



# Surface modification of phosphogypsum and application in polyolefin composites

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## Abstract

Phosphogypsum (PG) is one of solid wastes with large amount of yield and serious pollution, which has attracted wide attention. The aim of this study is to investigate filling performance of PG on polypropylene (PP) or high-density polyethylene (HDPE) matrix. In this work, PG was calcined initially to improve whiteness and fix impurities. X-ray diffraction (XRD) results showed that after calcined at 500 °C, the PG phase changed from  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{CaSO}_4$ . The modification effects of the three modifiers were evaluated by Fourier transform infrared spectra (FTIR), oil absorption value, water floatability, and contact angle analysis. The effects of weight fraction of PG in PP and HDPE matrix on mechanics and morphology were observed by tensile test, impact test, and scanning electron microscope. Scanning electron microscope (SEM) showed that modified PG can be dispersed uniformly in the matrix at low filling content. With the increase of PG filling content, the analysis of mechanical properties showed that the tensile strength of HDPE matrix increased, while the tensile strength of PP matrix decreased gradually. The impact strength of HDPE matrix would decrease, but the impact strength of PP matrix increased first and then decreased. Compared with calcium carbonate (CC), the mechanical properties of HDPE filled with PG performed better. The apparent density showed that polymer composites filled with PG have the characteristics of light weight.

**Keywords** Phosphogypsum · Polypropylene · High-density polyethylene · Composites · Mechanical properties · Modification

## Introduction

Phosphogypsum (PG) is a moist gray-white or gray-black, powdery solid, which is an industrial by-product discharged during the production of wet phosphoric acid. Along with the rapid development of phosphorus fertilizer industry, the annual production of PG worldwide was estimated around 280 million tonnes (Ding et al. 2019), and Chinese production of PG more than 75 million tonnes every year (Fu et al. 2020). PG consists mainly of calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), making up over 90%. Depending on different type of wet process, the pH value is 1.5~4.5 and exists a little smell (Li et al. 2019; He et al. 2018). Only about 30% of PG production in the world was reused in different

fields such as building materials (Rashad 2017; Tian et al. 2016), agriculture (Matveeva et al. 2021; Li et al. 2018), filling mining regions (Chen et al. 2017, 2018; Shi et al. 2021), ceramic (Syczewski et al. 2020), and rare earth recycling (Kulczycka et al. 2016; Rychkov et al. 2018; Cánovas et al. 2019). At present, the established PG landfills are main treatment method. Since PG contains phosphate, fluoride and sulfate, organic matter, and other harmful substances, however, it may result in severe contamination of atmosphere and groundwater (Zhang and Zou 2018).

According to phosphate ore composition and producing processes of phosphoric acid, the impurities of PG exist some differences. These impurities not only adhered to the surface of PG crystal, but also incorporated into the lattice of PG. They can be divided into three categories, including intergranular impurities, soluble impurities, and insoluble impurities. Because of complex impurities, PG has resulted in long setting time and low mechanical strength in building materials, and the utilization rate is not at a high level. Luckily, these impurities can be solved by pretreatment (Cai et al. 2021). Pretreatment methods mainly include

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lime neutralization (Liu et al. 2020a), water washing (Bai et al. 2009), pickling (Zhao et al. 2017), flotation (Zhang et al. 2022), ball milling (Dong et al. 2016), and calcination. These methods can be used as single approaches or in combination (Wang et al., 2020). Calcination is a worth considering method. It can not only change the PG phase, but also improve whiteness and fixed impurities. There are some reports about calcined PG in the works of other authors. In research work carried out by Liu et al. (2019), PG was calcined and made into embedded filler. The mechanical performance and thermal insulation performance of the product can meet the standard, and would not cause secondary pollution. Liu et al. (2020b) reported the mechanism of calcination modification of PG and its effect on the hydration properties of PG-based supersulfated cement. It was found that the calcination pretreatment can reduce the adverse reactions of PG and change the gypsum phase. Especially after calcination at 600 °C for 2 h, both early and later strength were significantly increased, which were almost twice of the reference specimen.

PG particles have some characteristics, such as hydroxyl adsorption, multicomponents, large surface area, and high surface energy, which will result in difficulties in application (Zhao et al. 2018; Muraleedharan and Nadir 2021). They are difficult to disperse uniformly in composites, and the ultimate properties of composites will be limited owing to agglomeration behavior. The surface modification of PG particles, however, can effectively improve interfacial adhesion and dispersion stability in polymer matrix (Sun et al. 2020; Denev et al. 2009; He et al. 2011; Lin et al. 2010). There are many surface modifiers in industry, such as long carbon chain fatty acids and their salts, long carbon chain cellulose, coupling agents, and unsaturated organic acids. Among them, long carbon chain fatty acids and their salts have the characteristics of low price and good modification effect. The general molecular formula of them is  $C_nH_{2n+1}COOMe$ , where  $Me$  stands for metal cation (such as  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Zn^{2+}$ ). One end of the molecule is carboxyl, which can be physically adsorbed or chemically reacted with the filler and wrapped on the surface of it. The other end is long carbon chain hydrocarbon, which has certain compatibility with the polymer due to the long carbon chain structure in the molecule. The long carbon chain structure has certain steric hindrance, which can weaken the particle agglomeration of the filler (Pan 2015). Therefore, the use of long carbon chain fatty acids and their salts can not only improve the hydrophobicity of inorganic powder surface, but also enhance the compatibility between PG and polymer matrix, improve its dispersion in composites, and prevent physical defects caused by interfacial repulsion.

Nowadays, polymer materials are widely used in all aspects of life. Filling inorganic powder in polymer materials is not only to reduce the cost, but also to obtain more

excellent properties of polymer materials. If can be used in polymer materials to strengthen and toughen PG as a waste inorganic powder material; it will realize the value-added resource of PG and the plastic reduction and quality improvement of polymer material industry at the same time. In research work carried out by Essabir et al. (2016), the purified PG (filling amount 0~40 wt%) was filled in PP matrix. It can be concluded that PG is potential reinforcing filler for the production of PP composites. Shan et al. (2020) focused their work on the melting blending of calcined PG and PP with different mass fractions. It is considered that added PG below 40 wt% can enhance the toughness of the composite and PG can improve the nucleation efficiency of  $\alpha$  crystal in PP material.

The aim of this study is to investigate the effects of different content of modified calcined PG on the properties of polymer. Therefore, the calcined characteristics and modified effect of PG were studied before filling in this work, as well as the morphology and mechanical properties of the polymer filled with modified PG of different content, through calcination to remove soluble impurities, improve whiteness, and change crystal phase. The good modification effect of calcium stearate was proved by oil absorption value, contact angle, water floatability, and FTIR analysis. Modified calcined PG can be used as reinforcing material for some properties in polymers.

## Experiment

### Materials

PP matrix PP450 was provided by Maoming Shihua, which is extrusion/coextrusion grade and the melt flow index is 45 g/10 min. HDPE matrix DGDA-6098 was provided by Qilu Petrochemical, which is injection molding grade, and the melt flow index is 8 g/10 min. PG came from Guizhou, China, which is a moist gray-black, powdery solid. The whiteness was 21.27%. Titanate coupling agent (PN-41B), sodium stearate, and calcium stearate are commercially available. CC was heavy calcium carbonate, which is a white powdery solid with a whiteness of 97.3%, commercially available. The average particle sizes of CC were 3.5  $\mu$ m (D50), and D10 and D97 were determined to be 0.26  $\mu$ m and 21.79  $\mu$ m, respectively.

