

Mechanochemical Surface Modification of Particles by Polymer Grafting

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Abstract

Mechanical energy released during stirred grinding promotes the polymerization reactions of styrene monomers on calcium carbonate and those of polystyrene on titanium dioxide surfaces and makes the surface modification by polymer grafting more efficient and with less initiating agent. Polymer grafting modification activated by mechanochemical effects improves the compatibility of calcium carbonate filler with the polymer matrix and the fluidity of alkyd varnish with modified titanium dioxide as the paint material. The process of polymer grafting modification activated by mechanochemical action and the changes of application properties of materials filled with modified powders are described, the interactions between the modifying agents and the surface of the powders is discussed.

INTRODUCTION

Surface modification is a key process in functional powder preparation. The chemical surface modification is the commonly used technology. Recently, however, surface modification with a combined action of modifying agent and mechanochemical effect is intensively studied [1–3], in this field, combined surface modification by polymer grafting has attracted particular attention of researchers [4–6]. The surface polymer grafting modification activated by mechanochemical effect uses monomer as well as polymer as the modifying agent, and usually is carried out in the vibrating mill at room temperature. The problem of the process is that it needs very long processing time. In our study, a stirred mill was used to carry out the grafting modification process to speed up the process. In this paper, some research results of mechanochemical surface modification of calcium carbonate and titanium dioxide by polymer grafting in stirred mill are introduced.

Titanium dioxide and calcium carbonate were taken as powder samples, while polystyrene

(PS), polypropylene (PP), low molecular weight polyethylene (PE) and monomer – styrene – were used as the modifying agents. Titanium dioxide has anatase morphology, its purity is 97 %, its density is 3.84 g/cm³ and the particle size is $d_{50} = 0.4 \mu\text{m}$. The purity of calcium carbonate is 98.38 %, the density is 2.71 g/cm³ and the particle size is $d_{50} = 7.01 \mu\text{m}$.

The apparatus in process study is a specially designed stirred mill made of stainless steel. The temperature inside the mill during treatment is kept unchanged within $\pm 1 \text{ }^\circ\text{C}$ by circulated water. Grinding medium is ZrO₂ balls with diameters 0.8–1.25, 1.6–2.0 and 2.0–2.5 mm. The mass ratio of the three fractions is 4 : 3 : 3.

BASIC PROCESS

The basic modification process using polymer as modifying agent is illustrated in Fig. 1.

The polymer modifying agent and powder first are fully mixed and crushed in a planet mill, the mixture material from planet mill with the added initiator are ground in a stirred mill

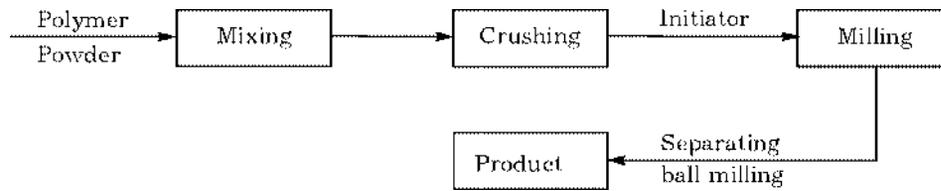


Fig. 1. The technology flowsheet of polymer as modifying agent.

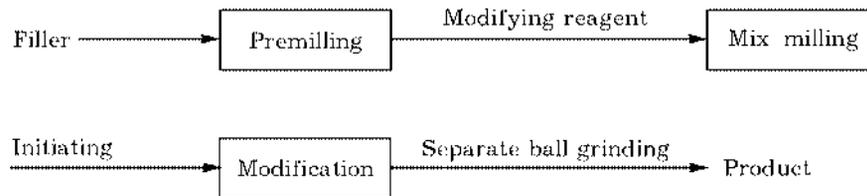


Fig. 2. Modification process using monomer as modifying agent.

within a definite period. After that, the milling balls are separated to get the prepared product.

