



## Modification and characterization of polypropylene

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### ABSTRACT

*For increasing the toughness of polypropylene and expanding its applications, the modification mechanism of polypropylene is discussed in this paper, and the inorganic particles (calcium carbonate) and organic plastic materials (polyethylene St) are used to modify the polypropylene in this article. The characterization of the polypropylene modified by calcium carbonate and St-modified shows much better toughness and mechanical strength than the pure polypropylene.*

**Key words:** Polypropylene(PP); Modification; Calcium Carbonate; Polyethylene (St) and Characterization

### INTRODUCTION

Polypropylene (PP) is an excellent plastic material with a high heat distortion temperature, excellent rigidity, electrical insulation, excellent resistance to folding and ease of molding. Therefore widely used in fiber, daily necessities, packaging films, industrial products, paints and other fields [1-3]. In the five common plastics, polyethylene and PVC production after domestic consumption is ranked second only to polyethylene. But also the existence of polypropylene notch sensitivity, poor toughness, mold shrinkage Japanese do not wear other shortcomings.

With the rapid development of the plastics industry, the industry needs to adjust the product structure, open up new areas of application, increasing the variety and new high-performance grades, strong research and development of technologies and modified PP modified products is extremely important, this paper modified polypropylene research.

### POLYPROPYLENE MODIFICATION EXPERIMENTAL METHOD

#### 1.1 THE MAIN RAW MATERIAL OF EXPERIMENTS

Polypropylene (powder), polypropylene (S1004, F401), ultrafine CaCO<sub>3</sub>, crystal nucleating agent (1MB); 5 ~ 7% octene, ethylene-propylene copolymer of 70%, crosslinking agent A, the crosslinking agent B, a dispersing agent A, monomer A, monomer B, the monomer c, antioxidant (1076), co-antioxidants (DSTP), liquid paraffin.

#### 1.2 THE MAIN EXPERIMENTAL EQUIPMENT

Twin-screw extruder, injection molding machine, computer-controlled electronic universal testing machine, plastic impact testing instrument and polarizing microscope

#### 1.2 EXTRUSION PROCESS

The first zone temperature: 170-175°C; second zone temperature (C): 175-180; third zone Temperature: 185-190°C; Fourth District Temperature: 195-200°C; die temperature: 190-195°C; feed rate (rpm): 500 to 600; screw speed (rpm): 200.

### 1.3 INJECTION PROCESS

The first zone temperature (C):170-175; second zone temperature (C): 180-185; third zone temperature (C):190-200; nozzle temperature (C) :200-210; injection time (s) 5; dwell time + cooling time (s): 10.

### 1.4GRAFTED POLYPROPYLENE SUSPENSION GRAFT TECHNOLOGY

Powdered PP, grafting monomer, a dispersing agent A, co-reactant, a dispersion time of deionized water, heated to 90 °C, the amount of BPO was added portionwise a solution of the reaction for 2 hours, filtered, washed and dried.

### 1.5 MECHANICAL TESTING

Tensile properties: with cMT5104 computer-controlled electronic universal testing machine according GB1048-79 test, the specimen gage length: 50mm; test speed: 50mIll, min (if not otherwise specified); test temperature:  $23 \pm 1\text{C}$ ; Bending Performance: with cMr5104 computer-controlled electronic universal testing machine according GB1048-79 test, the specimen span: 60mm; provisions deflection: 3.994 Shan; test speed: 2mm, m Rainbow test temperature:  $23 \pm 1\text{C}$ ; Impact: Impact Tester with cHARH7xcJ4 by GB1048.79 test, test temperature:  $23 \pm 1\text{C}$ .