### Experimental procedures

The experiment of PG calcined at 500 °C for 2 h was performed via high-temperature furnace, and removed as the furnace cooled. Then, calcined PG was added into high-speed mixer and heated to 40 °C. Subsequently, surface modifier was introduced into the mixer, mixed for 20 min,

removed, and reserved. Finally, the modified powder was dried for 2–4 h in an oven at 120 °C. All experiments in this work were performed under set conditions, in order to reduce the impact on modification.

PP and HDPE composites at various weight fractions with 10, 30, 50, 70, and 80 wt% of PG which was calcined at 500 °C (PP-10PG, PP-30PG, PP-50PG, PP-70PG, PP-80PG or HD-10PG, HD-30PG, HD-50PG, HD-70PG, HD-80PG) were produced by twin-screw extruder. Melt blending of such compositions were carried out on twin-screw extruder with the set temperatures of 180–200 °C from hopper to nozzle and the screw speed of 120 rpm. Then, the compounds were cooled in water bath and pelletized into pieces of 2–3 mm in length. After, the pellets were dried at 80 °C in oven and held there for 4 h. Last, the standard specimens for mechanical property measurements were prepared by injection-molding machine (HTF60W2, Ningbo, China). The melt temperatures from hopper to nozzle were set as 180–200 °C, and the mold temperature was 25 °C. Calcined PG filled polymer matrix; the samples of injection molded have complete surface and high finish. With increasing the filler content, the specimens became more opaque. The digital photographs of samples are exhibited in Fig. 1. The sizes of the samples are 80 mm × 10 mm × 4 mm.

## Characterization methods

The oil absorption values were measured by dioctyl phthalate (DOP), and the reported values were the average value of three separate measurements.

The surface hydrophilicity of PG powder was measured by contact angle analyzer (YY-GS130, Chengde, China), and the contact angle values were the average value of five tests.

The particle size distribution of PG powder was measured by laser particle size distribution instrument (BT-9300H). The whiteness of PG powder was measured by whiteness instrument (GQS-102). The particle size and whiteness value were the average value of three tests of different samples.

Tensile property at room temperature was studied by American Instron-5966 universal testing machine. The tensile test was carried out at crosshead speed of 50 mm/min.

The tensile fracture surface was characterized and the morphology was observed by Hitachi SU-1510 scanning electron microscope (SEM). Before SEM analysis, all the surfaces were sputtered with a thin layer of gold.

The chemical composition of sample was analyzed by X-ray fluorescence (XRF) spectrometry with ZXs Primus series spectrometer.

Crystallographic phase of PG after calcined at 500 °C was identified by XRD (Rigaku, Cu K $\alpha$ , 30 kV, 35 mA,  $\lambda=0.154$  nm). XRD data were obtained from 5 to 60° at scan rate of 2°/min.

Surface modification effect of PG particle was analyzed by Fourier transform infrared spectroscopy (FT-IR) (Thermo Fisher, USA). The scanning interval of test conditions is 4000 to 420 cm $^{-1}$ , and the resolution is 4 cm $^{-1}$ .

The Izod impact tests were carried out by impact tester (CEAST 9050) with an impact velocity of 1 m/s. The notched specimens were subjected to the impact test in the temperature of 25 °C.

## Results and discussions

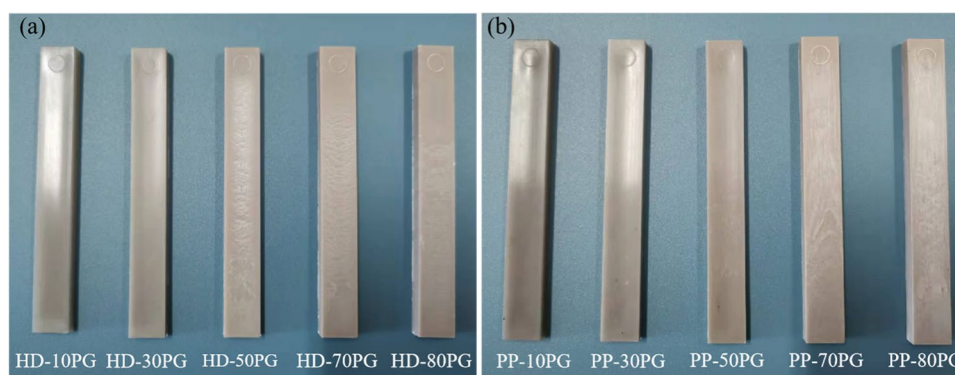
### Particle size analysis

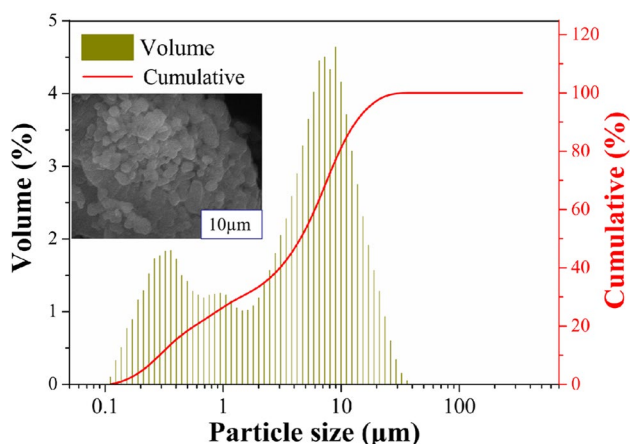
Particle size distribution and SEM graph of PG powder are shown in Fig. 2. The mean size of powder is 4.52  $\mu\text{m}$  (D50) based on volume distribution and 50% of the particles are less than 4.52  $\mu\text{m}$ . Besides, D10 and D97 were obtained to be 0.29  $\mu\text{m}$  and 19.53  $\mu\text{m}$ , respectively.

### Characterization of PG waste and calcine material

The main components of PG are CaO and SO $_3$ , and the rest are impurities such as silica, phosphoric acid, and hydrofluoric acid. The chemical compositions of PG are listed in Table 1 by X-ray fluorescence analysis. In order to explore

**Fig. 1** The digital photographs of injection molding samples



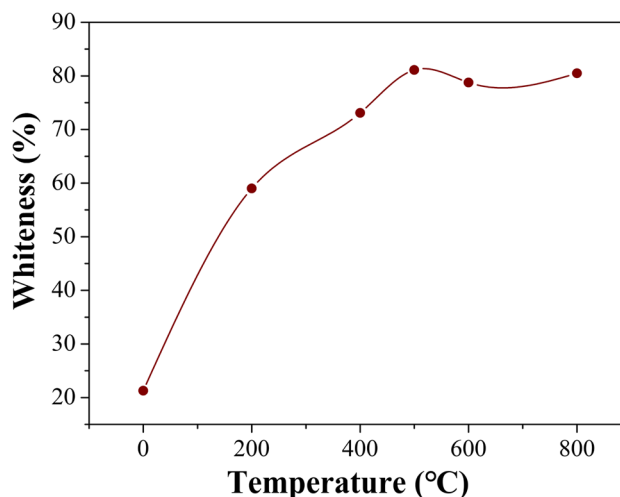


**Fig. 2** Particle size distribution and SEM graph of PG powder

the effect of different calcination temperature (0~800 °C) for 2 h on whiteness, an appropriate amount of raw PG was calcined in insulated furnace at heating rate of 10 °C/min. The whiteness increased over the first 500 °C before leveling off and stabilizing in at about 81.10% (Fig. 3). The photographs of raw PG and calcined PG at 500 °C are exhibited in Fig. 4.