The basic modification process using monomer as modifying agent consisting of three steps: premilling, mix milling and modification milling, is shown in Fig. 2. The modifying agent – monomer is added into the mix milling step, while a small amount of initiating agent is added at the modification milling step.

The functions of the steps and the relationship between them in the modification process can be explained as follows. Premixing in the stirred mill creates smooth and fully activated surface of particles for the further reactions with the modifying agent at the mix milling step. In the modification milling step, the surface polymerization is carried out because the decomposition of initiating agent and the production of surface radicals, originated from the mechanochemical effect and heat effect, cause surface grafting of the adsorbed monomer.

THE APPLICATION RESULTS OF MODIFIED PRODUCTS

The application results with the modified calcium carbonate as filler

The application test was carried out according to the following flowsheet. The mechanical and fluid properties of PH-888H polystyrene (with 15% rubber) (HIPS) with modified calcium carbonate and with non-modified calcium carbonate were measured for comparison. The results of the measurements are listed in Table 1.

It is evident from Table 1 that significant improvement in the melting fluid velocity is observed for HIPS with modified calcium carbonate filler. The tensile strength and bend strength of HIPS with modified filler are also increased to some extent. The impact strength has also been improved at low filling ratio. It indicates that the calcium carbonate particles after polymer grafting modification have bet-

TABLE 1

Comparison of the properties of PH-888H polystyrene HIPS with different dose of modified fillers

Sample	Impact strength, kg/m	Tensile strength $\times 10^6$, kg/m ²	Bend strength $\times 10^6$, kg/m ²	Melting fluid velocity $\times 10^3$, kg/10 min
HIPS	1153	2.07	3.04	13.86
HIPS + 15% CaCO ₃	1198	1.56	2.75	10.5
HIPS + 25% CaCO ₃	1067	1.62	2.79	12.06
HIPS + 15% modified CaCO ₃	1251	1.77	–	–
HIPS + 25% modified CaCO ₃	938	1.83	2.86	14.54

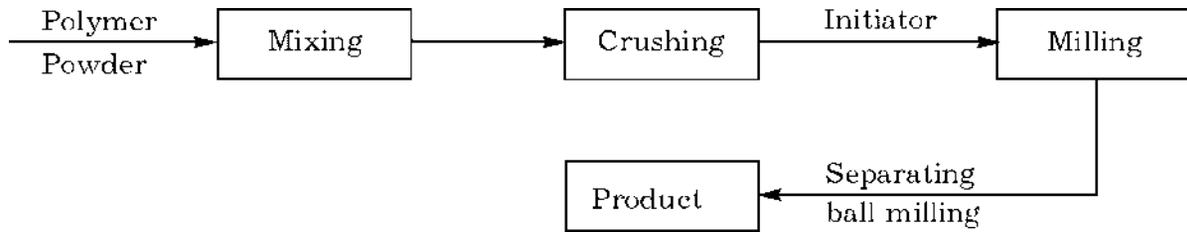


Fig. 3. The flowsheet of the application test.

ter compatibility with the matrix and can improve the processing performance of the polymer material.

The application results with modified titanium dioxide

Different titanium dioxide samples such as that modified by styrene, by polystyrene and non-

modified were mixed fully with alkyd varnish to prepare the suspension samples 1, 2 and 3, respectively, for the rheological measurements. Figure 4 is the relationship between the apparent viscosity of suspensions and the shear rates; Figure 5 is the flow curves of suspensions. Low apparent viscosity means high compatibility. It shows that titanium dioxide after polymer grafting modification is more compatible with alkyd varnish and can lower its apparent viscosity.