### 1.6 POLARIZING MICROSCOPE

Law melt tablet,tablet temperature  $220 \pm 5\text{C}$ , non-isothermal crystallization using natural cooling in air

### 1.7 X-RAY DIFFRACTION ANALYSIS

Japan Science Rigaku D / Max 2550/PCX ray diffraction, cu Ka radiation wavelength 0.154nm, excitation voltage 40kv, inspire current 300rnA

## RESULTS AND DISCUSSION

### 2.1 SUPERFINE CALCIUM CARBONATE MODIFIED POLYPROPYLENE

#### 1) Electron microscopy characterization

Figure 1 clearly see that there are obvious interface between the crystal ball, and calcium carbonate plus a superfine polypropylene photos can be seen, fine calcium carbonate added to make polypropylene spherulite, which also borders become more blurred, this is due to the presence of ultra-fine calcium carbonate, polypropylene crystallization process, promote the heterogeneous nucleation of polypropylene, and make part of the sub- $\alpha$  into  $\beta$  crystal ball crystal ball. It can be explained as follows: ① After ultrafine calcium carbonate surface treated with polypropylene polymer chain prone to physical and chemical combination can improve the binding force between the two phases when subjected to external shocks, ultra-fine calcium carbonate matrix will induce shear yielding deformation, absorb more impact energy, but too fine calcium carbonate content high, polypropylene melt easily reunion, when under attack, the formation of a large number of voids and cracks, causing a decline in the overall performance composite materials; presence ② superfine calcium carbonate crystallization can be used as a nucleating agent of polypropylene spherulites refinement, also resulted in the generation of crystal-induced B toughness of the composite material is improved; ③ polarizing microscope photographs.

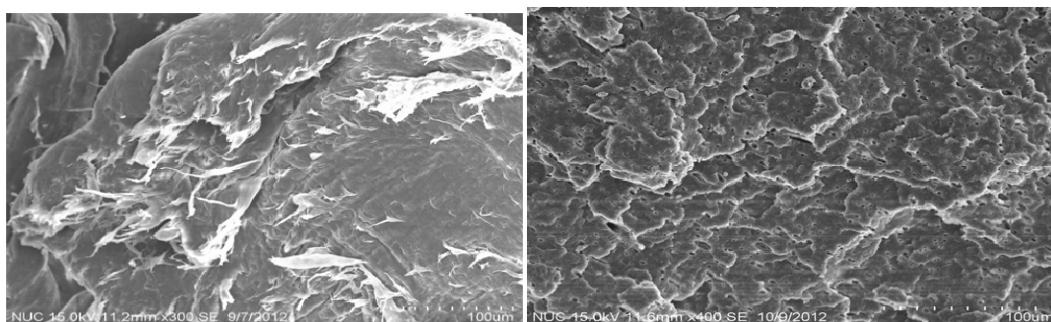


Fig.1 Polarized light micrograph of PP(left) and 10%CaCO<sub>3</sub>/90%PP(right)

Unmodified PP, the external force is likely to rupture phase interface; while the modified PP / CaCO<sub>3</sub> blends, the phase interface unclear, the surface treatment agent is formed between the substrate and a resilient filler material buffer layer, which can effectively transfer and stress relaxation interface, better able to absorb and disperse impact from outside, thereby improving the impact strength of the composite.

## 2) Calcium carbonate modified polypropylene x-ray diffraction analysis

Tab. 1 XRD data of CaCO<sub>3</sub>/PP

0.5%TMB/PP			0.5%TMB/(10%CaCO <sub>3</sub> &90%PP)		
Wc,x=53.46%; K=29.88%; S=30.34%			Wc,x=55.90%; K=28.81%; S=17.74%		
	2-Theta/°C	d(nm)		2-Theta/°C	d(nm)
(110)	13.721	6.4484	(110)	13.694	6.4613
(300)	15.650	5.6577	(300)	15.681	5.6464
(040)	16.503	5.3671	(040)	16.467	5.3787
(130)	18.094	4.8987	(130)	18.094	4.8985
(301)	20.613	4.3053	(301)	20.678	4.2920

Table 1 x-ray diffraction results showed that the presence of ultrafine CaCO<sub>3</sub>, reduced content of  $\beta$ -crystal, the degree of order  $\beta$  crystals decreased, indicating that the ultrafine crystal CaCO<sub>3</sub> affect  $\beta$  induced crystallization nucleating agent, and to facilitate increase in  $\alpha$  crystals[4].

Data show: The CaCO<sub>3</sub> is added to increase the crystallinity of PP, PP and increase the crystal size, the larger the lattice parameters are increased, wherein the b axis is most increased significantly [5].