### XRD analysis

The crystallographic structure and composition for PG were carried out by X-ray diffraction. The results showed that PG is essentially dominated by calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and trace amounts of quartz. The PG crystallographic phase however changed after calcination. The initial PG consists of dihydrate and it is almost completely dehydrated into anhydrite after calcination at 500 °C. Figure 5a illustrates that diffraction angles of raw PG are 11.6°, 20.7°, 23.3°, 26.5°, 29.1°, 31.0°, 33.3°, 43.2°, and 47.8°. The  $2\theta$  values of main peaks at 25 °C are 11.6°, 20.7°, 23.3°, and 29.1°, corresponding to lattice plane of (020), ( $-121$ ), (040), and ( $-141$ ), representing the main phase of dihydrate gypsum. In contrast, diffraction angles of PG calcined at 500 °C are 22.9°, 25.3°, 26.5°, 31.3°, 36.1°, 38.6°, 40.6°, 43.2°, 48.6°, 52.1°, and 55.7°. When the diffraction angle is 25.3° corresponding to lattice plane of (020), the spectrum shows a strong peak, which is the characteristic of anhydrous gypsum ( $\text{CaSO}_4$ ) as the main component of calcined PG. These sharp and strong peaks further confirmed that the product crystallized well. In addition, quartz is just an inert impurity, which exists in whole calcination process. Figure 5b studies the



**Fig. 3** Effect of calcination temperature on whiteness

crystal phase of modified and unmodified PG, and found that calcium stearate-modified calcined PG did not change the crystal phase of PG. However, the grain size of PG became larger after modification, indicating that calcium stearate was successfully coated on the grain of PG.

### Surface modification

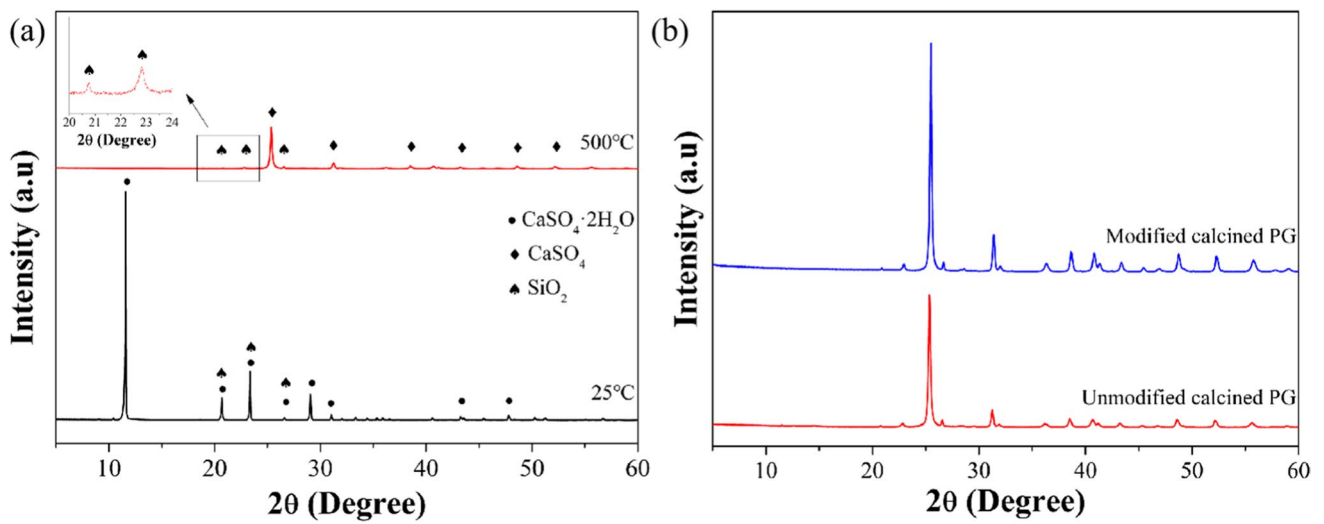
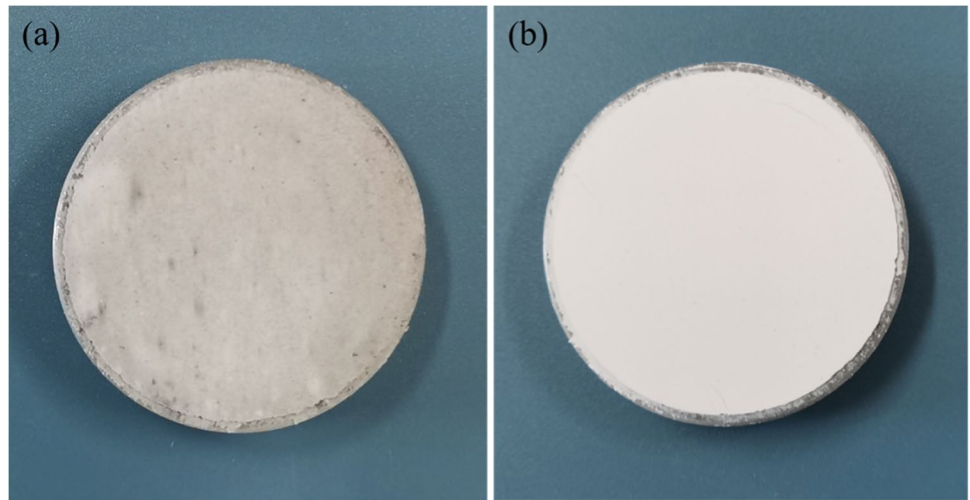
In this work, calcium stearate was used to change the polarity of inorganic powder. The modification processes of it are divided into two steps. Firstly, calcium stearate is hydrolyzed to form stearate radical. Then stearate radical reacts with the surface of inorganic filler. Stearate radical replaces the hydroxyl groups on the surface of inorganic fillers to form salts with lower solubility product than calcium stearate, which are wrapped on the surface of fillers. The specific modification processes of calcium stearate are shown in Fig. 6.

The experiment of modified calcined PG was performed via high-speed mixer, with 1 wt% modifier, the fixed modification time of 20 min, and the temperature of 40 °C. The purpose of experiment is to investigate modification effects of different modifiers on calcined PG. Oil absorption value and static contact angle are effective and direct way to reflect hydrophobic or hydrophilic properties of material. The oil absorption values of untreated and modified PG particles are exhibited in Fig. 7a. Obviously, the oil absorption value of untreated PG particle is 0.54 g, indicating typical hydrophilicity property. The oil absorption value of calcined PG modified by calcium stearate

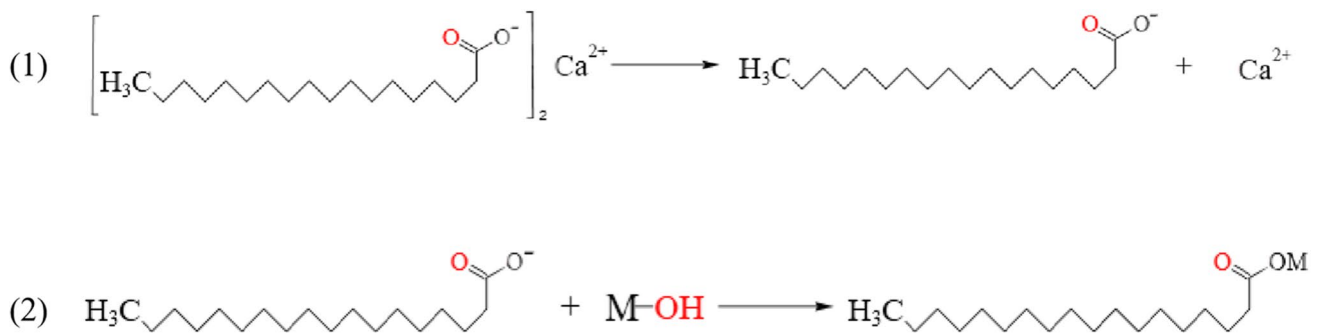
**Table 1** Chemical composition of PG raw material

