

RESEARCH ARTICLE

Synthesis of an eco-friendly composite of palygorskite-gypsum associated ore using corn starch and waste biomass

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Abstract: Composite materials were prepared with palygorskite-gypsum associated ore, modified corn starch and corn stalk as raw materials, glycerin as plasticizer, ammonium persulfate as initiator, KH-560 as organosilane coupling agent and linseed gum as adhesion promoter. Tensile strength, flexural resistance and compressive strength were used as the evaluation criteria to investigate the optimal ratio of composite material. The effect of the content of palygorskite-gypsum associated ore and glycerol, the ratio of modified starch to corn stalk as well as the ratio of initiator to coupling agent on the mechanical properties was investigated. Composite materials were characterized by means of SEM, FT-IR, XRD and TG/DTG. The impact on the environment of composite material was evaluated via measuring the degradation and bacteriostatic properties. The degradation rate of the composite reached 52.7% when the degradation time was 42 d and the composite had a good antibacterial property.

Keywords: palygorskite-gypsum associated ore, corn stalk, corn starch, degradation, bacteriostatics

1 Introduction

Palygorskite (Pal) ore is a layered non-metallic clay mineral that the main components are hydrated magnesium and aluminosilicate, and its theoretical chemical formula is $Mg_5Si_8O_{20}(OH)_2 \cdot 4H_2O$ [1]. According to metallogenic factors, palygorskite ore can be divided into hydrothermal ore and sedimentary ore, which have differences in the size of crystals, microstructure, thermal stability, chemical composition and theoretical composition. Palygorskite has unique 3 D nanoclub-like crystal structure, abundant nanopores, stable framework structure and surface functional groups, which has excellent colloidal properties, adsorption properties, carrier properties and reinforcing properties [2, 3].

Although palygorskite clay reserves are abundant in Linze, China, the formation of palygorskite crystals is accompanied with a large amount of gypsum, kaolinite, a little of montmorillonite and limestone due to the inland salt lake lacustrine sedimentary geology. Palygorskite clay consists mainly of gray palygorskite clay and brick-red palygorskite clay with palygorskite content of 20%-50% in this area. The single crystal are shape as short stick and diameter is about 100 nm. Most of the palygorskite is attached to the surface of sediment and the corresponding associated minerals has a low-grade. Thus, the existing methods, such as milling, acid treatment, organic modification and heat treatment limits its application due to complicated process, environmental pollution and difficulty in separation [4-7]. Some of the associated mineral clays with low palygorskite content are discarded, which causes a great waste of clay resources. The large amount of gypsum in clay ore is the main raw material for the production of gypsum cementing and gypsum building products as well as the retarder of Portland cement. After treatment at different temperatures, the product has higher compactness and strength, better heat insulation, abrasion resistance and water resistance. However, the volume expands slightly during coagulation and hardening of gypsum lead to a poor water resistance and impermeability, which is improved by adding nano-clay.

Crop straw is a kind of renewable bio-organic polymer materials, which includes rich cellulose and hemi-cellulose. It has advantages of wide sources, low price, good toughness, high specific strength, low density, biodegradation and biocompatibility [8,9]. However, the resistance of crop straw in high temperature is poor and it is susceptible to aging. Crop straw, as the reinforcing

phase of inorganic mineral products, could improve the mechanical and thermal insulation properties and reduce the cost of products of composite materials.

The processability and dispersibility as well as the mechanical properties of composite materials can be improved by adding nano-clay [10]. Meanwhile, agricultural wastes have attracted more attention, because they could improve the performance of composite materials and reduce the cost of materials as a filler or toughener [11]. Davachi therefore, an environmentally friendly composite material was prepared with biomass and palygorskite-gypsum associated ore as raw materials, which not only used low-grade clay resources and waste biomass effectively, but also improved the mechanical properties, compressive strength and antibacterial performance of the composite material. According to demand, the composite material could be processed into egg trays, flower pots, seedling bowls and heat insulation gaskets and other items.

2 Material and methods

2.1 Raw materials

Methylbenzene, ethanol, glacial acetic acid, sodium hydroxide, potassium permanganate, tributyl phosphate and sulfate (all of AR) were all provided by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Ammonia (concentration was 25%) and sodium chlorite (AR) were purchased from Damao Chemical Reagent Factory (Tianjin, China). Borax and ammonium persulfate (APS) were purchased from Yantai Shuangshuang Chemical Co., Ltd.. Glycerin was obtained from Tianjin Kaitong Chemical Reagent Co., Ltd.. Linseed gum (AR) was provided by the Shanghai Yuanye Biological Technology Co., Ltd.. Corn starch, corn stalks and palygorskite-gypsum associated ore were all derived from Linze Fenjun Mining Co., Ltd. The mineral composition of each layer of the associated ore was shown in Table 1.