## 3) Influence on the mechanical properties of calcium carbonate modified polypropylene

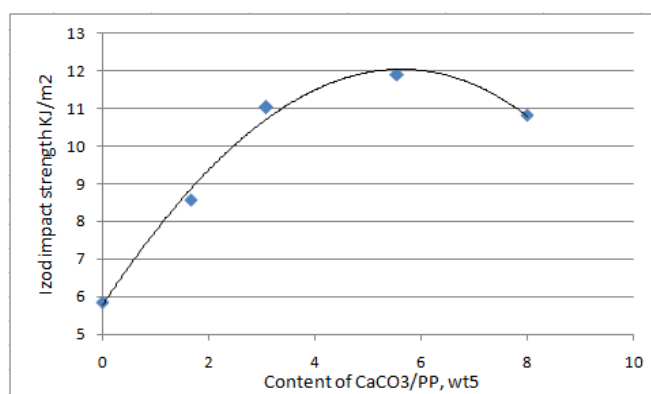
As it shows in Table 2, when A is CaCO<sub>3</sub> beneficial to improve the tensile properties of polypropylene monomer is covered, when B is CaCO<sub>3</sub> monomer is coated to improve the bending properties of polypropylene favorable, and when C is CaCO<sub>3</sub> monomer when coated polypropylene favorable impact performance improvement.

Tab. 2 Effect of monomer on the mechanical properties of PP

Items	Tensile strength (Mpa)	Tensile modulus (Gpa)	Flexural strength (Mpa)	Flexural modulus (Gpa)	Izod impact strength (KJ/m <sup>2</sup> )
CaCO <sub>3</sub>	36.4	1.27	34.67	0.87	6.26
Monomer A	37.3	1.38	35.45	0.88	6.88
Monomer B	3.18	1.25	40.98	1.04	7.45
Monomer C	36.35	1.03	32.03	0.79	7.84

## 4) The impact of calcium carbonate filler content notched impact strength of PP

Experimental results show that the notch impact strength of PP increases to improve the first CaCO<sub>3</sub> content decreased and reached the maximum at about 5%. This is because the surface effect of nanoparticles, resulting in a composite system when under attack, will produce more than the presence of micro-cracks in general filler absorb more impact energy, thereby preventing further development of cracks and passivation, but if filler content is too big, too close to the particles, micro-cracks are likely to develop into a macroscopic crack, making the notch impact strength, shown in below Fig2.

Fig. 2 Effect of CaCO<sub>3</sub>/PP content vs izod impact strength5) Ultrafine CaCO<sub>3</sub> on the performance of the modified cross-linked polypropylene

It can be seen from Figure 3 and 4, a similar variation of the mechanical properties of ultrafine CaCO<sub>3</sub> modified crosslinked PP, PP modified with ultrafine CaCO<sub>3</sub>, with the tensile strength of ultra-fine CaCO<sub>3</sub> content increases the composite modulus of elasticity and the gap impact intensity firstly increased and then decreased, compared with the ultra-fine CaCO<sub>3</sub> modified PP, significantly lower strength and modulus, and toughness is significantly higher, which is a long-chain alkyl structure crosslinkers B related.

Notched impact strength of the composite increases as the CaCO<sub>3</sub> content first increased and then decreased and reached the maximum at about 5%. This is because the surface effect of nanoparticles, resulting in a composite system when under attack [5], will produce more than the presence of micro-cracks in general filler absorb more impact energy, thereby preventing further development of cracks and passivation, but if filler content is too big, too close to the particles, micro-cracks are likely to develop into a macroscopic crack, making the notch impact strength.

