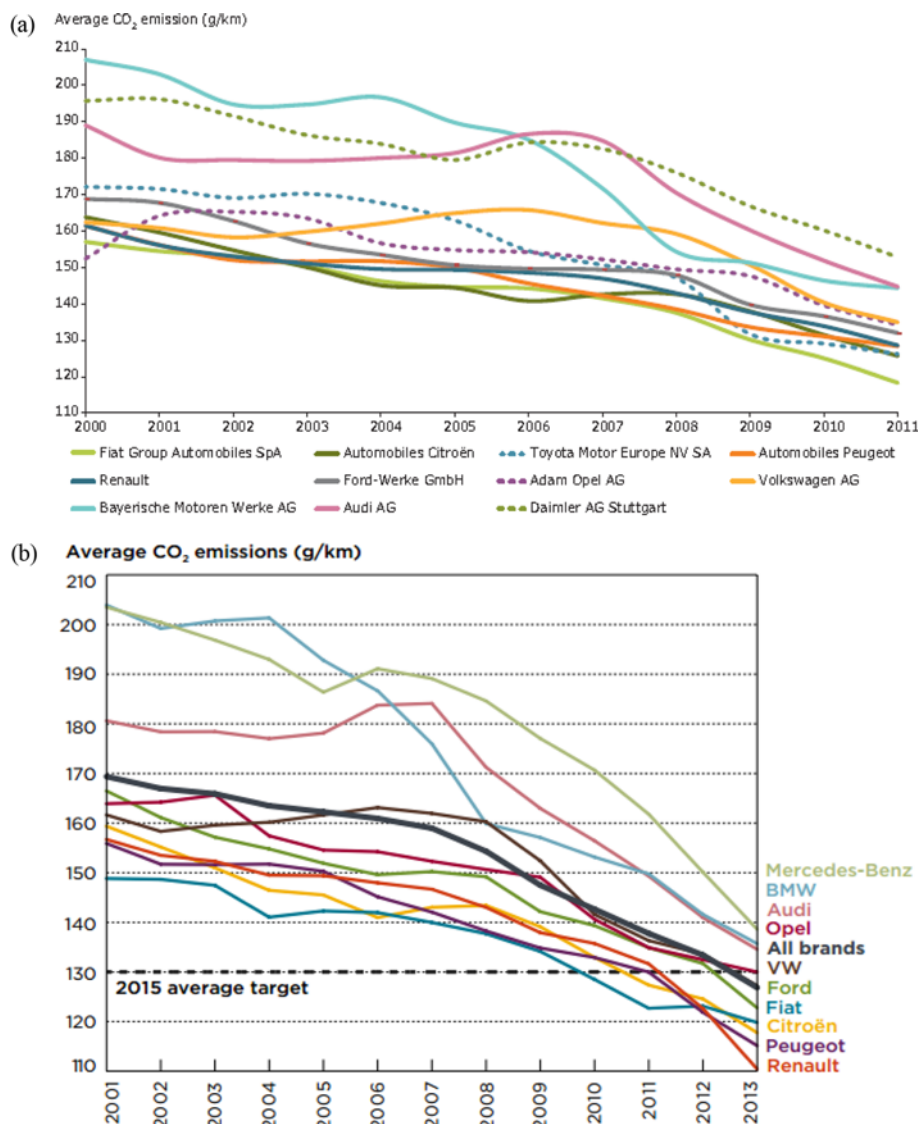


Fig. 4. (a) CO<sub>2</sub> emissions from passenger cars (source: Adapted from reference 19). (b) CO<sub>2</sub> emissions by branded passenger cars (source: Adapted from reference 20).

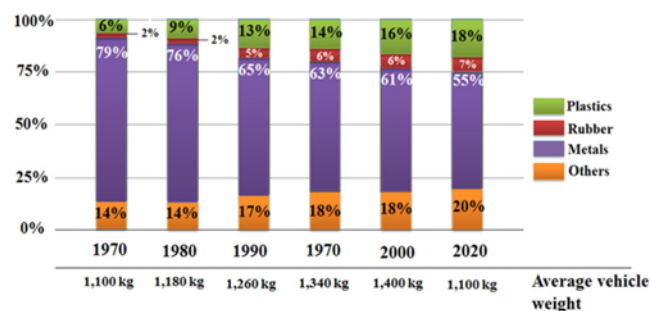


Fig. 5. Average plastics weight in total vehicle weight (source: Adapted from reference 21).

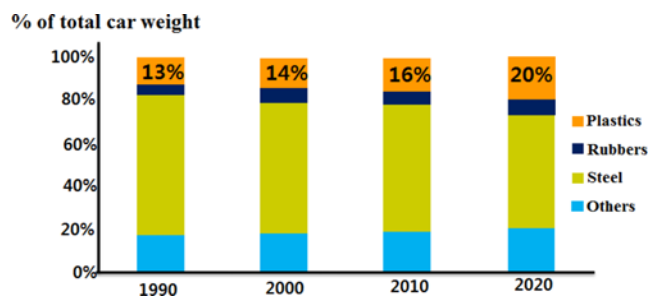


Fig. 6. Average plastics weight in total vehicle weight (source: Adapted from reference 22).

Different kinds of polymers and polymer composites are used for automotive parts having different sizes and shapes. The major advantage of plastics is not only controlling the car's body weight and

fuel consumption, but also allowing the production of safety systems without excessive cost. Fig. 5 [21] and Fig. 6 [22] show car manufacturers use 200–300 kg of plastics in today's cars. Tables 2 [19] and 2-1 [20] show the relation between CO<sub>2</sub> emissions and

**Table 2. Relation between the car weight and CO<sub>2</sub> emissions (source: Adapted from ref. 19)**

Manufacturer	Average mass (kg)	Average CO <sub>2</sub> /km		
		2011	2010	2009
Maruti Suzuki India Ltd.	934	104	104	104
Chevrolet Italia	1,092	113	118	122
Mitsubishi Motor Europe BV (MME)	1,046	120	127	*
Honda Automobile China CO	1,146	125	126	*
Magyar Suzuki Corporation Ltd.	1,163	128	137	138
Honda Motor CO	1,372	142	144	*
Suzuki Motor Corporation	1,242	148	144	146
Audi Hungaria Motor KFT	1,444	149	*	*
BMW M GmbH	1,629	153	156	*
Mitsubishi Motors Corporation (MMC)	1,589	154	165	*
Saab Automobile AB	1,699	155	175	184
Honda of the UK Manufacturing	1,450	161	162	*
Fuji Heavy Industries Ltd.	1,582	170	179	178
Jaguar Cars Ltd.	1,900	189	197	196
Chrysler Group LLC	2,005	192	215	216

**Table 2-1. Average plastics weight among total vehicle weight (source: Adapted from ref. 20)**

Worldwide top selling vehicles manufacturer	Average mass (kg)	Average CO <sub>2</sub> g/km
		2013
Ford F150 (USA)	2,359	255
Toyota Corolla (Australia)	1,280	154
Volkswagen Golf (EU)	1,180	85
Wuling Hong Guang (China)	1,106	171
Chevrolet Aveo (Mexico)	1,080	144
Toyota Aqua (Japan)	970	61
Volkswagen Gol (Brazil)	845	151
Maruti Alto 800 (India)	565	103

car weight.

