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Study on Preparation Technology and Mechanical Properties of Polypropylene/Montmorillonite Nanocomposites

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Abstract. In this paper, the polypropylene/montmorillonite nanocomposites were prepared by two-step process. The influence of technical formulae and preparation conditions on mechanical property of nanocomposites was studied through orthogonal experiment. The optimal technical formulae were as follows: mass percentage of montmorillonite was 2%, mass percentage of compatibilizer was 15%. The optimal preparation conditions were as follows: processing temperature was 200℃, screw speed was 50rpm. Montmorillonite achieved the nanometer-scale dispersion in PP/MMT nanocomposites

1. Introduction

PP is one of the most widely used general plastics in the form of fabrics, films and so on, due to its well-source, excellent heat-resistance, safety, non-toxic along with low cost. However, the defect of brittleness, poor mechanical properties, low hardness and high molding shrinkage has restricted its use in many fields [1]. To resolve these problems, studies, which purpose was to strengthen and toughen mechanical properties of PP, had been a very active subject in the field of polymer science. In recent years, it has become a research hotspot to study nanocomposite [2-5]. Inorganic filler with nanoscale dimension was added to PP matrix by various peculiar methods. Due to size effect and surface effect, mechanical properties of nanocomposite were more excellent than PP.

Currently, there are two categories of PP/inorganic nanocomposite: PP/layered silicate nanocomposites and PP/inorganic rigid particles nanocomposites. melt intercalation[6.7]was a simple, effective and environmentally friendly method, which process was intercalate polymer directiy into silicate layers. As the temperature was above the softening temperature.

Due to the nonpolarity of PP and the polarity of inorganic nanoparticles, surface modification of inorganic nanoparticles and adding of compatilizer were carried out in order to increase their compatibility and improve the dispersity of tne inorganic nanoparticles in PP matric.ZHANG Liangjun[8] thought that there were three kinds of interface interaction between layered silicate and PP matric: (1) PP chains were connected (adsorbed) direct to the siloxane atoms of silicate layer

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inert surface; (2) Alkyl chains dissolved in PP matrix in different degree; (3)Binding effect between PP chains and groups of silicate layer inert surface.

In this paper, PP/PP-g-MAH/MMT[9,10] nanocomposites were prepared by two-step process in a variety of experimental conditions with silicate of layer structure-montmorillonoid (MMT) as inorganic filler and PP-g-MAH as compatilizer, and mechanical property of nanocomposite was studied.

Experimental

Materials. Montmorillonoid, CEC=90mmol/100g, Zhejiang FengHong clay co., LTD; Hexadecyl trimethyl ammonium Bromide(HTAB), analytical pure, Tianjin Fuchen Chemical Reagent Factory; Polypropylene, technical grade, melt index: 10.9g/min, Daqing Petrochemical Company; PP-g-MAH, grafting ratio: 1.0%, Chengdu Jinniu Seven New Technology Application Research Institute.

Instruments. Experimental instruments were showed in Table 1.

Table 1 Experimental instruments

Instrument	Model	Manufacturer
Twin screw extruder	002-1085	HAAKE, Germany
Torque rheometer	RHEOCORD90	HAAKE, Germany
automatic sheeter	2002	TETRAHEDRON, England
Compression moulding press	YX-50	Shanghai Weili Machinery Factory
Blunt thick machine	6050	CEAST, Italian
tensile testing machine	4467	INSTRON, England

Experimental scheme and steps. At room temperature, a solution of MMT(3 wt%) and water was put in a beaker, violent stirred for 1h, stood for 2h, removed sediment and reserved. HTAB solution was added dropwise into the MMT solution after the MMT solution was heated to 75℃. The reation was carried out for 4h.The solutionwas cooled, quiet placed, filtrated. The sediment filtered out was washed with water several times to remove halide ions (there was no white precipitate when $AgNO_3$ was added dropwise into the filtrate). The sediment filtered out was dried to constant weight under a drying oven at a certain temperature, and then levigated, forced through a sieve of 200 meshes. Organic montmorillonite was obtained.

Firstly, master batch of PP-g-MAH and organic montmorillonite was prepared by melt blending. Masterbatch after drying and appropriate homopolymer polypropylene pellets extruded, cooled, prilled and dried to obtain PP/ PP-g-MAH / MMT composites with the twin-screw under the same process conditions.

