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# Graft modification of chlorinated polypropylene and coating performance promotion for polypropylene



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## ABSTRACT

Butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA) and acrylamide (AM) were successfully grafted onto chlorinated polypropylene (CPP) via the solution polymerization. Under the optimum conditions, graft ratio turned out to be 14.9% and the fastness reached 100%, which fully satisfy the requirements in the coating industry. This paper studied the various factors on the graft ratio and optimized the grafting process via the orthogonal experiments. The mechanism of graft polymerization was proposed based on the FT-IR and DSC results. The mechanism that grafted CPP (g-CPP) promotes the adhesion between polypropylene (PP) and the topcoat was discussed in accordance with the ESCA results. Compared with CPP, the rheological properties and thermal behaviors of g-CPP were improved dramatically. The processing parameters were demonstrated to have great influence on adhesion properties.

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## 1. Introduction

PP is one of the most promising thermoplastic polymer materials in plastic automotive parts and packages. It often requires to be painted to enhance the cosmetic appearance. However, the drawback of inherently poor adhesion constrains the application of PP. This obstacle is overcome by several traditional techniques, such as corona treatment, flame treatment, plasma treatment or chemical treatment, etc. [1–7]. Although they can improve the polarity of the PP surface to increase the surface energy and adhesion properties, there is serious degradation on the PP surface for the first three processing methods, especially in a damp environment [8]. Adhesion promoter has been discovered to promote the adhesion properties. The typical adhesion promoter for PP is based on chlorinated polypropylene (CPP) [9–14]. CPP is usually combined with other resins to provide mechanical and rheological properties [15–19]. However, to authors' knowledge, the bonding mechanism of the PP substrate with g-CPP is not completely unequivocal. And the factors that govern the application of CPP have yet to be fully defined.

In this paper, we shall first briefly introduce the synthesis of the graft copolymer, which is applied as the promoter in the field of PP coating. After a statement of the adhesion mechanism, various processing parameters involving the fastness are investigated. The results obtained provide a group of foundations for the modification of polyolefines. It is of great value for the molecular design and the application in the coating and adhesive industry.

## 2. Experimental section

### 2.1. Materials

Chlorinated polypropylene (containing Cl 31%) is purchased from Jinzhujiang Chemical Co. Ltd. (Guangzhou, China). MMA, BA, AA, AM are supplied by Tianjin Chemical Reagent Research Institute. 5# coating and PP coated paper are obtained from Zeafee Co. Ltd. (Shanghai, China) and Quanzhou Lichang Co. Ltd. (Fujian, China), respectively. All monomers of acrylates have been distilled under vacuum.

### 2.2. Grafting procedure

A three-necked flask, with a mechanical stirring bar and a reflux condenser, was charged with chlorinated polypropylene and the mixed solvent of ethyl acetate and toluene. The mixture was stirred and heated to 60 °C to dissolve CPP, followed by introducing half of the dissolved initiators. After the installation was bubbled with nitrogen, the graft liquid was dripped for 1.5 h. The graft liquid is composed of the graft monomers, solvent, and half of the initiators per the formulation. Meanwhile, the temperature was raised to boiling point for 7 h. Afterwards, the products were discharged and cooled before weighting ( $M_0$ ).

The nonvolatile content (X) was determined gravimetrically as the weight ratio between the pure polymer and the total amount of the products in the formulation.

The g-CPP samples were purified as follows. The products were dissolved into the concentration of 6% at 60 °C in toluene, subsequently precipitated with 10 times the volume of methanol at

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room temperature, then conducted the process above again. The precipitates were collected and refluxed in an extractor for 24 h, during which the mixed solvent of methanol and toluene was used as the extraction agent. Finally, the purified samples were dried at 60 °C in a vacuum oven. Graft ratio (*G*) is calculated based on the following equation:

$$G = \frac{M_1 - M_0XY}{M_0XY} \times 100\%$$

Where  $M_1$  is the total weight of the pure *g*-CPP; *Y* is the weight ratio between the CPP and the initial reactants in the formulation.

### 2.3. Preparation of the PP/*g*-CPP/coating samples

The product was diluted in the mixed solvent of toluene, ethyl acetate and methanol (volume ratio=1:1:0.02) to obtain desired promoter at 5% solids.

The PP paper, repeatedly wiped with acetone, was coated with the promoter at a 5 μm wet film thickness using a scraper and then dried in an oven at 80 °C for 10 min. Upon cooling, 5# coating was coated on the promoter to obtain a 15 μm thick film with a winding bar. Then the PP paper was baked in an oven at 90 °C for 20 min again. The samples were preserved for the adhesion test and adhesion mechanism analysis.