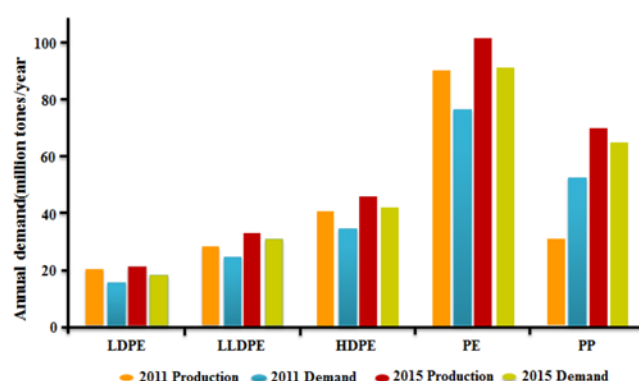
## GLOBAL DEMAND FOR POLYPROPYLENE

Globally, polymer demand has been rising at different ratios in various regions. Among the major thermoplastics, polypropylene shows the highest demand. Fig. 7 shows the global supply/demand/forecast of polypropylene (2014) [23].

From a survey of the literature, several types of polymers are used in automobiles: high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), composites, and acrylonitrile-butadiene-styrene (ABS). Among all the automotive polymers, polypropylene has the highest consumption owing to its easy forming properties and availability at lower prices than other materials, followed by polyurethanes (17.6%), ABS (12.8%), composites (11.5%), HDPE (10.2%), polycarbonates (7%), and PMMA (4.4%).

### 1. Global Consumption of Polypropylene by Region

Polypropylene consumption patterns vary from region to region

**Fig. 7. Global polypropylene supplies to outstrip demand in 2015 (source: Adapted from reference 23).**

depending on the structure and balance of end uses in the industries in each region. Fig. 8(a) [24] and Fig. 8(b) [25] show the global consumption growth rate by polymer (2005-2012 and 2012-2017, respectively) and Fig. 8(c) presents the global polypropylene consumption growth rate by region [26].

Globally, the major polypropylene and polyethylene (PE) consumption growth centers are Asia, Central and Eastern Europe, South America, Central and South America, and the Middle East. Based on Platts petrochemical analysis, Asia and Africa are both expected to have the strongest growth polypropylene consumption rates, 6% and 5%, respectively. Within Asia, consumption of polypropylene in China exceeded eight million metric tons from 2005-2013. Global PP consumption is growing in terms of key end-use sectors in the region. The PP demand and consumption rate are also positive in Europe, as PP usage has increased in various fields. PP compounds are widely used in automotive applications, electronics and electrical industries, and building and construction.

In general, major polypropylene consumption lies in injection-molding applications in industrialized countries (Table 3) [27]. The



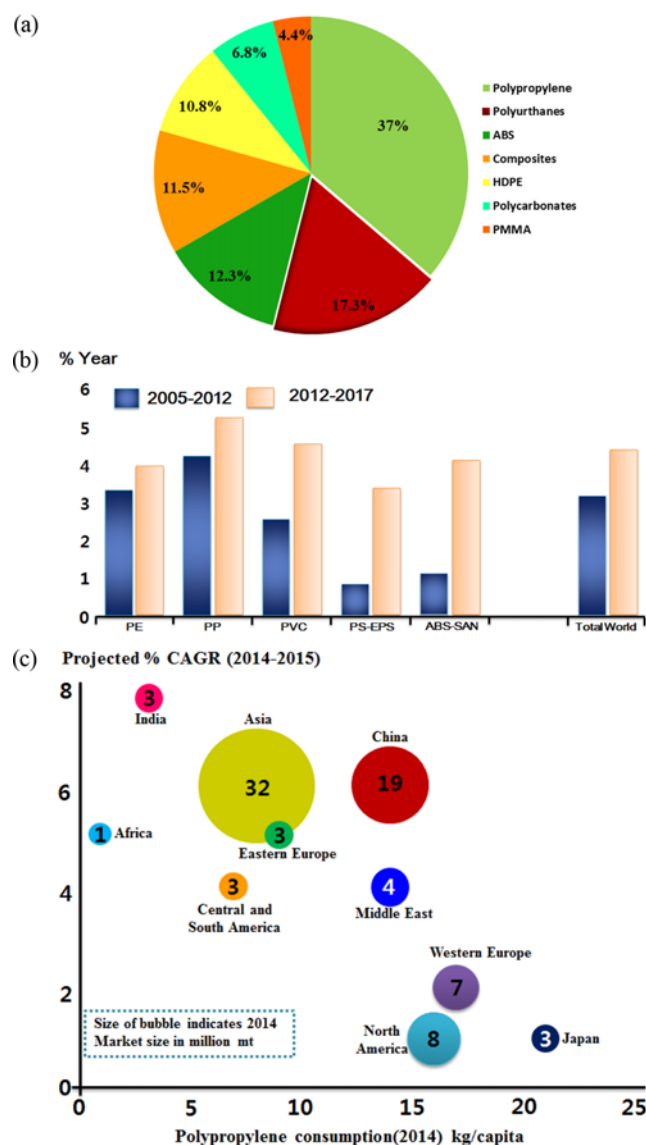


Fig. 8. (a) Global consumption of polypropylene in passenger cars (source: Adapted from reference 24). (b) Global consumption growth rate, by polymer (2005-2012) and 2012-2017) (source: Adapted from reference 25). (c) Global consumption of polypropylene growth rate by region (2014) (source: Adapted from reference 26).

applications of polypropylene have also widely spread into the agricultural sector for making agricultural bags, tarpaulins, and fishing nets along with other uses such as stockings and home appliances.

## 2. Polypropylene for Plastics

Polypropylene is a homogeneous material that has the same corrosion resistant properties throughout, thus eliminating the need for additional treatments such as re-coating the inside or outside to guard against corrosion. Handling, installation, and relocation of polypropylene equipment are easier because polypropylene is lighter than most other materials used in fabrication. The light weight allows for less expensive structural supports and concrete floors. Meanwhile, more than one-third of communities collect plastic beyond bottles. In the US, polypropylene recycling rates are increasing, even in the absence of a "formal stream".

The advantages of polypropylene include low density, good stiffness/impact balance, chemical and thermal resistance, reduced environmental impact, good moisture vapor barrier properties, hot fill and retort capability, and microwavable properties. The low density of polypropylene reduces the environmental impact. Polypropylene produces less solid waste by weight than PET, PS, and PVC, respectively. Polypropylene and high-density polyethylene (HDPE) produce significantly less CO<sub>2</sub> equivalent by weight than PET, PS, and PVC. Recycled polypropylene is being used in many diverse applications. In the US, polypropylene recycling rates are increasing dramatically.