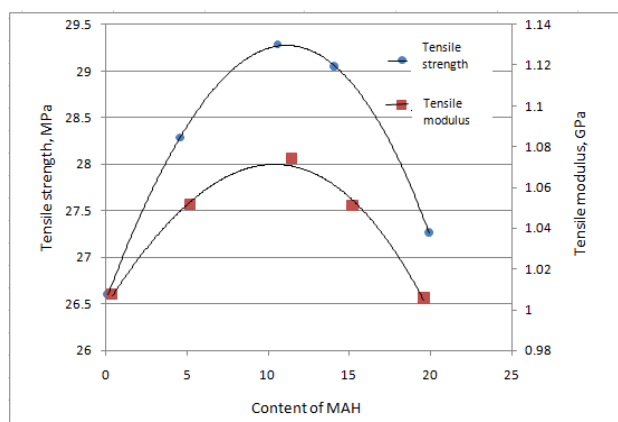


Fig.3 Effect of content CaCO<sub>3</sub>/PP on the tensile strength

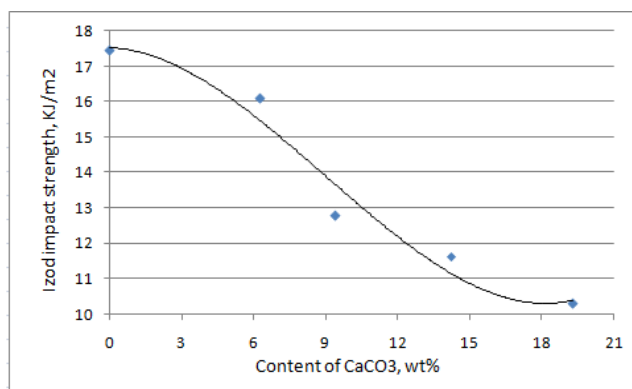


Fig. 4 Effect of content CaCO<sub>3</sub> on izod impact strength

According to the results, impact strength with gap filler, coated polymer ratio increases continuously improve High. This is because after in situ emulsion polymerization, forming with elastic Core-shell particle structure of the cladding layer due to the presence of the polymer, significantly reduced from the surface of CaCO<sub>3</sub>. The energy, reduce agglomeration of nano CaCO<sub>3</sub> during melt mixing[6], it can be uniformly dispersed in the PP: Long chain polymer by entanglement with the matrix resin and the matrix resin CaCO<sub>3</sub> improved compatibility, increasing Strong interfacial adhesion of the filler and the matrix, thereby increasing the notched impact strength of the composite system, if the filler, The coating polymer is relatively small, due to the large presence of the homopolymer of the monomer coating, and the polyethylene photopolymer[7]. Propylene compatibility there are some differences, when the material is under attack, leaving the gap is easy to form stress concentration Impact strength.

Tab. 3 Effect of velocity on the CaCO<sub>3</sub>/PP

Velocity (rpm)	Tensile strength (Mpa)	Flexural strength (Mpa)	Flexural modulus (Gpa)	Izod impact strength (KJ/m <sup>2</sup> )
CaCO <sub>3</sub>	29.3	32.06	1.28	16.26
Monomer A	30.1	33.54	1.33	16.28
Monomer B	29.98	33.73	1.26	15.65
Monomer C	29.94	34.82	1.31	15.34

#### 6) Screw speed of impact modified polypropylene ultra-fine calcium carbonate

Table 3 shows that the screw speed has little effect on the mechanical properties of ultrafine CaCO<sub>3</sub> hiding acidic polypropylene, mainly because in the case already have a certain speed, then increase speed to enhance superfine polypropylene matrix resin CaCO<sub>3</sub> the dispersion is not.

## 2.2 GRAFTED MODIFICATION OF PP

### 1) Reaction mechanism grafted polypropylene

A radical initiator in the reaction suspension grafted polypropylene, PP is formed first macromolecular radicals; the radical B is prone to lead to bond breaking reaction of polypropylene degradation. After the addition of styrene, since the stabilizing effect of the benzene ring conjugated, PP macro radicals styrene monomer and easily connected to the first styrene-based macromere to form a stable free radical, this reaction in the whole system is the predominant the reaction, then the reaction with the styrene-based monomer is the reaction of free radical molecules. We know that for copolymerization monomer, which is the determining factor of two monomer reactivity ratios the monomer reactivity ratio study judged by the following formula [8].

Where  $r_i$  ( $i = 1, 2$ ) for the reactivity ratio.  $Q, e$  in the formula  $Q$  is a measure of the effect of the monomer;  $e$  is a value characterizing the polarity effect of conjugated monomers. The basic principle is that, if the  $Q$  value close to the size of the two monomers, then the two monomers copolymerizable prone contrary, if the  $Q$  value of the size of the two very different monomers, indicates that they are not prone to the copolymerization reaction.