Compound	CaO	SO <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	F <sup>-</sup>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
wt%	48.7	42.3	3.32	3.10	1.17	0.309	0.263	0.253	0.191	0.162

**Fig. 4** The photographs of PG: **a** raw PG and **(b)** calcined PG at 500 °C



**Fig. 5** **a** XRD of raw PG and calcined PG at 500 °C. **(b)** XRD of modified and unmodified calcined PG



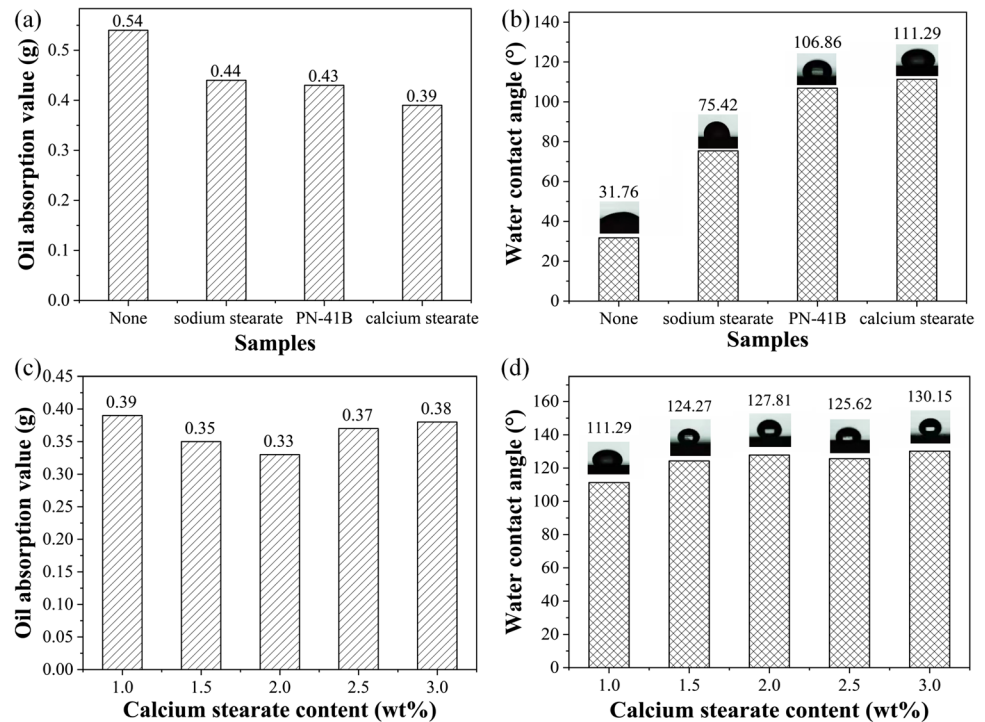
**Fig. 6** Modification mechanism of calcium stearate

decreased from 0.54 to 0.39 g. The oil absorption values of calcined PG are similar after modification with sodium stearate and titanate coupling agents. On the other hand, the water

contact angle ( $\theta$ ),  $\theta < 90^\circ$  and  $\theta > 90^\circ$ , can indicate that the surface is hydrophilicity or hydrophobicity, respectively. As can be seen from Fig. 7b, the static contact angle of untreated



**Fig. 7** Oil absorption value and contact angle of modified calcined PG: (a and b) 1 wt% different modifiers and (c and d) different content of calcium stearate



PG particle is  $31.76^\circ$ . Samples modified by three different modifiers' static contact angle increased from  $31.76$  to  $75.42^\circ$ ,  $106.86^\circ$ , and  $111.29^\circ$ , meaning that the surface properties are changed from hydrophilic to hydrophobic.

On the basis of above research, the effect of different calcium stearate content on calcined PG modification is shown in Fig. 7. It can be clearly observed that oil absorption value of modified calcined PG (Fig. 7c) decreased first and then increased rapidly, with increasing calcium stearate amount, and reached the minimum values at 2 wt%. As can be seen from Fig. 7d, the contact angle of 2 wt% is second only to 3 wt%, which is  $127.81^\circ$ . In addition, the comprehensive result analysis is helpful to establish the best reaction conditions. Namely, the modification effect of 2 wt% calcium stearate is the best and most economical.

Afterward, the experiments of water floatability were conducted with calcined PG (Fig. 8). Among the 1% modifiers (1–3 represent sodium stearate, titanate coupling agent, and calcium stearate, respectively), the calcined PG modified by sodium stearate and titanate coupling agent was placed on water and immediately submerge large amounts of powder. While powder modified by calcium stearate was placed on water only a small amount of it sank. After stirring and standing for 24 h, however, all three powders were immersed in water. The powder modified by calcium stearate with different content (4–7 represent 1.5 wt%, 2 wt%, 2.5 wt%, and 3 wt%, respectively) did not sink immediately, and floated well on the water. After standing for 24 h, only a little powder sank, and the floatability was excellent.

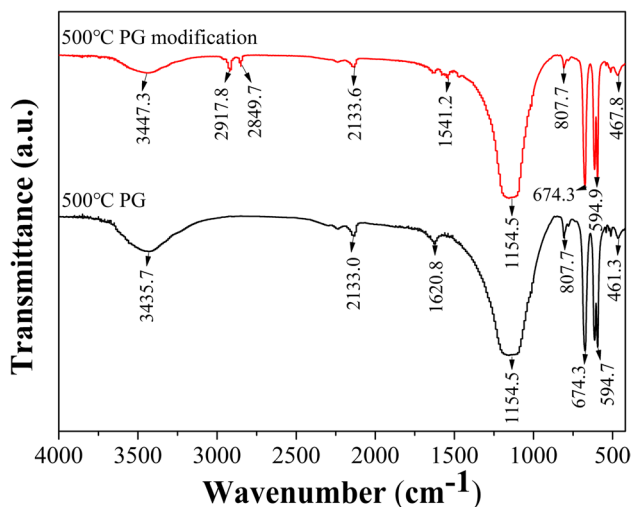
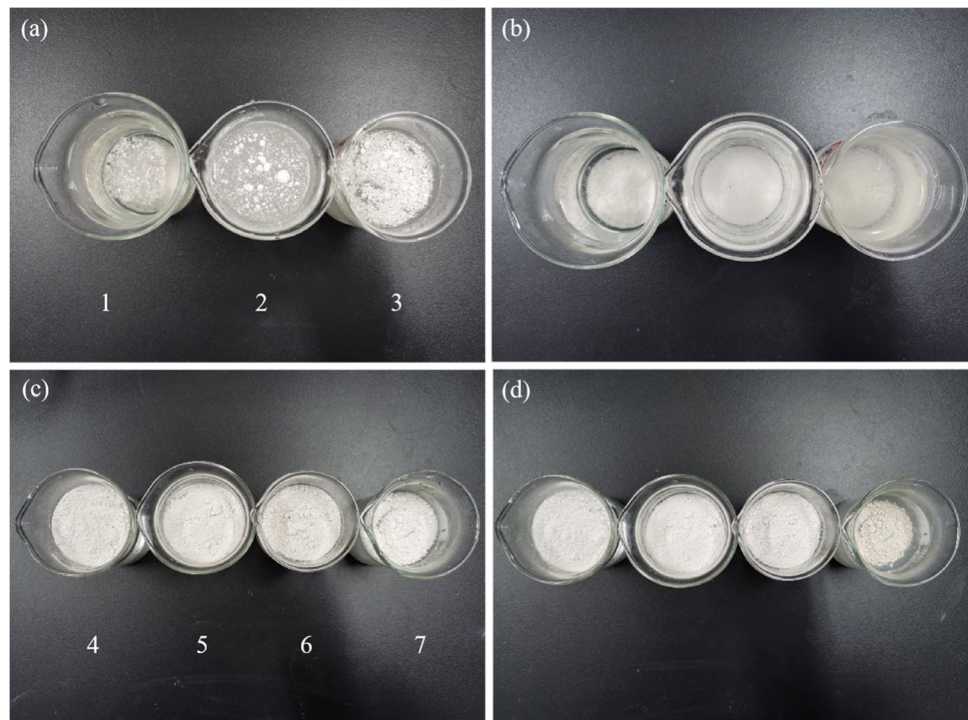
The FTIR spectrum analyses of PG and PG modified by 2 wt% calcium stearate were carried out, and the resulting spectra are presented in Fig. 9. The bands at  $3447$  and  $3435\text{ cm}^{-1}$  are attributed to the tensile vibration of Si–OH groups. In addition, it is clear that there are two distinct bands at  $2917$  and  $2849\text{ cm}^{-1}$  in the FTIR spectrum of modified calcined PG, arising from antisymmetric and symmetric stretching vibrations of the C–H group, which do not exist in the FTIR spectrum of unmodified calcined PG. The absorption band at  $2133\text{ cm}^{-1}$  is attributed to P–OH stretching of phosphoric acid residues. The peak at  $1620\text{ cm}^{-1}$  indicates the presence of crystalline water. It is possible that PG absorbed moisture during storage. The peak at  $1541\text{ cm}^{-1}$  is methylene bending vibration absorption peak. The strong absorption band at  $1154\text{ cm}^{-1}$  is associated with stretching vibrations of S=O related to sulfate groups. The vibrations at  $674$ ,  $594$ ,  $467$ , and  $461\text{ cm}^{-1}$  are related to the presence of metal oxides. It can be seen from the figure that the modified PG retains the original characteristic peak without offset and enhancement, indicating that calcium stearate did not destroy the PG structure. Therefore, the above results showed that calcium stearate is successfully coated on the surface of calcined PG particles.