After making a small opening on the sample to separate the coating partially from the PP substrate, the coating was slowly peeled from the substrate with the mode of 180° peel. Stripping schematic diagram is shown in Fig. 1.

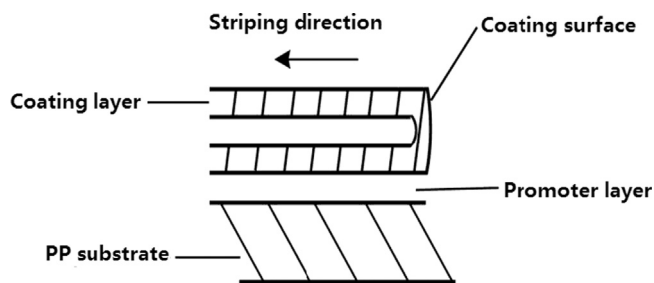


Fig. 1. The diagram of 180° peeling.

### 2.4. Analysis

FT-IR spectra was recorded using a FTIR PERKIN ELMER PARATON 1000 spectrophotometer after 64 scans at a resolution of 2 cm<sup>-1</sup>.

Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 204 thermal analyzer. The samples were heated from 10 to 100 °C at a rate of 5 °C/min under nitrogen atmosphere.

Static rheological properties were characterized on the capillary rheometry. The diameter of the capillary is 0.5 mm and *L/D* ratio is 40:1.

Thermogravimetry (TGA) were carried out by the NETZSCH TG 209 thermogravimetric analyzer at a heating rate of 10 °C/min.

Electron Spectroscopy for Chemical Analysis (ESCA) experiments were implemented on the X-ray photoelectron spectrometer. The grazing angle was kept at 70° (except the coating surface after peeling was 90°).

The fastness was performed in accordance with DIN EN ISO 2409. In this test a cross-cut was made onto the dried coated PP substrates using a cross-cut knife, and an adhesive tape was applied under uniform pressure covering the cross-cut, where after the tape was torn off in a single movement. This tape test was then repeated in a perpendicular direction to the first test. The fastness is defined as the percentage of the non-peeling parts.

## 3. Results and discussion

### 3.1. Orthogonal experimental analysis of graft reaction

A number of experiments we have conducted show that the amount of AM, CPP and BPO and the reaction temperature have pronounced influence on the graft ratio.

We have chosen the orthogonal experiments to investigate the optimum conditions, fixing BA/MMA ratio of 1:2, AA content of 6%, reaction time for 3.5 h. The results are described in Table 1. It is plain from Table 1 that the dosage of AM has the most influential on graft ratio. Within our measured range, the fastness is strengthened with the increase of the graft ratio. However, from the theory, the increasing number of polar groups destroys the crystalline structure of the CPP and makes the promoter polarity contrary to the substrate polarity as a result of declining the fastness, when the graft ratio is excessive. Therefore, we choose

Table 1  
The intuitionist analysis results of L9(3<sup>4</sup>) orthogonal experiment.

	Number	CPP content (%)	AM content (%)	BPO content (%)	Temperature (°C)	Graft ratio (%)	Fastness (%)
Index	1	1(20)	1(3)	1(1.33)	1(89)	8.09	92.3
	2	1	2(3.5)	2(2.00)	2(93)	14.90	100
	3	1	3(4)	3(2.67)	3(97)	7.37	88
	4	2(25)	1	2	3	9.76	97
	5	2	2	3	1	14.81	99.3
	6	2	3	1	2	8.52	93.8
	7	3(30)	1	3	2	10.53	97.9
	8	3	2	1	3	9.57	96.5
	9	3	3	2	1	8.86	94.8
Graft ratio (%)	<b>K<sub>1</sub><sup>a</sup></b>	30.36	28.38	26.18	31.76		
	<b>K<sub>2</sub><sup>a</sup></b>	33.09	39.28	33.52	33.95		
	<b>K<sub>3</sub><sup>a</sup></b>	28.96	24.75	32.71	26.7		
	<b>AVG K<sub>1</sub></b>	10.12	9.46	8.73	10.59		
	<b>AVG K<sub>2</sub></b>	11.03	13.09	11.17	11.32		
	<b>AVG K<sub>3</sub></b>	9.65	8.25	10.90	8.9		
	<b>R<sup>a</sup></b>	1.38	4.84	2.44	2.42		

<sup>a</sup> **K<sub>1</sub>** sum of three grafting rate of the level 1; **K<sub>2</sub>** sum of three grafting rate of the level 2; **K<sub>3</sub>** sum of three grafting rate of the level 3; and **R** the value of the largest minus the smallest among **AVG**.

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