Tab. 4 the  $Q$  and  $e$  value of monomers

Monomer	$Q$	$e$
MAH	0.86	3.69
St	1.00	-0.80

It can be seen from the above data in the table, and MAH-grafted styrene monomer  $Q$  value is very close, so when the Added a suspension system grafted styrene macromer after formation of styryl radicals, MAH contents can vary And the styrene-based macromer easily radical copolymerization reaction, so that it by grafting monomers more benzene Ethylene grafted onto the polypropylene chain length so that they have a greatly increased rate of graft.

### 2) Grafted polypropylene melt flow rate

It can be seen from Table 5, the content of MAH increases, the melt flow rate is gradually reduced, and the addition of St, particularly the melt flow rate decreases. These data illustrate: In the process of grafting of the suspension, with the increase of the content of MAH, st can effectively inhibit the degradation of polypropylene was added to improve the rate of grafting of polypropylene, so that the polypropylene melt flow rate is reduced .

Tab. 5 MI of grafted PP

Item	Neat PP	PP-g-MAH (2.5%)	PP-g-MAH (5.0%)	PP-g-MAH (7.50%)	PP-g-MAH-St (2.5%+2.5%)
MI(g/10min)	10	8.7	7.3	6.8	4.9

### 3) Infrared spectra of grafted polypropylene

After extraction grafted polypropylene film by pressing 200C by infrared spectroscopy analysis of the samples.

Fig. 5 shows the MAH appeared characteristic peaks 1659 $\text{cm}^{-1}$  and 3145  $\text{cm}^{-1}$  Department indicates MAH grafted on a polypropylene molecular chain.

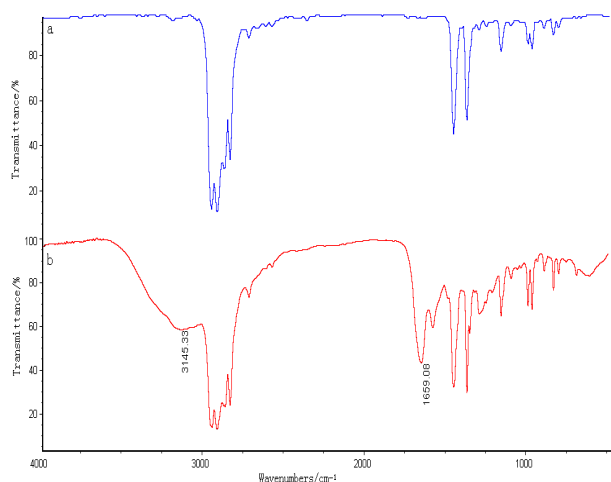


Fig. 5 FTIR spectra of PP-g-MAH

## 4) Grafted polypropylene orthogonal

Select the b (34) orthogonal table 6; select the experiment filler / coating polymer ratio, and grafted polypropylene content the filler content of the composite of three factors.

From the experimental results described in below table 6 it can be seen its optimum conditions: A>B>C. As can be seen from the poor image of the factors Ring degree: A, B, C, i.e., the filler / coating polymer maximum ratio of grafted polypropylene content on the impact Times, minimal impact composite filler content.

Tab. 6 The results of orthogonal experiment

Items	monomer C	PP-g-MAH, wt%	Encapsulating St, wt%	Izod impact strength (KJ/m <sup>2</sup> )
1	10:1	10	2.5	12.6
2	10:1	7.5	5.0	11.8
3	10:1	5.0	7.5	11.4
4	7.5:1	10	5.0	13.5
5	7.5:1	7.5	7.5	10.4
6	7.5:1	5.0	2.5	10.6
7	5:1	10	7.5	10.4
8	5:1	7.5	2.5	9.5
9	5:1	5.0	5.0	10.1
K1	35.8	36.1	32.4	
K2	33.9	31.2	35.6	
K3	30.1	32.3	32.4	
k1	11.9	12	10.7	
k2	11.5	10.6	11.5	
k3	9.8	10.6	10.6	
R	2.2	1.7	1.2	

## 5) Grafted polypropylene impact on the notched impact strength

According to the results of orthogonal experiment, notched impact strength increases with the content of the grafted polypropylene continuous improvement and the maximum at about 10%. This is because a polar group grafted monomer to improve the polarity of the PP, and PP to improve the interaction between the elastic covering layer to improve the notched impact strength of the composite system.