Orthogonal experiment had two aspects: the mixing temperature and screw speed of preparation technology and the dosage of montmorillonite and compatilizer. The influence of the factors what were mentioned above on properties of composites was studied by mechanical properties testing. L9(3^4) orthogonal experiment was adopted, and investigation factors and levels were as Table 2.

Table 2 Factor and level

Level	Mixing temperature /℃	Screw speed /rpm	Dosage of montmorillonite /(wt%)	Dosage of compatilizer /(wt%)
1	a_1（170）	b_1（50）	c_1（2）	d_1（10）
2	a_2（185）	b_2（80）	c_2（4）	d_2（15）
3	a_3（200）	b_3（100）	c_3（6）	d_3（20）

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Characterization of composites. Composite pellets were squashed into a thin section with an automatic sheeter according to GB9352-88 at 210℃ under pressure of 45 tons. Different molds were selected to obtained 1mm and 2mm thin section respective. Thin section was transferred to compression moulding press of 50 tons to finish cold pressing. 1mm thin section was sliced into dumbbell-like test pieces, and 2mm thin sections were sliced into rectangular. The dumbbell-like test pieces were used to study the tensile strength, tensile modulus and other mechanical properties of composites with tensile testing machine according to GB/T1040-92, and tensile speed was 50 mm/min. The rectangular test pieces were used to study the flexural strength and modulus of composites with tensile testing machine according to GB/T9341-2000, crosshead speed was 2mm/min.

The optimized composites and pure PP were frozen in liquid nitrogen and then quickly smashed. The fracture surfaces were sputter coated with gold with JFC-1600 ion sputtering equipment. The fracture surface morphology of the composites was observed on a JSM-6360LA scanning electron microscope with an acceleration voltage of 20kV.

Results and discussion

Optimization of preparation conditions and technique formula. Results of orthogonal experiment were as Table 3. (sample 0 was pure PP)

Table 3 Conditions and results of L9(34) orthogonal experiment

Number	Mixing temperature /℃	Screw speed /rpm	Dosage of montmorillonite /(wt%)	Dosage of compatilizer /(wt%)	Tensile strength /Mpa	Flexural modulus /Mpa
0	a_3	b_1	-----	----	25.50	1129.0
1	a_1	b_1	c_1	d_1	34.42	1807
2	a_1	b_2	c_2	d_2	33.79	2187
3	a_1	b_3	c_3	d_3	32.27	1656
4	a_2	b_3	c_1	d_2	33.31	2333
5	a_2	b_1	c_2	d_3	33.31	1884
6	a_2	b_2	c_3	d_1	32.83	1892
7	a_3	b_2	c_1	d_3	34.36	1692
8	a_3	b_3	c_2	d_1	35.27	1748
9	a_3	b_1	c_3	d_2	33.85	2081
I	100.48	101.58	102.09	102.52	Tensile strength	
II	99.45	100.98	102.37	101.46	Important order: a>c> d > b	
III	103.48	100.85	98.95	99.94		
T	4.03	0.73	3.42	1.52		
I	5650	5772	5832	5447	Flexural modulus	
II	6109	5771	5819	6601	Important order: d>a>c>b	
III	5521	5737	5629	5232		
T	588	35	203	1369		

Table 3 was the conditions and results of L9(34) orthogonal experiment. It can be seen from Table 3 that tensile strength and flexural modulus of composites which were prepared in a variety of experimental conditions all increased obviously Comparing with pure PP(number 0). The tensile strength increased by 25%~35% generally,and the best (number 0) was 40%. The flexural modulus

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increased overtly too. The best (number 4) was 107%, and the least was 50%. Those factors indicated that the two-step process optimized the mechanical property of PP clearly.

Optimal preparation conditions. In order to analyze further factors which affect the performance of composite and the best level, various experimental data were calculated according to the principle of the orthogonal table. The results were summarized in table 3. With the influence of mixing temperature on the tensile strength as an example, calculation method was as follow: First of Ⅰ was the sum of the result (tensile strength) corresponding mixing temperature level a1 (170 ℃) in the table 3. Range was T=max{I, II, III} - min{I, II, III}. Calculation method of II, III was the same. The effect of three factors on flexural modulus was calculated by the same method.

The multi-index comprehensive balance sheet was gained by range analysis of experimental result, and was showed in Table 4.