Recent studies support the evaluation of thermal behavior by thermo-gravimetric analyzer for rejected polypropylene, plastic pellets and plastic films collected from the chemical industry, plastic packaging industry and Municipal Solid Waste Plants. These researchers investigated the kinetic parameters also by using several methods such as Coats-Redfern, Ozawa and Kissinger methods [28] and compared them. Based on their comparisons between Coats-Redfern and Ozawa methods, they concluded that magnitudes of activation energy varied, and it indicates the thermal degradation of plastic waste follows a two-dimensional diffusion mechanism. By Ozawa method, thermal degradation of plastic waste follows three-dimensional diffusion mechanisms.

## 3. Global Scenario of Polypropylene in Automobiles

There are many examples in modern cars of weight savings made possible by plastics: plastic bumpers are up to 10.4 kilograms lighter, engine covers are 4.2 kilograms lighter, and plastic fuel tanks are

Table 3. PP global consumption by region - 2011-2015 (source: Adapted from ref. 27)

Country name	2011 kt	2012 kt	2013 kt	2014 kt	2015 kt	AAGR growth 15×10	%World 2015
North America	7,758	7,940	8,133	8,338	8,553	2.5%	13.4%
Central/South America	2,772	2,965	3,177	3,395	3,624	6.9%	5.7%
Western Europe	7,620	7,772	7,933	8,100	8,273	2.1%	12.9%
Japan	2,543	2,666	2,798	2,908	3,026	4.5%	4.7%
China	2,567	2,678	2,744	2,769	2,795	1.5%	4.4%
Other Asia/Pacific	14,965	16,049	17,195	18,426	19,735	7.2%	30.8%
Middle East	6,551	6,855	7,165	7,474	7,794	4.6%	12.2%
Africa	3,476	3,363	3,810	4,003	4,200	4.7%	6.6%
India	1,281	1,344	1,419	1,506	1,601	4.7%	2.5%
Total World	2,936	3,251	3,600	3,985	4,403	10.7%	6.9%

**Table 4. Polymers used in a typical cars (source: Adapted from ref. 29)**

Component	Main types of plastics	Weight in av. car (Kg)
Bumpers	PP, ABS, PC/PBT	10.0
Seating	PUR, PP, PVC, ABS, PA	13.0
Dashboard	PP, ABS, SMA, PPE, PC	7.0
Fuel systems	HDPE, POM, PA, PP, PBT	6.0
Body (incl. panels)	PP, PPE, UP	6.0
Under-bonnet components	PA, PP, PBT	9.0
Interior trim	PP, ABS, PET, POM, PVC	20.0
Electrical components	PP, PE, PBT, PA, PVC	7.0
Exterior trim	ABS, PA, PBT, POM, ASA, PP	4.0
Lightening	PC, PBT, ABS, PMMA, UP	5.0
Upholstery	PVC, PUR, PP, PE	8.0
Liquid reservoirs	PP, PE, PA	1.0
Total		105.0

five kilograms lighter than their conventional counterparts (Table 4) [29].

Plastics utilization in the automobile industry is mainly targeted at mass reduction and simultaneous reduction of carbon dioxide emissions according to automobile manufacturers. These factors affect the material cost and research activity investments by companies. Some global automobile manufacturers (GM, BMW, Nissan, Chrysler, Mercedes, Volkswagen, Toyota, Ford, and Honda)

use polypropylene with different combinations of filler composites for car body parts. The key advantage of polypropylene is an excellent balance of high impact strength/stiffness, improved function integration capability, noise reduction, lighter components, possibility of reducing overall system costs, vibration resistance, a wide operating temperature range ( $-40^{\circ}\text{C}$  to  $+120^{\circ}\text{C}$ ), and chemical resistance. Fig. 9(a) shows the PP compounds used in automotive applications, and the effects of PP compounds on mechanical properties are presented in Fig. 9(b) [30].

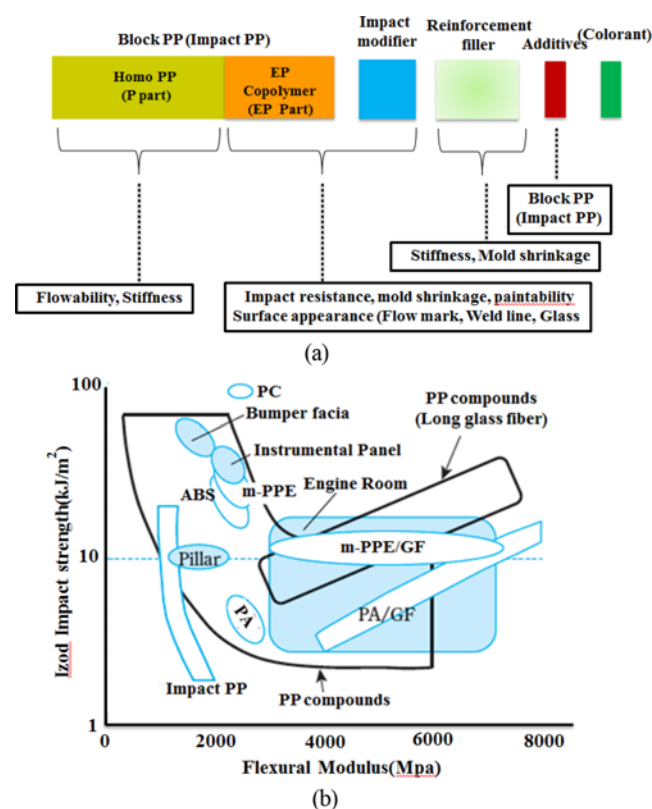
#### 4. Effects of Polypropylene Composites on Mechanical Properties

PP composites have significant effects on mechanical properties in automotive applications depending on the mineral fillers with different particle shapes and sizes. Polypropylene with suitable functional mineral fillers or additives can provide higher stiffness and impact resistance for desired automobile applications. There are many research reports available about polypropylene with different coated and uncoated fillers. Researchers have investigated the influence of nano clay (other than calcium carbonates) on mechanical properties of polypropylene by applying dihydroxylation at high temperature. Based on their analysis, flexural modulus and the deflection temperature for the pp nano composites were much higher than the virgin pp [31].

Micron size powdered filler materials are widely used in the plastics industry. Based on detailed research investigations [32], the most influential mechanical properties such as tensile strength, impact resistance, and flexural modulus of a polymer are all affected by the addition of a filler. The flexural modulus rises as filler aspect ratio is increased. A high aspect ratio of particles and a higher modulus lead to higher composite stiffness.

The major final conclusions from the above research investigations are as follows:

- The mechanical properties of PP/filler composites depend on a uniform dispersion of the mineral particles;
- Micro-sized particles are suitable for achieving higher impact and tensile strength;
- The stiffness of composites is enhanced by high loading and a high aspect ratio;



**Fig. 9. (a) Component of pp compound for automotive application (b) mechanical properties of PP compounds (source: Adopted and modified data from Ref. 29).**

iv) High aspect ratio fillers create large stresses in the polymer near the filler edges;

v) Low aspect ratio fillers lend medium stiffness but enhance the impact strength.