## Calcined PG filled in HDPE or PP matrix

### Tensile properties of composites

In general, mechanical properties of polymer composites reinforced with rigid particles are function of particle size,

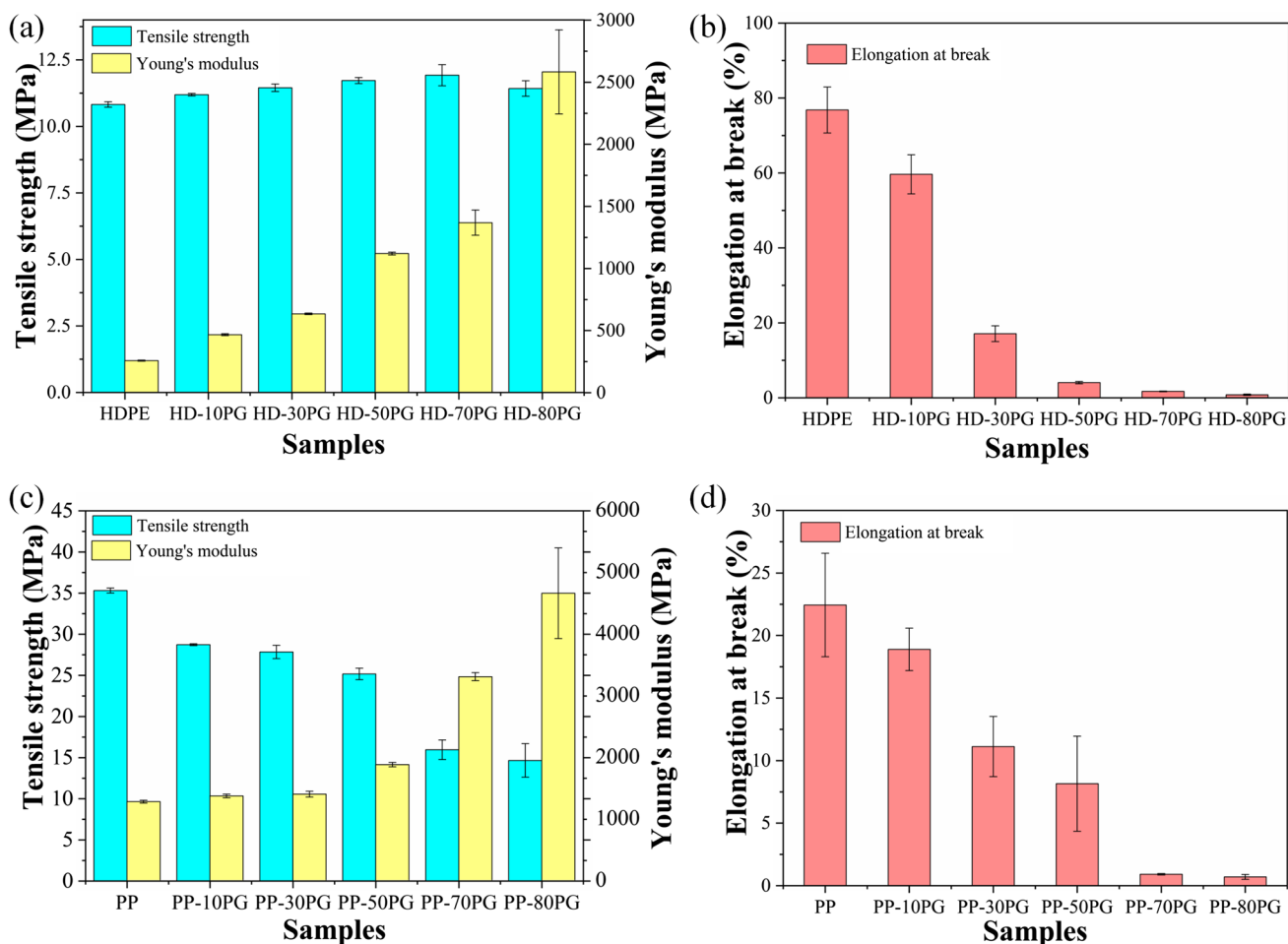
**Fig. 8** Water floatability of calcined phosphogypsum: (a and c) before standing and (b and d) after standing, (1–3) 1% different modifiers and (4–7) different content of calcium stearate



**Fig. 9** FTIR spectra of unmodified and modified calcined PG

degree of dispersion, interfacial adhesion, and particle loading (Essabir et al. 2016). Fig. 10a and c indicate the effects of filler weight fraction on the tensile properties such as tensile strength and Young's modulus in HDPE or PP matrix. As shown in Fig. 10a, the tensile strength and the Young's modulus of neat HDPE were obtained to be 10.82 MPa and 257.76 MPa, respectively. It is observed that after incorporation of modified calcined PG into HDPE, tensile strength of PG/HDPE composite increased from 10.82 MPa of neat HDPE to 11.92 MPa of HD-70PG. The modified calcined

PG has strong adhesion on the surface and improves the rigidity of the composite. The propagation of cracks would be curbed when the composite is stressed. When modified calcined PG was filled in HDPE, the tensile strength of the composite would increase gradually (Luo et al. 2020). It can be also seen that Young's modulus of PG/HDPE composite increased with the addition of modified calcined PG in the studied weight fraction range (10, 30, 50, 70, and 80 wt%), since Young's modulus of the filler is higher than matrix material (Kaya et al. 2018). When 80 wt% modified calcined PG was added into HDPE, the Young's modulus of HDPE increased by 902%. The tensile strength and the Young's modulus of PP were obtained to be 35.31 MPa and 1271.04 MPa, respectively (Fig. 10c). While 80 wt% modified calcined PG was introduced into PP, the tensile strength of PG/PP composite decreased from 35.31 MPa of neat PP to 14.66 MPa of PP-80PG. The addition of rigid particles in PP matrix would generate a stress concentration zone, resulting in the debonding of the interface under stress. The probability to generate this decohesion increases with particle load, which would also lead to premature fracture of samples. This condition can also be confirmed by SEM. When modified calcined PG was filled in PP, the tensile strength of the composite would decrease gradually. While 80 wt% modified calcined PG was introduced into PP, the Young's modulus of PG/PP composites increased by 266%. The Young's modulus of HDPE composites increases more than that of PP composites, indicating that the modified PG greatly improves the rigidity of HDPE composites. Because



**Fig. 10** Tensile properties of the HDPE and PP composites with different PG content, including Young's modulus, tensile strength, and elongation at break: (a and b) HDPE matrix and (c and d) PP matrix

the Young's modulus of PP matrix is high, the Young's modulus of PP increases slightly.