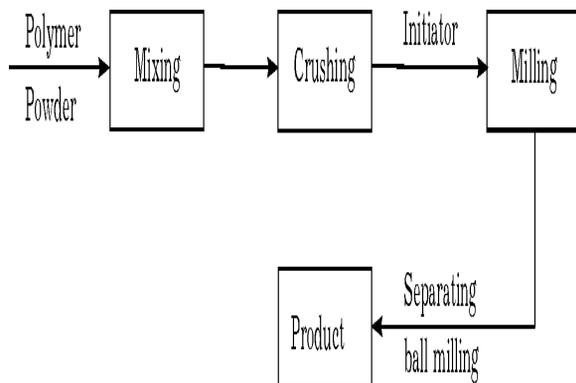


Fig. 4. Relationship between the apparent viscosity of suspensions and shear rates: 1-3 - samples 1-3, respectively.

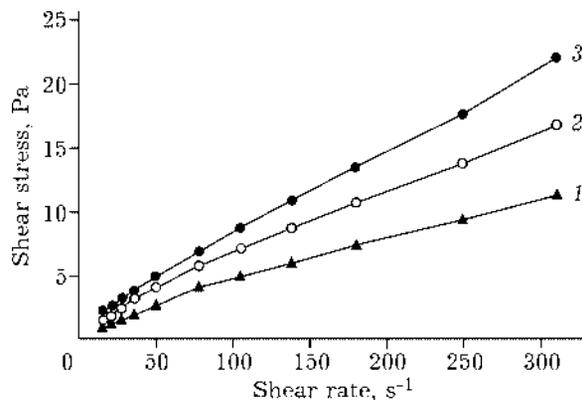


Fig. 5. Flow curves of suspensions: 1-3 - samples 1-3, respectively.

MODIFICATION MECHANISMS [7, 8]

Mechanism of calcium carbonate modification by using monomeric styrene

Typical IR spectrum of calcium carbonate is shown in Fig. 6, a, a series of characteristic bands of calcium carbonate were found at 1420, 870 and 711 cm^{-1} . After modification, besides the characteristic bands of calcium carbonate, the characteristic bands of PS and C-O-C are found as shown in Fig. 6, b.

Many mechanoactivated CO_3^{2-} and calcium surface sites in hydroxyl form are produced on calcium carbonate surface during ultrafine grinding. These mechanoactivated hydroxyl calcium ions are the active sites capable of interacting with styrene monomers. On the other hand, the covalent bonds between carbon and oxygen in carbonate anion include C-O σ bond and Π_4^6 bond that accept electrons. After accepting radical electrons or big Π bond of styrene, anionic radicals are produced to initiate styrene polymerization on the surface. Thus, the mechanoactivated carbonate anions act as initiating agent to produce anionic radicals and initiate styrene polymerization on the surface.

The results of XPS spectrometry show that before modification the atom content ratio