Polymer processing by radiation or irradiation influence the polymer physical, thermal and mechanical properties. PP/LLDE blends with different monomers are highly influenced in their rheological and thermal properties by electron beam irradiation. After introducing irradiation, LLDPE/PP is highly effective for crosslinking or branching [33].

The size and shape of the mineral particles can affect the mechanical properties, such as the stiffness, tensile, and impact strength. In recent years, diverse nanomaterials with wide unique properties have been used as filler materials for polypropylene. Due to their higher surface area, nanomaterials combined with polymers are advantageous to form nanocomposites. Based on various research investigations, micro-sized particle sizes have a limited influence on the Young's modulus of composites, but with nano-size particles the modulus can be increased. Nanocomposites show superior mechanical properties over composites with micro-sized particles.

### CALCIUM CARBONATE FILLERS FOR POLYPROPYLENE

Calcium carbonate ( $\text{CaCO}_3$ ) is one of the most abundant mineral fillers used in the plastics industry with a specific particle size, to meet polymer resins requirements. Among the various mineral fillers, calcium carbonate ( $\text{CaCO}_3$ ) is one of the most important, versatile and widely used fillers for polypropylene in terms of weight. The main motivation to use this mineral is economical. The automotive industry has been one of the driving forces for the increased consumption of functional fillers in plastics. Precipitated calcium carbonate is widely used in different industries including paper-making, plastics, coating, etc. [11].

#### 1. Calcite Filled Polypropylene

Among the three polymorphs of calcium carbonate, calcite is an economical, nontoxic, and thermodynamically more stable poly-

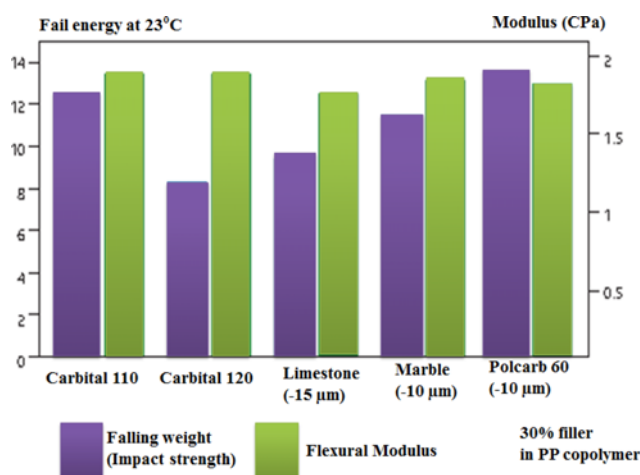


Fig. 10. Effect of calcium carbonate type on impact strength (source: Adopted and modified data from Ref. 31).

morph over a wide range of temperature. Calcite is used as an additive in plastics, and helps to decrease surface energy, opacity, and surface gloss. Calcite filler provides superior appearance and color consistency among various available fillers. In addition, if the particle size is carefully controlled, calcite can help increase the impact strength, elongation at break, notched izod impact strength, and flexural modulus (stiffness). Accordingly, calcite is the preferred filler in many industries and has advantages over other commercial fillers. IMERYS, a world leading international supplier of white minerals, fillers and extenders based on calcite calcium carbonates, measured the mechanical properties of different calcium carbonates (different sizes and shapes) with polypropylene (see Fig. 10) [34].

The addition of calcite-filled calcium carbonate provides an excellent balance of stiffness and impact, and can enhance toughness with polypropylene resins. In Table 5, the mechanical properties of calcium carbonates fillers with polypropylene are presented [35-57]. Fig. 11 shows the dispersion of calcium carbonates in PP

Table 5. Summary of calcite calcium carbonate as fillers in polypropylene/calcium carbonate composites

$\text{CaCO}_3$ polymorph	Size ( $\mu\text{m}$ or nm)	Selected resins	Remarks	Ref.
Calcite	100 nm	Polypropylene homopolymers	Improvement of stiffness, toughness and synergistic improvement of mechanical properties	35
Calcite	70 nm	Isotactic Polypropylene homopolymers	Improvement of mechanical properties such as Young's modulus, tensile yield stress and impact strength	36
Calcite	1.2 $\mu\text{m}$	Isotactic Polypropylene	$\text{CaCO}_3$ treated with stearic acid and admicellar treated displayed lower tensile strength, Young's modulus, and flexural strength, but higher impact strength	37
Calcite	50 nm	Isotactic Polypropylene	Addition of nm- $\text{CaCO}_3$ increases the crystallization rate of iPP from the molten state	38
Calcite	50-100 nm, 40-70 nm, 100-250 nm, 1 $\mu\text{m}$	Isotactic Polypropylene	$\text{CaCO}_3$ nanoparticles coated with maleated polypropylene can promote nucleation of iPP crystals	39
Calcite	21-39 nm	Polypropylene	Mechanical property of tensile strength is enhanced as the amount of nano $\text{CaCO}_3$ is increased	40

