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RESEARCH ARTICLE

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# Surface modification of $CaCO_3$ filler and its characterization using inverse gas chromatography (IGC)

**Abstract** A $CaCO_3$ filler was treated by generally used coupling agents and a special one — ethylene-octene copolymer (POE)-*g*-maleic anhydride (MAH). Fourier transform infrared spectroscopy (FTIR) results show that the special coupling agent POE-*g*-MAH, in a chemical reaction with $CaCO_3$, can produce an interfacial layer stronger than simple physical adhesion attained with usual coupling agents. Inverse gas chromatography (IGC) was used to investigate the surface free energy of $CaCO_3$ after surface modification and to optimize the monolayer content of coupling agents. Based on the IGC results, it can be deduced that the monolayer cover is around 1.9% for $CaCO_3$ treated with a titanate coupling agent. Scanning electron microscope (SEM) observation results show that the separated morphology existed in the ternary composites containing $CaCO_3$ after surface treatment with coupling agents, whereas the core-shell morphology was obtained in the ternary composites with POE-*g*-MAH. The encapsulation of the $CaCO_3$ filler treated with POE-*g*-MAH was caused by the strong chemical reaction between the elastomer and $CaCO_3$ particles.

**Keywords** surface modification, coupling agent, POE-*g*-MAH, inverse gas chromatography (IGC), morphology

## 1 Introduction

The main purpose of incorporating inorganic rigid particles such as calcium carbonate into thermoplastics is to decrease costs and change tensile and impact properties. Recently, it has been found that the simultaneous enhancement of toughness and stiffness can be achieved in the polymer/rigid particles system [1,2]. For those reasons, particulate-filled polymers have been a subject of increasing interest in both industry and research. However, the mechanical characteristics of these materials are significantly influenced by poor filler-polymer matrix interaction. Surface treatment of fillers is one of the techniques often used to modify interactions in particulate-filled polymers. Among all the rigid fillers used in polymer matrix, calcium carbonate is one of the most preferred. However, there are two obvious disadvantages for calcium carbonate. Firstly, the higher surface energy and unstable thermodynamic state of calcium carbonate induce the poor dispersion of fillers. Secondly, the poor compatibility between calcium carbonate and polymer as the result of hydrophilic characteristics of $CaCO_3$ will influence the mechanical properties of final composites.

In this paper, a $CaCO_3$ filler was treated by generally used coupling agents and a special one — POE-*g*-MAH. Inverse gas chromatography (IGC) [3,4] as a new characteristic method was chosen to investigate the surface free energy of $CaCO_3$ after surface modification and to optimize the monolayer content of coupling agents. The effect of surface modification of the rigid calcium carbonate on the morphology of polypropylene (PP)/ethylene-octene copolymer (POE)/$CaCO_3$ composites was analyzed.

## 2 Experimental

### 2.1 Materials

Polymer matrix materials used in this study were polypropylene (PP) T30S supplied by Xi'an Yanlian Industrial Group Company. The rigid particle used was calcium carbonate from Xi'an Zhongxin Fine Chemical Factory, while the elastomer used, ethylene-octene copolymer (POE) EG8150, was supplied by Dupont Dow Elastomer Company. Maleic anhydride (MAH) and benzoyl peroxide (BPO) supplied by Xi'an Chemical Reagent Factory were used as the grafting monomer and

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initiator respectively. The coupling agents used were titanate (NDZ-101) from Nanjing Shuguang Chemical Group Company. Aluminate coupling agent (DL-2411-A) came from Fujian Yuanke Material Company, while rare-earth coupling agent (WOT) was from Guangdong Weilinna Functional Material Company.

### 2.2 Surface modification of calcium carbonate with coupling agents

$CaCO_3$ particles were first dried in an oven at 120°C for 3 h and then mixed with various amounts of the coupling agent immediately in a high-speed mixer for 10 min. The weight ratio of the coupling agent to $CaCO_3$ particles was in the range from 0.5% to 2.5%.