On the other hand, to study ductile behavior of the composite, the elongation at break of PG/HDPE and PG/PP composites is shown in Fig. 10b and d. It can be seen that elongation at break decreases significantly with increase of PG content. The results showed 98.97% decrease between neat HDPE and HD-80PG. The elongation at break between neat PP and PP-80PG decreased by 96.88%. It can be monitored that the ductility of the composite would decrease significantly with the share of calcined PG in the samples. This ductility loss is the result of lower plastic energy in the composite, which is due to the plastic deformation of the neat polymer matrix limited by the addition of rigid particles.

To illustrate the effect of modification, this study also compares tensile properties of PP and HDPE matrix filled with modified and unmodified calcined PG. Because of the poor fluidity of the unmodified calcined PG-filled matrix, it was decided to choose 70 wt% for comparison. As can be seen from Table 2, the presence of modified calcined PG did

not significantly improve tensile strength of the composite. However, compared with unmodified calcined filled matrix, elongation at break and Young's modulus would get better.

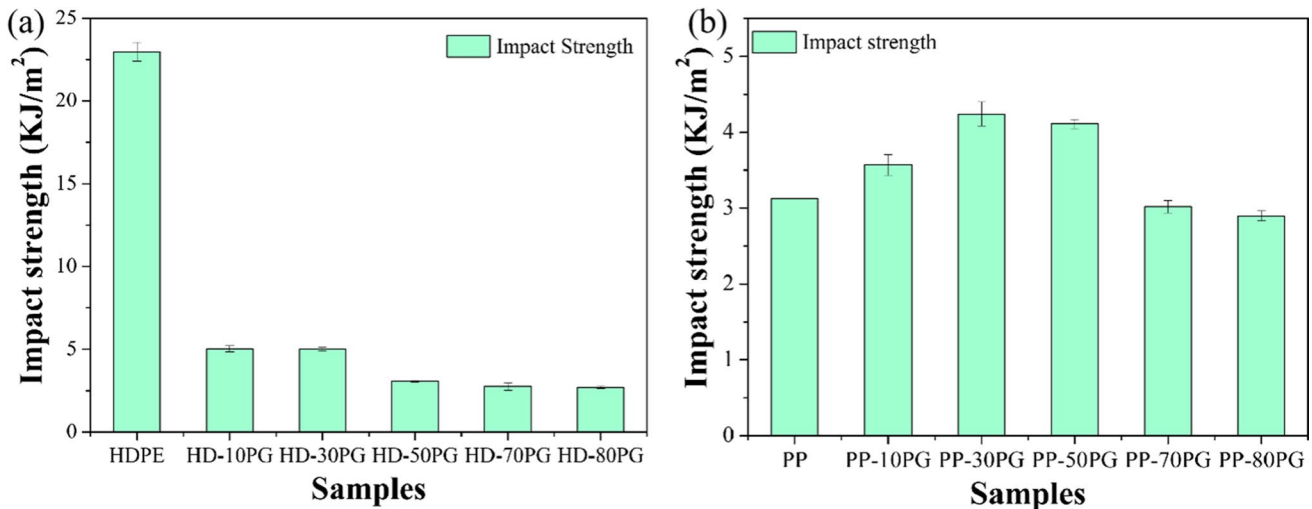
#### Izod notch impact toughness

Izod notch impact strength of the HDPE and PP composites with different PG content is presented in Fig. 11. In Fig. 11a, it may be noted that adding calcined PG to HDPE would decrease the impact strength of matrix. The impact strength of neat HDPE and HD-10PG are 22.98 kJ/m<sup>2</sup> and 5.02 kJ/m<sup>2</sup>, respectively. With the increase of calcined PG, the impact strength of HDPE composites decreased gradually. The impact strength of HD-80PG is 2.69 kJ/m<sup>2</sup>. The strikingly different features and fracture zones were shown in neat HDPE and PG/HDPE composites. Macroscopically, the fracture surface appeared highly ductile in neat HDPE and less ductile or brittle-like in PG/HDPE composites. The HDPE material to experience high-ductile behavior, but calcined PG offers resistance to



**Table 2** Comparison on tensile properties of PP- and HDPE-filled unmodified and modified calcined PG

Samples	Unmodified calcined PG filling			Modified calcined PG filling		
	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
HD-10PG	10.53	34.53	380.61	11.17	59.56	468.70
HD-70PG	11.72	1.62	1649.57	11.92	1.70	1368.84
PP-10PG	28.60	14.72	1364.03	28.73	18.89	1363.63
PP-70PG	15.83	0.62	3573.95	15.96	0.91	3297.17

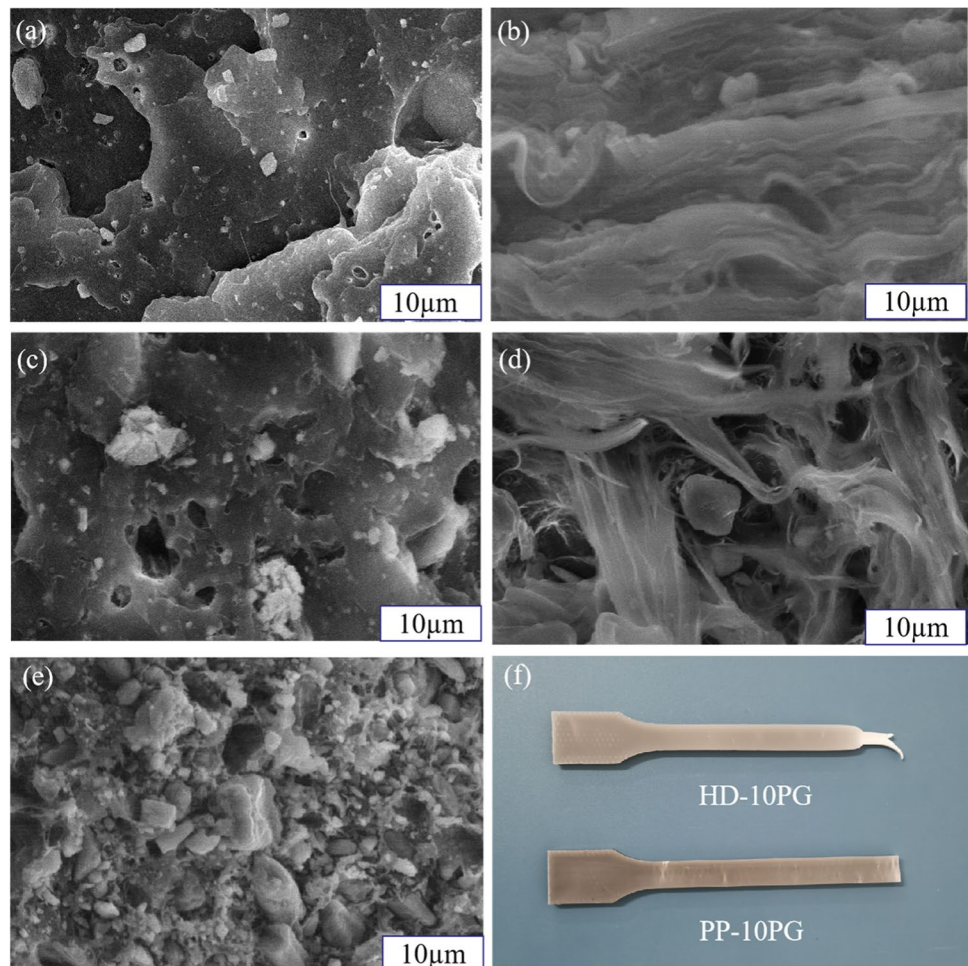
**Fig. 11** Impact strength of the HDPE and PP composites with different PG content: **a** HDPE matrix and **(b)** PP matrix