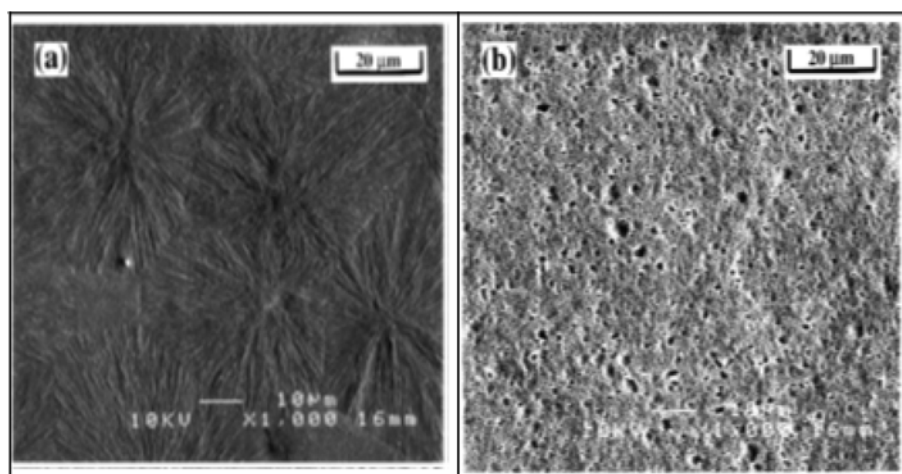


Table 5. Continued

CaCO <sub>3</sub> polymorph	Size (μm or nm)	Selected resins	Remarks	Ref.
Calcite	44 nm	Polypropylene	Izod impact tests suggest that the addition of CaCO <sub>3</sub> nanoparticles to polypropylene significantly increases its impact strength (by almost 300%)	41
Calcite	2.8 μm	Polypropylene composite fibers	The creation of agglomerates can be suppressed by establishing calcite homogenization conditions during spinning with a shear rate of 100-250 s <sup>-1</sup>	42
Calcite	1.85 μm	Polypropylene homopolymer	Enhancement of toughness and ductility	43
Calcite	4.0 μm and 2.9 μm	Polypropylene homopolymer	Addition of lower content of CaCO <sub>3</sub> with lower particle size tends to decrease the composite viscosity	44
Calcite	70 nm	Maleic anhydride-modified polypropylene Licomont AR 504 (PP-g-MA)	Young's modulus increased significantly (25%) when unmodified, 9-wt% commercial grade CaCO <sub>3</sub> was used with PP-g-MA	45
Calcite	1.32-4.20 μm	Polypropylene	Larger CaCO <sub>3</sub> particle size (4.20 μm) with PP showed higher impact strength	46
Calcite	2.5 μm	iPP powder	Pimelic acid (PA), a new surface modifier treated CaCO <sub>3</sub> to make PP/CaCO <sub>3</sub> composites showed better tough ness and a notched impact strength value, 19.79 kJ/m <sup>2</sup> , which is 3.64 times greater than that of pure PP	47
Calcite	0.07-1.9 μm	Polypropylene	A polypropylene-CaCO <sub>3</sub> composite showed a significantly higher modulus and improved toughness, and the notched Izod fracture energy was raised from 2 up to 40-50 kJ/m <sup>2</sup>	48
Calcite	1.1 μm	Copolypropylene	50 wt% calcite with copolypropylene showed higher elongation at break and the impact strength	49
Calcite	1.9 μm-10.5 μm	Syndiotactic poly propylene	Untreated CaCO <sub>3</sub> with syndiotactic poly propylene showed a higher Young's modulus with an increasing amount of CaCO <sub>3</sub> , whereas treated CaCO <sub>3</sub> (with stearic acid) showed the reduced mechanical properties such as tensile strength and Young's modulus, but improved impact resistance	50
Calcite	1.1 μm	Poly(propylene-co-ethylene) CoPP) and poly(propylene-coethylene-co-1-butene) (TerPP)	Calcite filled CoPP and TerPP composites showed good improvement in Young's modulus by successive increments of the filler but at the same time higher loadings of filler decrease the yield stress, elongation at break, and impact strength in both systems	51
Calcite	0.07, 0.7 & 3.5 μm	iPP Accpro 9346	The 0.7 μm diameter CaCO <sub>3</sub> particles enhanced the mechanical properties such as modulus and Izod impact energy beyond those that of an unfilled matrix. Initial addition of fillers enhanced strain at break but at higher loadings it decreased	52
Calcite	0.07 μm	PP1 is a homopolymer, PP2 is a propylene-ethylene copolymer, and PP <sub>3</sub> is a mixture of PP1 and PP2 (PP1 : PP2=1 : 1, weight ratio)	Precipitated calcium carbonate filled with PP1 with average particle size 0.07 μm enhanced the yield strength. When the filler content was appropriate, the three pp nano composites improved impact strength	53
Calcite	0-0.135 μm	Iso-polypropylene with 4.5 wt% of ethylene KS001P	The coated CaCO <sub>3</sub> with PP composite dispersed homogeneously and improved the mechanical properties such as stiffness and toughness	54

**Table 5. Continued**

CaCO <sub>3</sub> polymorph	Size (μm or nm)	Selected resins	Remarks	Ref.
Calcite	t-PCC (1-5 μm), n-PCC (40-50 nm) and ns-PCC (40-50 nm (width) and 150-200 nm length)	Polypropylene	Strong interaction of ns-PCC with the matrix caused an increase in yield and tensile strength	55
Calcite	1 μm	Polypropylene (GWE 27 PP)	Surface modified PCCs considerably enhanced the impact strength and flexural modulus	56
Calcite	70-90 nm	Polypropylene Homopolymer (grade H501-HC)	CaCO <sub>3</sub> nanoparticles greatly affected the mechanical properties such as elastic modulus and yield stress	57
Calcite (from recycled clam shell waste	2.27 μm	Polypropylene	PP with different filler weight ratios (100 : 0, 95 : 5, 93 : 7, 90 : 10, 85 : 15, 80 : 20 and 70 : 30) tested the mechanical properties and it enhances the as impact strength, flexural modulus and flexural strength of pp composite	58
Calcite mixed with little aragonite (from modified clam shell waste such as CS, FCS, ACS)	<4 μm	Polypropylene (T30S)	Calcite mixed with little quantity of aragonite with pp composite (5, 7 and 15 wt%, respectively) to achieve better mechanical properties such as good fracture toughness & stiffness	59
Calcite (from modified clam shell waste FCS)	2-4 μm	Polypropylene (T30S)	Calcite with pp composite (15 wt%) to achieve better mechanical property toughness	60
Calcite (from furfural modified clam shell waste F-MCS)	2-4 μm	Polypropylene (T30S)	Calcite with pp composite (15 wt%) to achieve better mechanical property toughness	61

**Fig. 11. SEM micrographs (a) pure PP and (b) nanocomposite with 9.2 vol% filler (source: Adopted and modified data from Ref. 40).**

composites [43].

A statistical analysis and a 2<sup>2</sup> factorial experimental design were employed to evaluate the effects of the rheological performance of polypropylene/calcium carbonate composites (Fig. 12) [46]. From this analysis, we observed that the addition of lower content of filler

with lower particle size leads to decreased composite viscosity due to better dispersion of the filler in the polymer matrix.

A recent study evaluated the feasibility of using recycling clam shell waste containing calcite with an average particle size of 2.27 μm for use as a filler in the polymer industry. The recycled bivalve

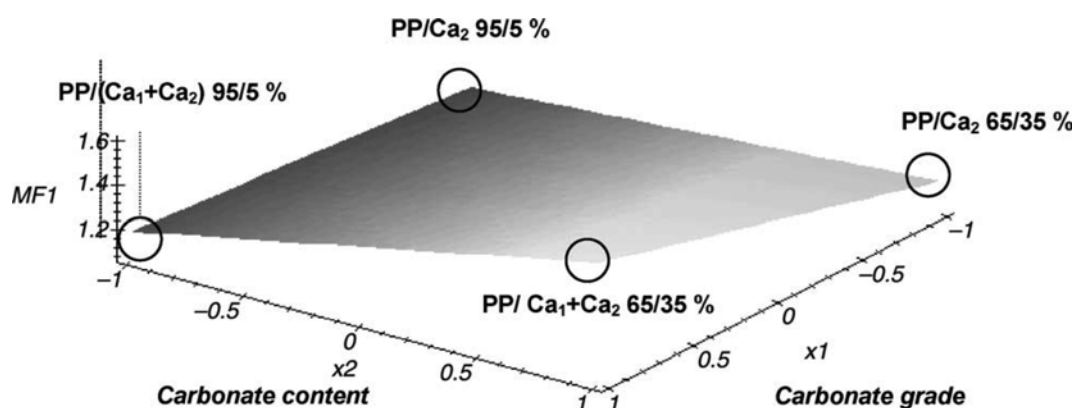


Fig. 12. Effects on grade and content of mineral fillers in the composite melt flow index values (source: Adopted and modified data from Ref. 43).

shell is a calcite calcium carbonate source that can potentially be used as a bio-filler for polymers. Researchers evaluated the surface free energies of the surfaces of clam shell waste (CS) by using inverse gas chromatography with the Dorris-Gray method and the Schultz method and also investigated clam shell waste with polypropylene (PP) composites and measured the mechanical properties. The results demonstrated that clam shell waste (CS) significantly enhances the mechanical properties of PP composites, including the impact strength, flexural modulus, and flexural strength [58]. Furthermore, modified clamshell waste (CS), furfural modified filler (FCS) and acid modified filler (ACS), enhances the mechanical properties (good fracture toughness and stiffness of PP composites) relative to commercial calcium carbonate [59-61].