### 2.3 Preparation of POE-*g*-MAH

POE-*g*-MAH was prepared in our laboratory. POE of 8 g and MAH of 0.7 g were first dissolved in 200 mL xylene. Then BPO of 0.1 g dissolved in 40 mL xylene was added into the POE and MAH mixture within 3 h at 130°C. After that $CaCO_3$ of 8 g was filled into the mixture solution, reacting for 1h at 70°C. The POE-*g*-MAH/$CaCO_3$ was last prepared by using 150 mL acetone as the precipitation solution.

### 2.4 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of samples were obtained using a WQF-310 FITR spectrometer. Potassium bromide plates of $CaCO_3$ both untreated and treated with coupling agents were prepared and analyzed .The characterization of POE-*g*-MAH was also analyzed by FTIR.

### 2.5 Inverse gas chromatography (IGC)

IGC measurements were carried out using a GC900 chromatograph. Stainless-steel columns 50 cm long and 3 mm in diameter were filled with pre-treatment $CaCO_3$ sifted between 80 mesh and 100 mesh and attached to a gas chromatograph equipped with a highly sensitive flame ionization detector. The columns filled with particles were then preconditioned at 150°C for about 24h under nitrogen carrier gas flows. The optimum carrier gas flow (nitrogen) is 20 mL/min. The temperature of the injector is controlled at 150°C and the detector at 200°C. Measurements were performed between 50°C and 120°C. Alkanes including n-hexane, heptane, octane, nonane and decane were used to determine the dispersive component of the samples.

### 2.6 Preparation of ternary composites

PP/POE/$CaCO_3$ ternary composites at a fixed weight ratio (60:20:20) were prepared using a Haake RHEOCORD 90 internal mixer set at a barrel temperature of 180°C and rotor speed of 50 $\text{min}^{-1}$. Melting blending time was 10 min.

### 2.7 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) AMRAY-1000B was used to observe the morphology of the PP/POE/$CaCO_3$ ternary composites. Samples were cooled in liquid nitrogen and then fractured. The SEM micrographs were taken from the fractured surfaces of the samples, etched with heptane to remove POE at 80°C and then coated with gold.

## 3 Results and discussion

### 3.1 IGC results

#### 3.1.1 Surface energy characteristics of coated and uncoated $CaCO_3$

In this work, IGC was used to determine the surface energy of coated and uncoated calcium carbonate. At the infinite dilution, a method for estimating the London-dispersive component of surface free energy $\gamma_S{}^D$ and the free energy per methylene group was used. $\Delta G^{CH_2}$value can be obtained from the difference in $\Delta G_a^0$ for adjacent members of a homologous series of linear alkanes from the relationship from the IGC was proposed by Henry's law [5]:

$$\Delta G^{CH_2} = -RT\ln\frac{V_n^{C_{n+1}}}{V_n^{C_n}} \tag{1}$$

The equation that Dorris and Gray derived may be rearranged to solve for $\gamma_S{}^D$, so that:

$$\gamma_S^D = \frac{\left(\Delta G^{CH_2}/N\alpha_{CH_2}\right)^2}{4\gamma_{CH_2}} \tag{2}$$

Where $\frac{V_n^{C_{n+1}}}{V_n^{C_n}}$ and $V_n^{C_n}$ are the retention volume of alkanes with $n$ and $n$+1 numbers of carbon atoms. N is Avogadro's number. $\alpha$ is the cross sectional area of the methylene group $(0.06\ \text{nm})^2$ and $\gamma_{CH_2}$ is the surface energy of a solid consisting of only $-CH_2$-groups, i.e., polyethylene (35 mJ/$\text{m}^2$ at 20°C).

Figure 1 displays variations of the net retention volume of the n-alkanes against the number of carbon atoms, measured on the calcium carbonate treated by using three kinds of coupling agents and POE-*g*-MAH. All experimental points fall on straight lines. The slope of the lines allows calculation of the dispersive component of the surface free energy of the samples. Fig. 1 shows that the slope of lines decreases as the temperature increases.