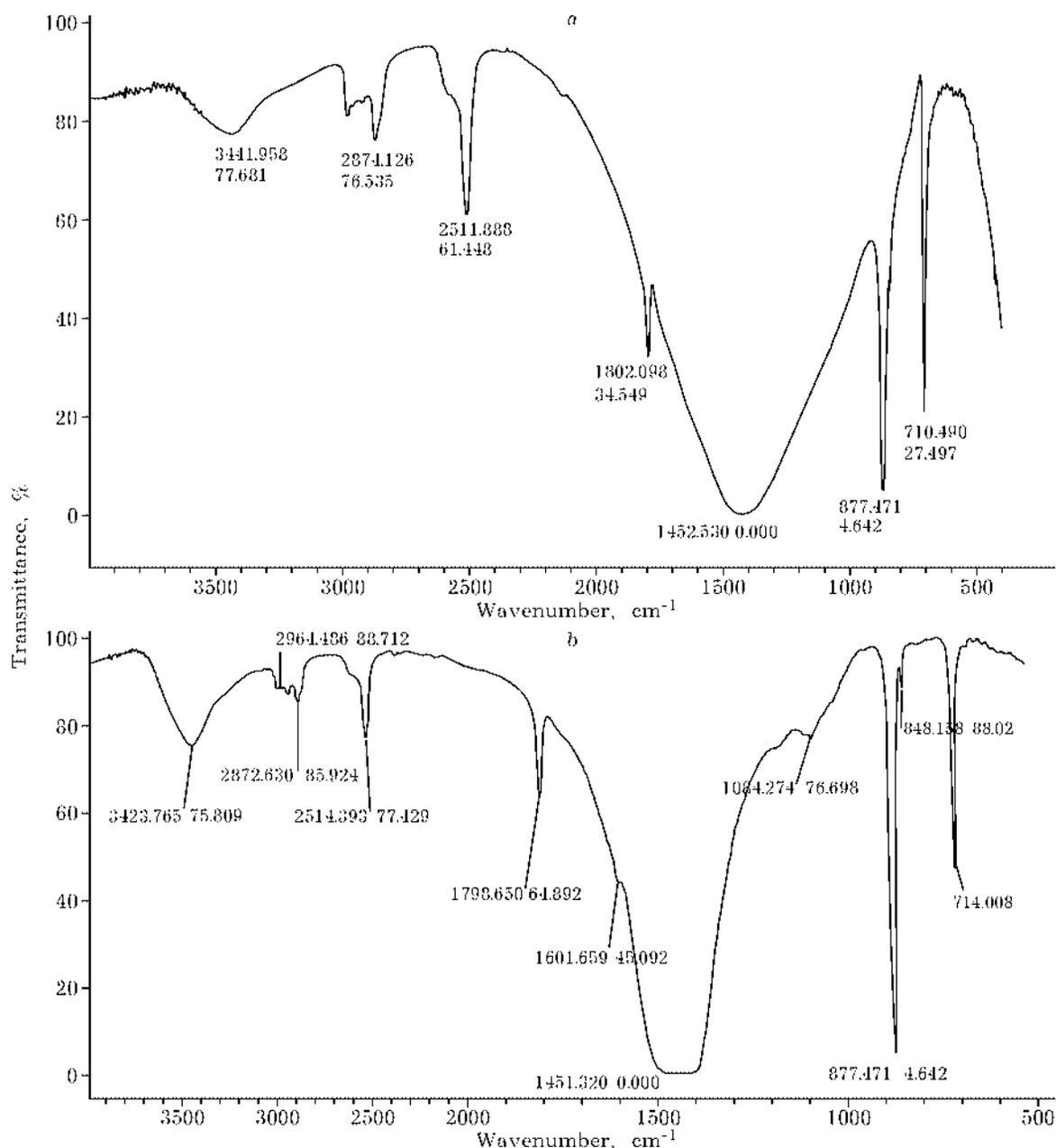


Fig. 6. IR spectrum of calcium carbonate before (a) and after (b) modification.

(C : O : Ca) is 1 : 2.8 : 1.07, that is close to the stoichiometric content of calcium carbonate, whereas after modification, the ratio of carbon, oxygen and calcium atom numbers of surface constituent changes to 1 : 2.2 : 0.93. The amount of organic carbon on the surface increases markedly, and the chemical shifts of all C, O and Ca atoms are positive, towards higher position.

All these results indicate that chemical interaction occurs between the modifying agent

and the calcium carbonate surface, and the modified layers are formed on the surface.

The mechanism of TiO₂ grafting modification by using polystyrene

Figure 7, a is the infrared spectra of the original TiO₂ sample and Fig. 7, b of the modified sample. It is observed in Fig. 7, b that the absorption peaks of benzene ring at 1599 cm⁻¹,