## 2. Aragonite Precipitated Calcium Carbonate Filled Polypropylene

Aragonite-precipitated calcium carbonate is the second polymorph of calcium carbonate and is a thermodynamically metastable form. Aragonite PCC has a slightly greater average index of refraction than calcite. Hence aragonite is expected to have better performance properties as a filler in the paper and plastics industries when compared with calcite [62,63]. Aragonite PCC is often used as a filler in the rubber, plastic, paint, pigment, and paper industries. In particular, aragonite PP, which is characterized by needle-shaped particles with a very high aspect ratio, increases the bending and impact strength of rubber and plastics. Aragonite whiskers are much better than calcite as fillers in polyvinyl or polypropylene (PP) composites, enhancing the tensile strength, impact strength, glass transition temperature, and decomposition temperature [64]. Some researchers used mixed composites with different particles

sizes. The mechanical properties such as the yield strength, flexural strength, modulus, and impact strength of PP/CC25/CC0.07 hybrid composites were higher than those of single filler composite. The authors used 25  $\mu\text{m}$  needle-like aragonite precipitated calcium carbonates [53]. While making PP composites with CaCO<sub>3</sub> polymorphs, the morphology of the polymorphs has a significant impact on the mechanical properties and the thermal properties.

Aragonite calcium carbonates (particle size is 57  $\mu\text{m}$ ) were extracted from the conch shell of *rapana thomsiana* and used as a filler for epoxy resin. This resin was modified with diglycidyl ether of bisphenol A (DGEBA), p-aminobenzoic acid (p-ABA), and triethylbenzylammonium chloride (TEBAC) systems were applied for the evaluation of thermal behavior of composite [65].

Recently, aragonite pcc filler was applied for both polypropylene and polyvinyl alcohol composites [66]. The morphology of aragonite precipitated calcium carbonate is similar to wollastonite (needle-like, aspect ratio 20  $\mu\text{m}$ -100  $\mu\text{m}$ ). Recently, wollastonite has been used as a filler for polypropylene, especially for bumpers. In the same manner, aragonite PCC is versatile mineral filler for polypropylene composites in the automobile industry due to its needle-like morphology. Aragonite PCC with PP (mixed with other polymorph calcite) (Table 6) enhances the mechanical properties of plastics.

## 4. Vaterite-Precipitated Calcium Carbonate Filled Polypropylene

Vaterite is the thermodynamically least stable form of calcium carbonate and it can be converted into calcite over time. The geological origin of this bio-mineral is rare. Some researchers [67] reported that vaterite is available with carbonate dust grain formation in astrophysical implications. The aforementioned study suggested that vaterite could be a mineral component combined with

Table 6. Summary of aragonite precipitated calcium carbonate as fillers in polypropylene/calcium carbonate composites

CaCO <sub>3</sub> polymorph	Size ( $\mu\text{m}$ )	Selected resins	Remarks	Ref.
Aragonite	25 $\mu\text{m}$	Polypropylene homopolymers (F401, homopolymer)	The mechanical properties such as yield strength, flexural strength, modulus and impact strength of the PP/CC25/CC0.07 composites was higher than that of single filler composite	53
Vaterite	100 nm	Polypropylene	Enhanced tensile strength and Young's modulus with vaterite composite. The crystallization temperature and crystallinity of the composite were higher than those of other composite forms	88

carbonate dust and it is possible to form its polymorphs on planetary surfaces. A recent study [68] demonstrated the synthesis of vaterite in the presence of the organic additive diethylene triamine penta acetic acid (DTPA) at higher temperatures with different morphologies, and in the presence of leucine (L-leucine) [69], N-(2-hydroxy ethyl) ethylene diamine-N, N, N<sup>1</sup>-triacetic acid (HEDTA) [70], poly(acrylic acid) PAA [71,72], and dyes [73]. Several papers have specified the characteristics of vaterite in terms of thermodynamic aspects [74], structure [75], crystal growth, nucleation, and orientation at a molecular level [76,77]. High aspect ratio single crystal rods of vaterite were obtained within membranes [78].

Synthetically, vaterite is often observed as a transient phase that converts into calcite via dissolution-precipitation [79], and some evidence has been presented on the structural variability and the origin of synthetic vaterite with multiple structures [80-82]. In the absence of organic additives or membranes synthesis of pure vaterite is particularly rare. Nevertheless, vaterite has wide advantages in biomedical applications, personal care, advanced biomaterials, as coating agents for controlling rapid degradation, and in improving biocompatibility, as well as in construction and building material applications, due to its unique physical and chemical properties and economical strengths [83-87].

From a thorough survey of the literature, vaterite filled polypropylene related research has been limited. Only one group [88] has reported on the use of vaterite as a filler in PP/CaCO<sub>3</sub> composites. In addition, the finest spherulite of polypropylene was used for vaterite. Therefore, vaterite is considered a suitable nucleating agent for polypropylene (Table 6).

## CONCLUSIONS

Polypropylene is often filled to enhance its rigidity, a requirement that becomes a key factor at higher temperatures. Fine grade fillers such as calcium carbonates can improve the toughness compared to other grades of marbles, which typically have a broader particle size distribution. Increased polymer use favors increased use of calcium carbonate as a functional filler in polypropylenes and composites.

Among the three polymorphs of calcium carbonates, calcite is used widely as a functional filler for polypropylene due to its thermodynamic stability. Aragonite precipitated calcium carbonate is meanwhile seeing growing use as a functional mineral filler for polypropylene, mainly owing to its needle-like morphology, which is similar to the needle-like morphology of wollastonite.

The main advantage of these calcium carbonates in terms of application as fillers is the possibility of making controlling particle size and shape possible, and they are more easily dispersed during mixing compared to other polymers used in the paper and plastics industries. Talc, kaolin, and clay minerals enhance the mechanical properties, but they are associated with asbestos. Asbestos is an environmental hazardous mineral that is not safe to use and is banned in most countries. Calcium carbonate, on the other hand, is a safe and abundant mineral that offers cost benefit in terms of its use in polymers. The carbonation process is useful for synthesizing calcium carbonate polymorphs with a wide variety of morphologies. Notably, it is economical, eco-friendly, and less energy consuming

compared to other conventional methods.

The purpose of the present review on calcium carbonate fillers for polypropylene composites is to realize further economical and environmental advantages. Calcium carbonate manufacturing is not complicated. The findings of the present study are quite significant in the polymers industry. Overall, the outlook for calcium carbonate fillers is bright. With expansion and growing demand within the automobile industry in coming years, the demand for calcium carbonate fillers in the plastics industry (bumpers and other body parts of cars) is expected to grow vastly.