plastic deformation (Tanniru et al. 2006). Therefore, the impact strength of neat HDPE is greatly decreased after adding PG. It can be seen from Fig. 11b that with the addition of PG, the toughness of PG/PP composites increased first and then decreased obviously. The impact strength of neat PP is 3.13 kJ/m<sup>2</sup>. When the mass fraction of PG is 30%, the notch impact strength of PG/PP composites is 4.24 kJ/m<sup>2</sup>, which is 35.5% higher than that of neat PP. However, when the filling amount of PG is continuously increased, the notch impact strength of PG/PP composites decreased with the increase of PG filling amount. The notch impact strength of PP-80PG composites is only 2.90 kJ/m<sup>2</sup>. There are stress concentration effects on the composite with existence of inorganic particles. It is easy to cause microcracks in the surrounding resin and absorb certain deformation work, therefore increasing the notch impact strength of the composite. With the gradual increase of PG addition, however, the spacing between particles decreased. The microcracks caused by impact penetrated and formed large cracks, which decreased the notch impact strength of PP composites. Therefore, when the mass fraction was greater than 50%, the notch impact strength of PP/PG composites decreased.

### Structural and morphological analyses

The SEM micrographs are used to investigate morphological representation of tensile fracture surfaces in PP and HDPE composites. The micrograph (Fig. 12) shows tightly stacked shape of PG/PP and PG/HDPE. Owing to difference between PP and HDPE matrix, PP has poor ductility and clean section, while HDPE matrix has strong ductility after tensile fracture (Fig. 12f). It is noticeable that modified PG is better distributed in PP matrix compared with unmodified PG in same matrix (Fig. 12a and c). The tensile fracture surface is relatively complete in Fig. 12c, which is a typical brittle fracture. The compatibility of calcined PG in the matrix is poor, and the calcined PG would be pulled out when subjected to tensile force. There are many voids, indicating that unmodified calcined PG has poor toughening effect on PP. In Fig. 12a, it can be found that the compatibility between calcined PG and PP has been improved to some extent after modification with calcium stearate. However, there are still exposed calcined PG on the fracture surface; the stress cannot be efficiently transferred from the matrix to the filler. Therefore, the tensile properties of composites would decrease. Orientation of HDPE matrix after fracture

**Fig. 12** SEM images and tensile fracture photograph of composites: **a** PP/10 wt% modified PG, **(b)** HDPE/10 wt% modified PG, **(c)** PP/10 wt% unmodified PG, **(d)** HDPE/10 wt% unmodified PG, **(e)** PP/80 wt% modified PG, and **(f)** tensile fracture appearance

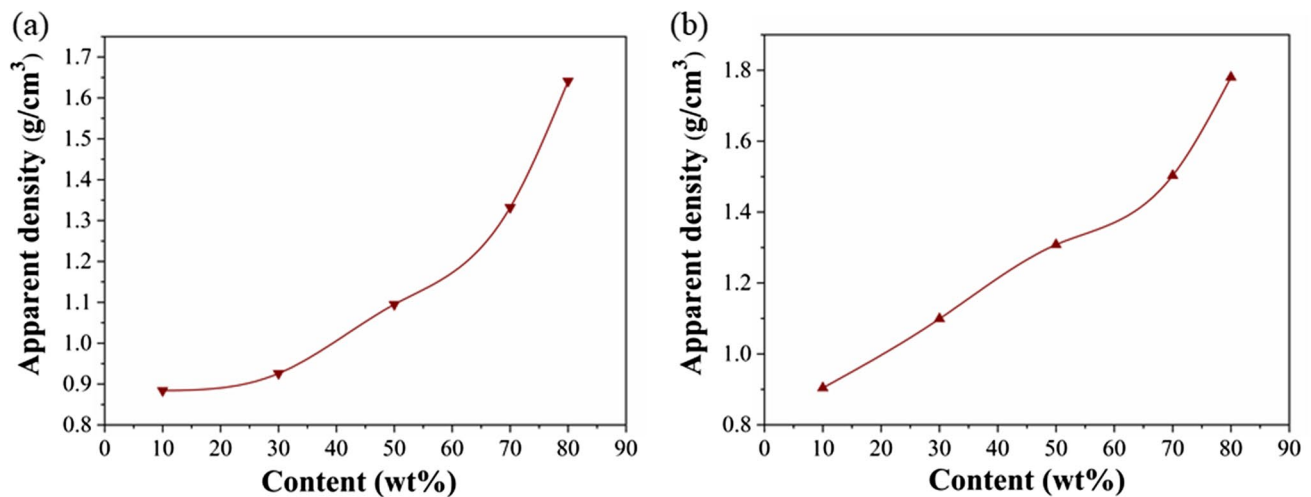


exhibited similarities in modified composites, but matrix fracture of unmodified composites seems to be omnidirectional (Fig. 12b and d). This irregularity could be attributed to demonstrating lower matrix strength under stress. It can be clearly seen in Fig. 12b that the modified calcined PG has better compatibility with HDPE matrix. The PG is basically compatible with the matrix, and there is no obvious bare PG. There are good interfacial compatibility and adhesion between the filler and the matrix; therefore, the tensile strength increased to some extent. It can be concluded from XRD that the grain size of modified PG became larger. Through the Scherer equation, the grain size of modified PG is 38 nm and that of unmodified PG is 34.6 nm. It can be seen from SEM that the grain size of unmodified PG was small, but unmodified PG was easy to agglomerate in the matrix, resulting in the decline of mechanical properties. The modified PG was better dispersed in the matrix, which improved the properties of the polymer. When filling amount became high enough, however, the modification effect of calcium stearate was not obvious. As can be observed from Fig. 12e, agglomerate particles obviously and poor distribution were exhibited in PP matrix of filled 80 wt% PG. It can

be concluded that mechanical test results are obtained to be in harmony with the SEM images of composites.