The dispersive component of surface free energy against the column temperature in the case of different kinds of $CaCO_3$ is shown in Fig. 2. The component decreases with

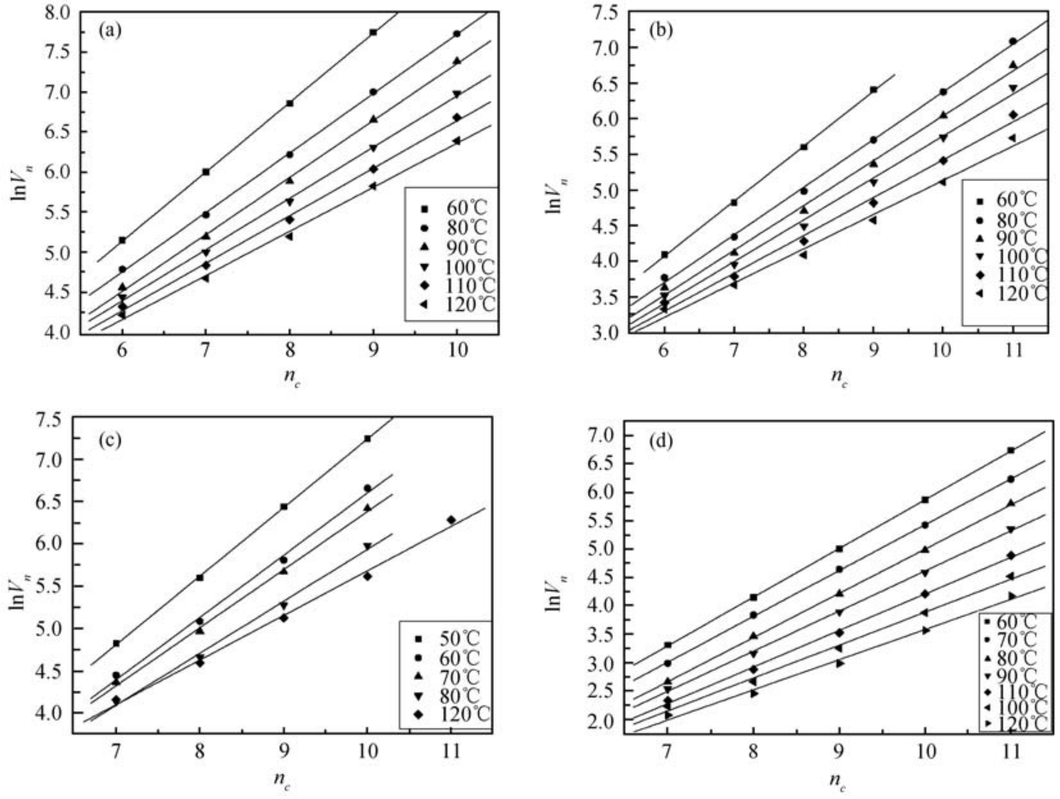


**Fig. 1** $\ln v_V$ plotted against number of carbon atoms in *n*-alkane at different column temperature for calcium carbonate samples (a) DL-2411-A aluminate coupling agent; (b) NDZ101 titanate coupling agent; (c) WOT rare-earth coupling agent; (d) POE-*g*-MAH surface treatment

an increase of the column temperature for all the samples, and the pure $CaCO_3$ has a sharper decline than calcium carbonate coated with 2.5% coupling agents. As to the pure $CaCO_3$, the dispersive component descends more sharply in the low temperature region than in the high temperature region. This indicates that in the low temperature region, the surface of the calcium carbonate adsorbs water from the air and then the hydroxyl group gathers on the surface. As the temperature rises, the hydration water is eliminated from the surface, causing the active groups of calcium carbonate to emerge between the gas/solid interfaces. This may be the reason why the dispersive component becomes stable in the higher temperature region. After the $CaCO_3$ is surface treated with coupling agents, the dispersive component of the samples becomes stable as the temperature changes. This variation is somewhat complex possibly because of the complex chemical changes on the surface of particles while coupling agents are added. The change depends on the difference of the functional groups on the surface and the alignment of those groups.

The surface characteristics of $CaCO_3$ have changed before and after surface modification. The dispersive component of surface free energy of treated $CaCO_3$ become more stable than pure $CaCO_3$. It can be deducted from Fig. 2 that $CaCO_3$ with rare-earth coupling agents has the lowest dispersive component, which is 20.455 mJ/m² at 90°C.