## ACKNOWLEDGEMENTS

The authors are very grateful to the Korea Institute of Energy Technology Evaluation and Planning through the ETI program, Ministry of Trade, Industry and Energy (Project No. 2013T100100021) for financial support of this research.

## REFERENCES

1. J. Aizenberg, J. Hanson, M. Ilan, L. Leiserowitz, T. F. Koetzle, L. Addadi and S. Weiner, *Fed. Am. Soc. Exp. Bio. J.*, **9**, 262 (1995).
2. M. Ukrainczyk, J. Kontrec, V. Babić-Ivančić, L. Brečević and D. Kralj, *Pow. Technol.*, **171**, 192 (2007).
3. J. Kontrec, M. Ukrainczyk, V. Babić-Ivančić, L. Brečević and D. Kralj, *Croa. Chim. Act.*, **84**, 25 (2011).
4. J. W. Ahn, J. H. Kim and S. J. Co, WO2007/078017 A1, July 12 (2007).
5. S. D. Skapin and I. Sondi, *J. Colloid Interface Sci.*, **347**, 221 (2010).
6. Pavel Fellner, Jana Jurisova and Ladislav Pach, *Acta Chim. Slov.*, **4**, 3 (2011).
7. P. Fellner, J. Jurisova, J. Kozankova and L. Pach, *Acta Chim. Slov.*, **5**, 5 (2012).
8. R. Beck and J. P. Andreassen, *Ame. Ins. Chem. Eng. J.*, **58**, 107 (2012).
9. J. Jiang, Y. Zhang, X. Yang, X. He, X. Tang and J. Liu, *Adv. Pow. Technol.*, **25**, 615 (2014).
10. S. M. El-Sheikh, S. El-Sherbiny, A. Barhoum and Y. Deng, *Colloids Surf., A: Phys. Eng. Asp.*, **422**, 44 (2013).
11. E. Dalas, P. Klepetsanis and P. G. Koutsoukos, *Langmuir*, **15**, 8322 (1999).
12. B. Cheng, M. Lei, J. Yu and X. Zhao, *Mater. Lett.*, **58**, 1565 (2004).
13. Z. Yao, M. Xia, H. Li, T. Chen, Y. Ye and H. Zheng, *Crit. Rev. Environ. Sci. Technol.*, **44**, 2502 (2014).
14. P. Stratton, *An overview of the North American Calcium Carbonate Market*, Roskill Information Services Ltd., October, 1 (2012).
15. J. W. Ahn, H. S. Kim, H. Kim, S. H. Yoon, J. S. Kim and G. W. Sung, *J. Ceram. Pro. Res.*, **3**, 62 (2002).
16. J. W. Ahn, J. H. Kim and H. S. Park, WO 2007/078018 A1, July 12.
17. J. K. Park, H. S. Park, J. W. Ahn, H. Kim and C. H. Park, *J. Korean Cry. Gro Cry Tech.*, **14**, 110 (2004).
18. Seasonal Fluctuation of Atmospheric CO<sub>2</sub>, National Oceanic and Atmospheric Administration (NOAA), [http://co2now.org/Current-CO2/CO2-Trend/seasonal\\_fluctuation-of-atmospheric-co2.html](http://co2now.org/Current-CO2/CO2-Trend/seasonal_fluctuation-of-atmospheric-co2.html) (2015).
19. CO<sub>2</sub> Emissions Performance of Car Manufacturers in 2011, European Environment Agency Report, 1 (2012).