#### Apparent density analysis

Apparent density is an important index affecting the utilization of materials, which is the ratio of mass to apparent volume of matter. Nowadays, average apparent density of most plastic building templates is  $1.6 \text{ g/cm}^3$  in the market. As shown in Fig. 13, the apparent density of PP and HDPE filled with calcined PG presented uniform upward trend. The results indicate an increase in the apparent density of composites with an increase in the share of calcined PG in samples. However, the apparent density of HDPE filled with calcined PG generally exceeds PP filled with calcined PG. The density of PP is smaller than HDPE; therefore, the same volume mass might also be smaller. The experiment about apparent density was performed for PP and HDPE filled with unmodified calcined PG. It is found that apparent density of matrix filled with unmodified calcined PG is higher than the apparent density of same matrix filled with modified calcined PG (Table 3). This performance indicates



**Fig. 13** Effect of calcined PG content on apparent density: **a** PP matrix and **(b)** HDPE matrix

**Table 3** Effect of PP and HDPE filled with unmodified PG or modified PG on apparent density

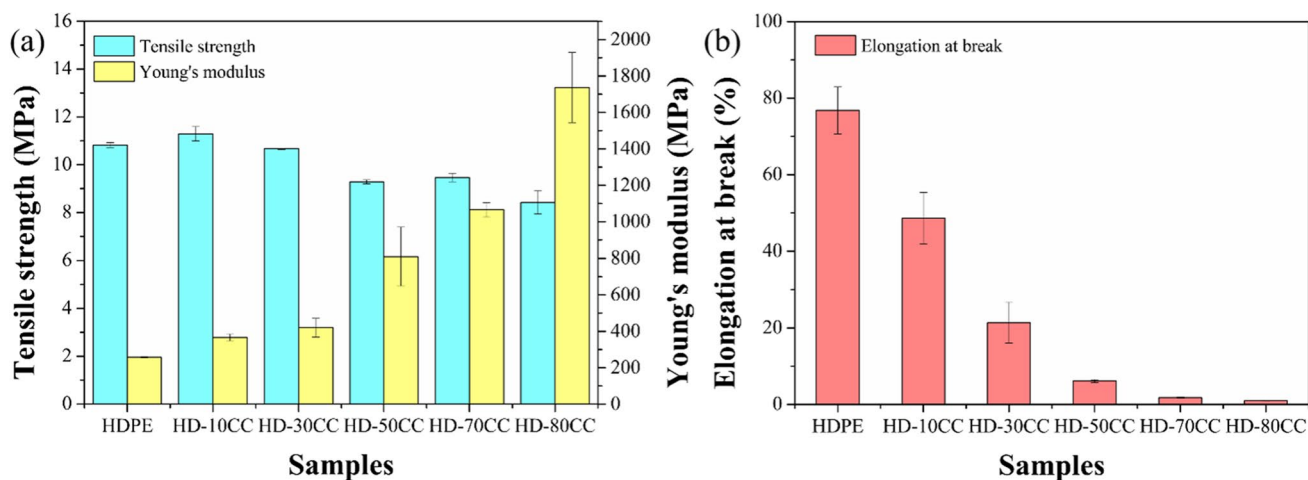
Samples	Unmodified calcined PG filling	Modified calcined PG filling
HD-10PG	0.936	0.904
HD-70PG	1.647	1.503
PP-10PG	0.925	0.884
PP-70PG	1.614	1.332

that the modified powder is better dispersed in the matrix. But the apparent density of composites mainly depends on the ratio of raw materials. And the apparent density of composites exceeds the average apparent density, only when filling amount of calcined PG exceeds 70 wt%. Compared with other building materials, PP and HDPE composites have the characteristics of lightweight. The apparent density can be adjusted via choosing different content of calcined PG to adapt to different conditions.

### Comparison of calcined PG and CC

This article compares tensile strength of HDPE filled with modified CC in same conditions. The results are shown in Fig. 14. It can be seen from the figure that the tensile strength of HD-10CC increased compared with neat HDPE. Then, the tensile strength decreased gradually, with the increased share of calcined PG in the samples. When 80 wt% modified CC filler was introduced into HDPE, the tensile strength of HDPE decreased from 10.82 MPa of neat HDPE to 8.42 MPa of HD-80CC. Because the surface modification of CC promoted the establishment of the connection point between inorganic

powder and polymer, the modified CC was easier to disperse in the HDPE matrix, therefore enhanced the tensile strength of the composite. However, with the increased amount of modified CC, the agglomeration state of powder would appear in the system, which would reduce the surface bearing capacity, resulting in the decrease of tensile strength. The increase continues in the Young's modulus with the increase of modified CC content. The Young's modulus of HD-80CC was 1736.57 MPa, an increase of 573.7% compared with neat HDPE. The Young's modulus of CC was higher than that of matrix, so the Young's modulus of HDPE composites would increase. The obtained values of the elongation at break indicate a decrease in elongation at break with an increase in the share of CC in samples. The results showed 98.7% decrease between neat HDPE and HD-80CC. This ductility loss is due to the plastic deformation of the neat polymer matrix limited by the addition of rigid particles. In the studied weight fraction range (10, 30, 50, 70, and 80 wt%), the tensile strength of HDPE filled with calcined PG is generally higher than HDPE filled with CC. But the HDPE filled with calcined PG is more brittle. There is no toughness of HDPE filled with 80% inorganic powder. The elongation at break is no distinction in same filling amount. The experiment of composites combine calcined PG with CC was also done to explore their filling performances (Table 4). The composite ratios are 7:3 and 9:1, and the filling amounts are 50 wt% and 70 wt%, respectively. It is found that the tensile strength of CC/HDPE composite is lowest and the tensile strength of calcined PG/HDPE composite is highest. There are little difference between elongation at break and Young's modulus. In conclusion, in terms of tensile mechanical properties, calcined PG is comparable to micron CC.



**Fig. 14** Tensile properties of HDPE composites with different CC content: **a** tensile strength and Young's modulus and **(b)** elongation at break

**Table 4** Tensile properties of HDPE filled with CC and calcined PG

Samples	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
$F_1$	11.48	6.415	770.01
$F_2$	11.02	1.813	1214.39
$F_3$	11.28	4.088	807.70
$F_4$	11.42	1.675	1338.78

$F_1$  calcined PG:CC (7:3) 50% filling amount,  $F_2$  calcined PG:CC (7:3) 70% filling amount,  $F_3$  calcined PG:CC (9:1) 50% filling amount,  $F_4$  calcined PG:CC (9:1) 70% filling amount

## Conclusions

With the increasing annual output of phosphate fertilizer, mass application of PG is mandatory. The removal of impurities and widespread use of PG are major challenges. In this work, the filling properties of PG in polymers were investigated. Based on the calcination, surface modification, and mechanical properties, the following conclusions were obtained:

1. Calcined at 500 °C for 2 h in high-temperature furnace, the crystallographic phase of PG would become  $\text{CaSO}_4$  and the whiteness of PG also reached highest.
2. According to oil absorption value, contact angle, water floatability, and FTIR analysis, the effect of 2 wt% calcium stearate-modified calcined PG is excellent. SEM showed that the modified PG is more uniformly dispersed in matrix than the unmodified PG.
3. Tensile strength and Young's modulus of PG/HDPE composites would increase as the filler loading increased; however, elongation at break and impact

strength would decrease with the increase of filler load. With the increase of PG filling content, the impact strength of PG/PP composites increased first and then decreased, but tensile strength and elongation at break would gradually decrease. Although calcined PG can improve some properties of the polymer, it will inevitably be accompanied by the reduction of other properties.

4. Compared with CC/HDPE composites, the mechanical properties of calcined PG/HDPE were more prominent, which indicated the possibility of application of modified calcined PG in the production of HDPE composites. The apparent density of unmodified PG-filled matrix was higher than modified PG-filled matrix, but the composite actually had the characteristics of light weight.

**Author contribution** Min Sun: experiment, writing original draft. Qing Sun: conceptualization, data curation, revising, funding acquisition. Jian Zhang: resources. Jiawei Sheng: project administration, review and editing, funding.

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**Data availability** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Declarations

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.



**Competing interests** The authors declare no competing interests.

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