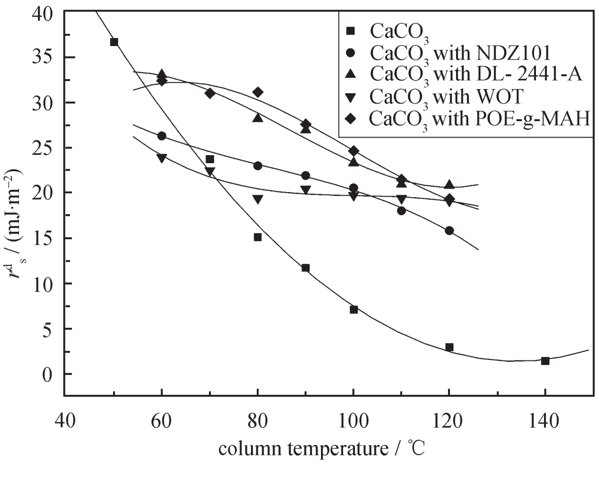


**Fig. 2** The dispersive component of surface energy of samples vs the column temperature

### 3.1.2 Monolayer cover

The content of coupling agents is one of the important factors showing a major influence on changes of surface free energy. Generally, the optimal content of a coupling agent is considered as the monolayer content. In this work, IGC was used to estimate the monolayer content via the relation between different contents of titanate coupling agents and their respective surface free energy as shown in Fig. 3. The content of titanate coupling agents are 1%, 1.5%, 2%, 2.5%.

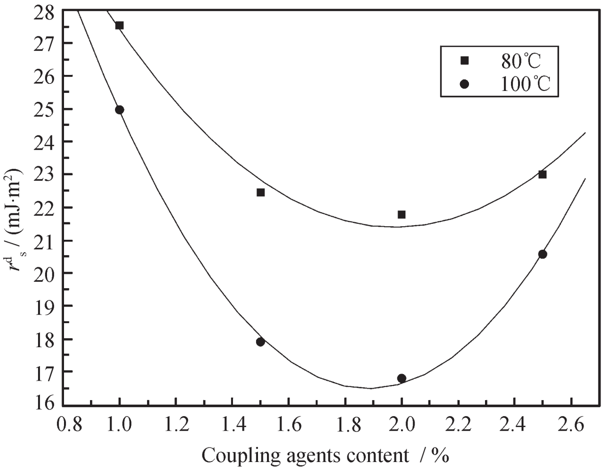


**Fig. 3** The London component of surface energy of samples vs the coupling agents content

The dispersive component of the treated $CaCO_3$ first decreases and then increases with an increase in the content of coupling agents, as shown in Fig. 3. It seems that the monolayer is related to the change in coupling agent content. It can be deduced that there is a change of the surface properties when the content of coupling agents is around 1.9%.

Initially, active sites of the surface of calcium carbonate are gradually occupied by the organic molecules, and the dispersive component of the surface energy decreased. But interestingly, the dispersive component ascends slowly with an increase in the content. This can be explained by the change in the way organic molecules align on the particulate surface when its content exceeds the monolayer coverage. Many organic groups dangle outside the surface instead of bonding to the active site on the surface of particles. The interaction of those groups with the probing alkane may contribute to an increase of the surface dispersive energy.

The long organic chain of coupling agents on the surface of $CaCO_3$ will prevent the aggregation of $CaCO_3$, which will be helpful for the dispersion of fillers in the polymer matrix. Based on the IGC results, the monolayer content is around 1.9% for titanate coupling agents.

### 3.2 Reaction on the surface of $CaCO_3$

The FTIR spectra of calcium carbonate modified with titanate coupling agent NDZ101 (1#), aluminate coupling agent DL-2411-A (2#) and rare-earth coupling agent WOT (3#) are presented in Fig. 4(a). Compared with spectra of the pure calcium carbonate, characteristic absorption peaks of methylene and methyl are at 2852 $cm^{-1}$, 2920 $cm^{-1}$ and 2960 $cm^{-1}$ in the spectra of (1#), (2#) and (3#), respectively. To check if the surface absorption is a chemical reaction or physical absorption, the calcium carbonate fillers modified with different coupling agents were extracted by xylene. FTIR results in Fig. 4(b) show that all characteristic absorption peaks of methylene and methyl disappeared. These results indicated that the treatment by traditional coupling agents was just surface physical absorption and not chemical reaction, indicating influence on the adhesion between polymer and fillers.