20. European vehicle market statistics pocket book, *The International Council on Clean Transportation*, 1 (2014).
21. D. Weill, G. Klink, L. Besland and G. Rouilloux, *Plastics. The future for Automakers and Chemical Companies*, AT Kearney, 1 (2012).
22. L. Burelle, *2012 Financial Results, Plastic Omnium*, 1 (2013).
23. P. Viswanathan, *Petrochemical Market Trends and Opportunities for South Asia*, <http://www.petrochemconclave.com/presentation/2013/Ms.PViswanathan.pdf> (2013).
24. Automotive plastics market for passenger cars, by type (Polypropylene, Polyurethane, HDPE, ABS, Polycarbonate & Composites), application (Interior, Exterior & Under Bonnet) & Geography-Trends and Forecasts to 2018, *markets and markets.com* (2013).
25. J. Richardson, *Market Outlook: Polymers World Turned on Its Head* (2013).
26. Hetain Mistry, *India to outweigh Chinese polyolefin/polypropylene demand growth over the next years, September 2014*, 1 (2014).
27. P. Callais, Outlook for PE and PP Resins, Townsend Solutions Presentation (2011).
28. S. Rana, J. K. Parikh and P. Mohanty, *Korean J. Chem. Eng.*, **30**, 626 (2013).
29. O. Wolf, C. Delgado, L. Barruetabena and O. Salas, Assessment of the Environmental Advantages and Drawbacks of Existing and emerging Polymers Recovery Processes, JRC Scientific and Technical Reports (2007).
30. Satoru Moritomi, Tsuyoshi Watanabe and Susumu Kanzaki, R&D report, *Sumi. Kag.*, **2010-1**, 1 (2010).
31. P. Pandey, S. Mohanty and S. K. Nayak, *Korean J. Chem. Eng.*, **31**, 1480 (2014).
32. J. M. Adams, *Clay Min.*, **28**, 509 (1993).
33. P. Dahal, J. H. Kim and Y. C. Kim, *Korean J. Chem. Eng.*, **31**, 1 (2014).
34. Carbital<sup>TM</sup> 110 and Carbital<sup>TM</sup> 120 in Polypropylene, *Technical Information Plastics* (2000).
35. M. Gahleitner, C. Grein and K. Bernreitner, *Eur. Polym. J.*, **48**, 49 (2012).
36. Y. Lin, H. Chen, C. M. Chan and J. Wu, *Eur. Polym. J.*, **47**, 294 (2011).
37. P. Rungruang, B. P. Grady and P. Supaphol, *Colloids Surf., A: Phys. Eng. Asp.*, **275**, 114 (2006).
38. H. Yuang, C. Guangmei, Y. Zhen, L. Hongwu and W. Yong, *Eur. Polym. J.*, **41**, 2753 (2005).
39. M. Avella, S. Cosco, M. L. Di Lorenzo, E. Di Pace, M. E. Errico and G. Gentile, *Eur. Polym. J.*, **42**, 1548 (2006).
40. S. Mishra, S. H. Sonawane and R. P. Singh, *J. Poly. Sci. Part B: Poly. Phys.*, **43**, 107 (2005).
41. C. M. Chan, J. Wu, J. X. Li and Y. K. Cheung, *Polymer*, **43**, 2981 (2002).
42. O. Durcova, P. Michlik and L. Knotek, *Polym. Test.*, **8**, 269 (1989).
43. A. Tabtiang and R. Venables, *Eur. Polym. J.*, **36**, 137 (2000).
44. M. C. G. Rocha, A. H. M. F. T. Silva, F. M. B. Coutinho and A. N. Silva, *Polym. Test.*, **24**, 1049 (2005).
45. P. Etelaaho, S. Haveri and P. Jarvela, *Poly. Compo.*, **32**, 464 (2011).
46. J. Zhang, B. Han, N. Zhou, J. Fang, J. Wu, Z. Ma, H. Mo and J. Shen, *J. Appl. Polym. Sci.*, **119**, 3560 (2011).
47. M. R. Meng and Q. Dou, *J. Mac. Sci., Part B: Phys.*, **48**, 213 (2009).
48. W. C. J. Zuiderduin, C. Westzaan, J. Huetink and R. J. Gaymans, *Polymer*, **44**, 261 (2003).
49. J. Biswas, H. Kim and S. Choe, *J. Appl. Polym. Sci.*, **99**, 2627 (2006).
50. P. Supaphol, W. Harnsiri and J. Junkasem, *J. Appl. Polym. Sci.*, **92**, 201 (2004).
51. J. Biswas, H. Kim, B. H. Lee and S. Choe, *J. Appl. Polym. Sci.*, **109**, 1420 (2008).
52. Y. S. Thio, A. S. Agon, R. E. Cohen and M. Weinberg, *Polymer*, **43**, 3661 (2002).
53. K. Yang, Q. Yang, G. Li, Y. Zhang and P. Zhang, *Polym. Eng. Sci.*, **47**, 95 (2007).
54. B. Cioni and A. Lazzeri, *Compo. Int.*, **17**, 533 (2010).
55. Tran Dai Lam, Tran Vinh Hoang, Duong Tuan Quang and Jong Seung Kim, *Mater. Sci. Eng.*, **501**, 87 (2009).
56. D. M. Ansari and G. J. Price, *J. Appl. Poly. Sci.*, **88**, 1951 (2003).
57. D. Eiras and L. A. Pessan, *Mater. Res.*, **12**, 517 (2009).
58. Z. Yao, L. Ge, X. Ji, J. Tang, M. Xia and Y. Xi, *J. Alloys Comp.*, **621**, 389 (2015).
59. Z. Yao, M. Xia, L. Ge, T. Chen, H. Li, Y. Ye and H. Zheng, *Fib. and Polym.*, **15**, 1278 (2014).
60. Z. T. Yao, T. Chen, H. Y. Li, M. S. Xia, Y. Ye and H. Zheng, *J. Hazat. Mater.*, **262**, 212 (2013).
61. M. Xia, Z. Yao, L. Ge, T. Chen and H. Li, *J. Comp. Mater.*, **28**, 1 (2014).
62. E. Dalas, E. Kallitsis and P. G. Koutsoukos, *J. Cry. Grow.*, **89**, 287 (1988).
63. H. Konno, Y. Nanri and M. Kitamura, *Pow. Technol.*, **123**, 33 (2002).
64. E. He, W. Shang and S. Chen, In: *Proceedings of the IEEE International Conference on Properties and Applications of Dielectric Materials*, **1**, 431 (2000).
65. F. Mustata, N. Tudorachi and D. Rosu, *Compo. Part B.*, **43**, 702 (2012).
66. Tran Dai Lam, Tran Vinh Hoang, Duong Tuan Quang and Jong Seung Kim, *Mater. Sci. Eng.*, **501**, 87 (2009).
67. D. M. Ansari and G. J. Price, *J. Appl. Poly. Sci.*, **88**, 1951 (2003).
68. S. J. Day, S. P. Thompson, J. E. Parker and Aneurin Evans, *Astro. Astro.*, **A&A 553, A 68**, 1 (2013).
69. S. Gopi, V. K. Subramanian and K. Palanisamy, *Mater. Res. Bul.*, **48**, 1906 (2013).
70. S. P. Thompson, J. E. Parker, S. R. Street and C. C. Tang, *Journal of Physics: Conference Series (Condensed Matter and Materials Physics Conference (CMMP10))*, **286**, 012030 (2011).
71. S. Gopi and V. K. Subramanian, *Ind. J. Chem.*, **52A**, 342 (2013).
72. Y. Y. Kim, N. B. J. Hetherington, E. H. Noel, R. Kroger, J. M. Char-nock, H. K. Christenson and F. C. Meldrum, *Angew. Chem., Int. Ed.*, **50**, 12572 (2011).
73. Yuya Oaki, Ryota Adachi and Hiroaki Imai, *Polym. J.*, **44**, 612 (2012).
74. Jiban Saikia and Gopal Das, *J. Env. Chem. Eng.*, **2**, 1165 (2014).
75. Lee Kabalah-Amitai, Boaz Mayzel, Yaron Kauffmann, A. N. Fitch, Leonid Bloch, Pupa U. P. A. Gilbert and Boaz Pokroy, *Science*, **340**, 454 (2013).
76. G. Wolf, E. Königsberger, H. G. Schmidt, L.-C. Königsberger and H. Gamsjäger, *J. Ther. Anal. and Calori.*, **60**, 463 (2000).
77. J. Wang and U. Becker, *Ame. Miner.*, **94**, 380 (2009).
78. Qiaona Hu, Jiaming Zhang, Henry Teng and U. Becker, *Ame. Miner.*, **97**, 1437 (2012).
79. A. S. Schenk, E. J. Albarracin, Y.-Y. Kim, Johannes Ihli and F. C. Meldrum, *Chem. Commun.*, **50**, 4729 (2014).



80. J. D. Rodriguez-Blanco, S. Shaw and L. G. Benning, *Nanoscale*, **3**, 265 (2011).
81. Giuseppe Falini, Simona Fermani, Michela Reggi, Branka Njegić Džakula and Damir Kralj, *Chem. Commun.*, **50**, 15370 (2014).
82. Amin Azdarpour, Mohammad Asadullah, Erfan Mohammadian, Radzuan Junin, Hossein Hamidi, Muhammad Manan and Ahmad Rafizan Mohamad Daud, *Chem. Eng. J.*, **264**, 425 (2015).
83. Raffaella Demichelis, Paolo Raiteri, Julian D. Gale and Roberto Dovesi, *Crys. Grow. Des.*, **13**, 2247 (2013).
84. Daria B. Trushina, Tatiana V. Bukreeva, Mikhail V. Kovalchuk and Maria N. Antipina, *Mater. Sci. Eng.*, **C 45**, 644 (2014).
85. A. Arizzi, G. Cultrone, M. Brümmer and H. Viles, *Cons. Buil. Mater.*, **75**, 375 (2015).
86. Yuki Sugiura, Kazuo Onuma and Atushi Yamazaki, *Chem. Lett.*, **44**, 20 (2015).
87. Shinya Yamada, Akiko Yamamoto and Toshihiro Kasuga, *J. Mater. Sci.: Mater. Med.*, **25**, 2639 (2014).
88. Lyu Gyu, Park Sangdae and Sur Gil Soo, *Korean J. Chem. Eng.*, **16**, 538 (1999).