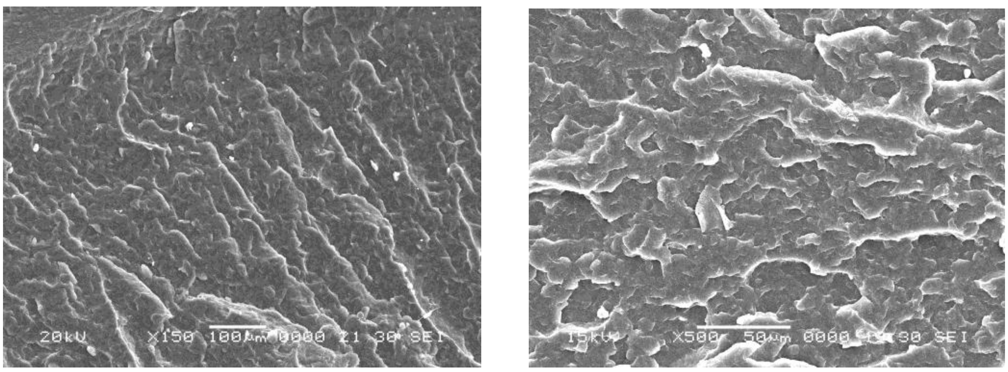
Table 4 consolidated balance sheet

Index	Important order Main→Secondary	Optimization levels
Tensile strength	acbd	$a_3b_1c_2d_2$
Flexural modulus	dacb	$a_2b_1c_1d_2$

Table 4 shows that the important order of various factors which influenced tensile strength was as follows: mixing temperature > montmorillonite content > compatibility content > screw speed. The important order of various factors which influenced flexural modulus was as follows: compatible content > mixing temperature > montmorillonite content > screw speed.

It can be seen from Table 4 that a_3, a_2 appeared only one time in optimization levels. Take high temperature of melt intercalation and good melt flowability into account, the dispersion of montmorillonite in the polymer became easily, and dispersion process did not need violent shearing. Meanwhile, nanocomposite contained more peeled structure. But too high mixing temperature would cause the degradation of polypropylene molecular, quaternary ammonium salt and compatilizer, leading to decrease of property of nanocomposite.So a_3 was chosed as temprature level;$b_1$appeared twice,so b_1 was chosed; c_1 and c_2 appeared one time respectively,because high montmorillonite content caused agglomeration again, montmorillonite content was controlled in lower level,so c_1 was chosed;d_1 was chose for d_1 appearing twice. In conclusion, after balancing synthetically index, the portfolio optimization was a_3, b_1, c_1 d_2. That was: mixing temperature was 200℃, screw speed was 50rpm, montmorillonite content was 2%, and compatible content was 15%.

Microtopography of nanocomposite. Fig 1(a) and (b) were SEM images of the fracture surfaces of pure PP and PP/MMT nanocomposite respectively.



(a) (b)

Fig 1 SEM photos of the fracture surfaces

(a) PP/MMT nanocomposite (b) pure PP

It can be seen from Fig 1(a) that.the fracture surface was smooth, edges and corners were spiculate, the direction of stress stripe was simplex, and there was no stress dispersion. Those were the feature of typical brittle fracture. Fig 1(b) was SEM images of the fracture surfaces of PP/MMT nanocomposite. The fracture surface has distinct fluctuation, and the direction of stress stripe was unordered. Those were the feature of typical ductile fracture. Structure of organic soil was subtle. Montmorillonite was glued into PP matrix, and there was no obvious interface between PP matrix and montmorillonite. These indicated that polypropylene/organic montmorillonite had formed PP/MMT nanocomposite.

Conclusion

1.The polypropylene/montmorillonite nanocomposite were prepared adopting two-step technology，the mechanical properties of the composite increased obviously.The reason was that the technology increase the length diameter ratio of screw, and increase the residence time of the composite , montmorillonite layers dispersed more uniform in PP matrix. 2.Processing temperature was the best important influence factor in all factors studied,the reason was that melting intercalation was enthalpy driven process,optimal high temprature increased the dispersibility of PP in the layers of montmorillonite to form nanocomposite.Screw speed was the last influence factor, content of montmorillonite and ingredient was between the both factors. 3.An optimum formulation to form nanocomposite was identified as follows: content of montmorillonite was 2%, weight fraction of ingredient was 15%.The optimal processing condition parameters were determined as the processing temperature at 200℃ and the screw speed at 50 r·min^{-1}. 4.In the polypropylene/montmorillonite nanocomposite prepared at optimal processing condition, montmorillonite conjoined strongly to PP matrix,and its layers were exfoliated into nanometer size .

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