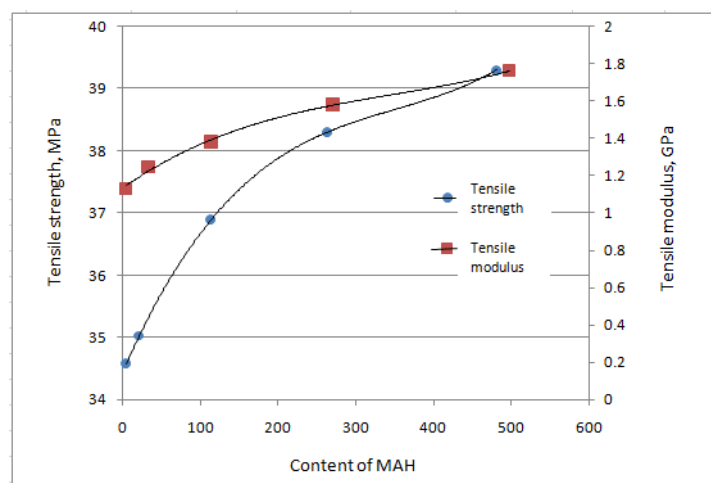


Fig.6 Effect of content MAH/PP on the tensile strength

As with a MAH content increases, more of PP macromolecules are protected, you can make PP moderately crosslinked to form three-dimensional network structure is conducive to absorb external impact energy; makes notched impact strength increased; mutually crosslinked PP increased interaction between the polymer chains, so easily slip occurs between polymer chains, causing the polymer chains to increase the force, thereby increasing the rigidity of the polymer chains to increase the pull-PP tensile properties, however, when the crosslinking agent to a certain extent, with the increase in the three-dimensional spatial network structure, and the crosslinking agent is easily prone to self-polymerization reaction, the resulting tensile and impact properties of PP declined .

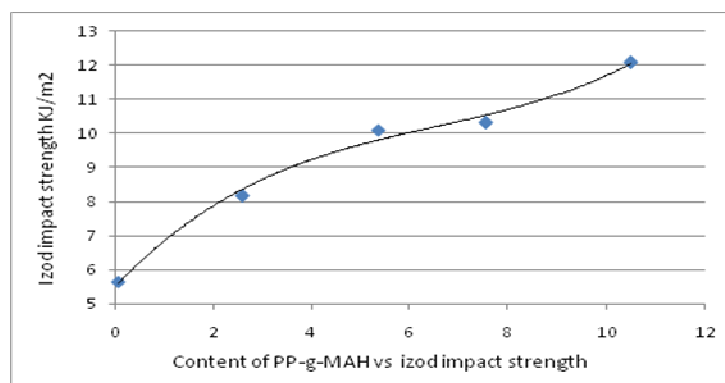


Fig. 7 The effect of the PP-g-MAH content vs izod impact strength

### CONCLUSION

The results show that the modified polypropylene its notch sensitivity, poor toughness and shrinkage greatly improved to meet the polypropylene in different fields of application. Meanwhile the study also received the following modified optimization program:

- 1) Superfine CaCO<sub>3</sub> modified PP, B. PP, PP always crosslinking, the mechanical properties showed a similar pattern. With increasing levels of ultrafine CaCO<sub>3</sub>, the mechanical properties of the composites showed a downward trend after the first rise, at about 10% can be obtained excellent overall performance composite materials.
- 2) The multi-cell suspension graft polypropylene has a melt flow rate decreased with increasing the content of the grafting monomer, the graft ratio relative increasing.
- 3) After three factors and three levels of orthogonal experimental study in situ polymerization grafted polypropylene showed that the optimum conditions were: polymer coated filler ratio 10:1; grafted polypropylene content of 10%; composite filler content of 5 %, and filler/polymer coated extent than the greatest impact, followed by grafted polypropylene content on composite filler content with minimal impact.

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