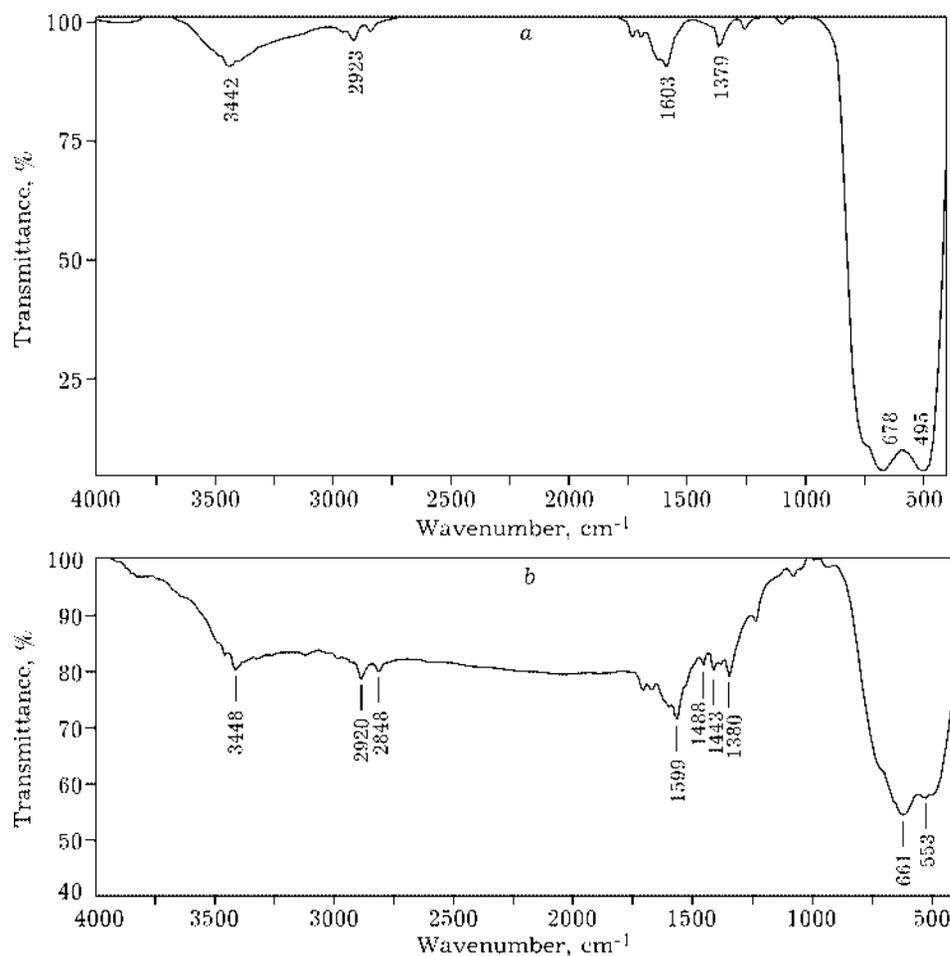


Fig. 7. Original (a) and modified (b) TiO_2 samples.

1488 cm^{-1} , 1380 cm^{-1} , 2920 cm^{-1} , 2848 cm^{-1} , the absorption peaks of carbonyl group in 1750 cm^{-1} and the absorption peaks of C–O bond in 1100 cm^{-1} appear, but the absorption peak of hydroxyl group is less changed after modification. These results indicate that the C–O bond is produced, at the same time, the hydroxyl group on the surface of titanium dioxide is not reacted in the process of modification and PS exists on the surface of titanium dioxide.

The XPS results of the original sample and the modified sample of titanium dioxide show that the relative number of oxygen atoms increases after modification. A substantial increment in oxygen chemical shift after modification shows that the chemical environments of oxygen atom have been changed and that the styrene fragments react with oxygen atom on the surface of titanium dioxide.

During grinding the fracture is predominant between O–O bonds to form electron-deficient oxygen atoms. The macromolecular radicals with strong oxidizing property created by initiating agent and mechano-chemistry can react with the electron-deficient oxygen atom to form C–O bond, or adsorb chemically on the surface of titanium dioxide by receiving electron from surface.

CONCLUSION

Mechanochemical surface modification by polymer grafting induces a compatible layer on particles by means of chemical adsorption.

The mechanical and fluid properties of plastics filled with modified calcium carbonate and the rheologic properties of paints with modified titanium dioxide were markedly improved.

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