Surface modification was also prepared by using POE-*g*-MAH. The characterization of POE-*g*-MAH was analyzed by FTIR as shown in Fig. 5. The spectra of POE-*g*-MAH and POE-*g*-MAH/$CaCO_3$ show the appearance of the 1784 $cm^{-1}$ and 1865 $cm^{-1}$ stretch vibration peaks corresponding to the symmetrical and asymmetrical acid anhydride bonds. Meanwhile, in the spectra of POE-*g*-MAH, the characteristic adsorption peaks of maleic acid after the hydrolyzation of the maleic anhydride at 1709 $cm^{-1}$ are observed. The FTIR results confirm the reaction between POE and MAH. Besides, the spectra of $CaCO_3$/POE-*g*-MAH show the characteristic adsorption

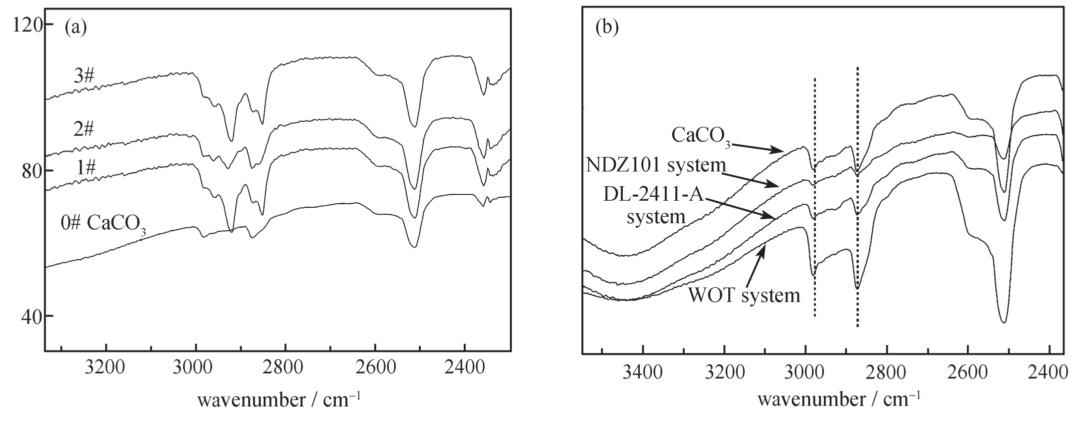


**Fig. 4** FTIR spectra of $CaCO_3$
(a) with coupling agents; (b) with coupling agent extracted with xylene

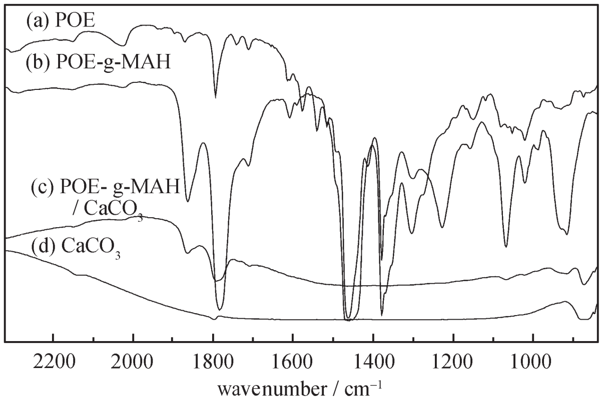
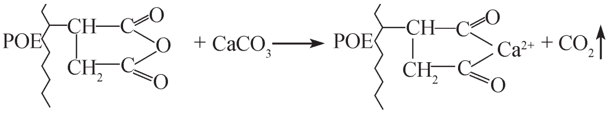


**Fig. 5** FTIR spectra of POE-*g*-MAH

peaks of $CaCO_3$. Together with the bubble phenomenon when $CaCO_3$ is added, it can be deducted that strong bonding between the POE elastomer and rigid particles $CaCO_3$ was the result of chemical reaction. The probable reaction is as follows:



Based on the results above, it can be concluded that the surface of $CaCO_3$ is encapsulated by the POE-*g*-MAH elastomer. Compared with physical absorption in the surface with coupling agents, POE-*g*-MAH/$CaCO_3$ composites will be the compatible agent and toughness agent for the preparation of ternary composites — a condition that will heavily influence the morphology and properties of ternary composites.

### 3.3 Morphology of the PP/POE/$CaCO_3$ ternary composites

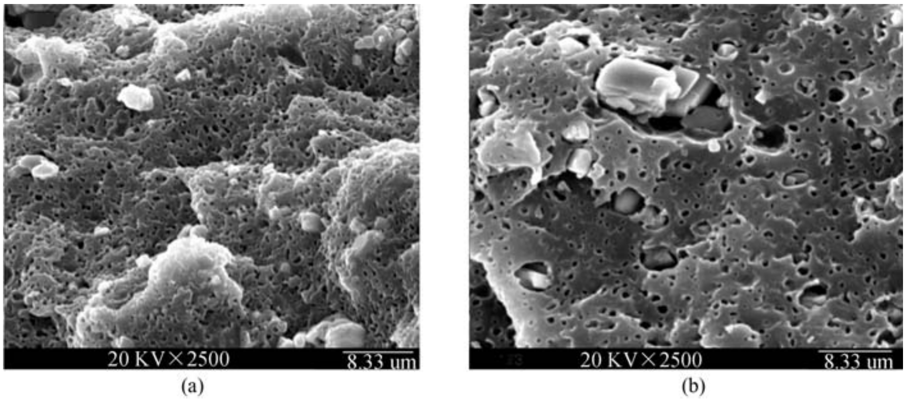
SEM micrographs of the etched fractured surfaces of PP/POE/$CaCO_3$ ternary composites are shown in Fig. 6. The dark holes represent POE elastomer droplets, which are dissolved out by a selective etching solution, whereas the brighter particles are $CaCO_3$ fillers. SEM micrographs reveal the separated dispersion of the POE and $CaCO_3$ particles in the PP matrix as shown in Fig. 6(a). However, for ternary composites containing the POE-*g*-MAH, the elastomer could encapsulate $CaCO_3$ particles due to the strong interaction between POE-g-MAH and $CaCO_3$, forming the core-shell inclusion structure. This is consistent with the FTIR results and reveals that the reaction between POE-*g*-MAH and $CaCO_3$ is much stronger than bonding between coupling agents and particles. In references [6,7], the encapsulated structure in the PP composites has a close relationship with mechanical properties. Finite element analysis [8] shows that the stress of rigid fillers will still be changed by the encapsulated elastomer when the thickness of the elastomer is 1/10 the diameter of fillers. Therefore, the simultaneous enhancement of toughness and stiffness will be achieved in the composites with such core-shell morphology.

## 4 Conclusion

IGC results showed that $CaCO_3$ fillers have a more stable surface free energy after surface treatment with coupling agents and POE-*g*-MAH. The rare-earth coupling agents have the most effective modification. IGC results also indicated that the monolayer cover was around 1.9% for $CaCO_3$ treated with a titanate coupling agent.

Compared to the simple adhesion layer caused by the coupling agents, the FTIR results indicated that the strong reaction between the POE-*g*-MAH and $CaCO_3$ occurred.

SEM observation results demonstrated that the separated morphology existed in the ternary composites containing $CaCO_3$ after surface treatment with coupling agents, while the core-shell morphology was obtained in the ternary composites with the POE-*g*-MAH. The encapsulation of the $CaCO_3$ fillers treated with POE-*g*-MAH was



(a) (b)

**Fig. 6** SEM spectra of PP ternary composites etched with heptane
(a) PP/POE/$CaCO_3$ (NDZ101 modification); (b) PP/POE-*g*-MAH/$CaCO_3$

caused by the strong chemical reaction between the elastomer and the $CaCO_3$ particles.

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