Table 1 Mineral content of different layers of Linze palygorskite-gypsum associated ore

Seam	Mineral content (%)								
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₂	K ₂ O	Fe ₂ O ₃	Ls	other
LP-I	0.4	1.4	5.2	15.2	32.0	0.9	1.5	41.5	1.9
LP-II	1.0	4.4	14.9	53.0	1.8	4.3	6.2	10.6	3.8
LP-III	0.6	4.6	8.7	30.7	13.5	2.1	4.5	32.8	2.5
LP-IV	0.0	0.4	1.6	5.0	40.6	0.2	0.5	50.6	1.1
LP-V	1.3	4.3	14.5	52.2	1.8	4.3	9.6	8.3	3.7
LP-VI	1.5	4.0	15.7	55.6	2.2	4.3	7.8	4.9	4.0

Notes: *Ls: Limestone; LP-I: Weathered layer; LP-II and LP-V: Gray palygorskite associated ore layer; LP-III: Mixed layer; LP-IV: Gypsum layer; LP-VI: Red palygorskite associated ore layer

2.2 Pretreatment of composite materials

2.2.1 Pretreatment of corn stalk

The corn stalk was cut into pieces, crushed, soaked and washed with water to remove sand and dust. It was dried in an oven at 80°C to constant weight and was sieved into 20-40 mesh (I), 40-60 mesh (II), 60-80 mesh (III), 80-100 mesh (IV), 100-120 mesh (V) and 120-140 mesh (VI), respectively. 10 g of corn stalk with different particle sizes was wrapped in filter paper and placed in Soxhlet extractors. After adding the mix solution of toluene/ethanol with volume ratio of 2 : 1, the reflux extraction was conducted at 90°C for 6-8 h to remove organic impurities, such as fat and biological wax. The straw was immediately put into constant temperature oscillator with 75°C, then 2 mL of glacial acetic acid and 3.5 mL of 10 mol/L NaClO₂ was added per 1 h, and this process was repeated 3 to 4 times until a white powder was obtained. The white powder was added into the mixed solutions of 8 wt% NaOH and 25 wt% of ammonia. It was agitated at 80°C for 2 h to increase the content of cellulose and remove hemi-cellulose. Finally, the mixture was filtered and the solid was washed to neutrality with deionized water and was dried at 80°C until the weight of the sample had no obvious change.

2.2.2 Pretreatment of palygorskite-gypsum associated ore

The palygorskite-gypsum associated ore from Zhengbei mountain in Linze County of Gansu Province was divided into six layers from top to bottom, named as LP-I (weathered layer), LP-II (gray palygorskite associated ore layer), LP-III (mixed layer), LP-IV (gypsum layer), LP-V (gray palygorskite associated ore layer) and LP-VI (red palygorskite associated ore layer), respectively. 500 g of palygorskite-gypsum associated ore raw soil from different layers was calcined at 400°C for 6 h to remove organic impurities, then distilled water with a solid-liquid

ratio of 1/5 was added and the mixture was stirred for about 8 h. Then, the suspension was left to layer. The solid was dried, ground and reserved.

2.2.3 Preparation of modified starch adhesive

The corn starch, distilled water, potassium permanganate and borax was mixed with mass ratio to 10 : 100 : 0.1 : 0.1. In order to adjust the acidity of suspension, certain amount of 8% sulfuric acid and glacial acetic acid were added. The suspension was transferred into the three-necked flask and was heated to 70°C for 15 min in a water bath. After the color of corn starch was changed from brown to milky white, a amount of 10 mol/L NaOH was added and stirred for 20 min to make it fully gelatinized.

2.2.4 Preparation of composite material

A certain amount of pretreated corn straw, modified starch adhesive and distilled water were mixed in the beaker and was heated to 70°C. Then, an appropriate amount of pretreated palygorskite-gypsum associated ore, modified corn starch, pretreated corn stalk, glycerin and dibutyl phosphate were added. After stirred for 60 min at 300 rpm, a certain amount of ammonium persulfate (APS), KH560 and linseed gum were added into the mixture when the temperature was dropped to 50°C. Finally, the uniformly mixed samples were rolled at 50°C for 2 min in an open mill and the samples were injected into the mold for cold pressing.

2.3 Performance test of composite material

2.3.1 The strength properties

The impact was measured by impact tester (XJJ-5, Chengde Shipeng Testing Equipment Co., Ltd., China). The pressed plate was ground in a prototype machine (100 mm × 10 mm × 4 mm, length × width × thickness). The compressive strength was measured via a microcomputer-controlled plastic tube pressure tester (Cangzhou Jilu Experimental Instrument Co., Ltd., China). The sample was pressed into a cylinder (46.92 mm × 10.00 mm, diameter × height) at a pressure of about 25 kN. The tensile strength was tested via the universal testing machine (Shanghai Hualong Co., Ltd., China). The sample was made into a dumbbell shape and the gauge length and the tensile speed was 50 mm and 10 mm/s, respectively. The width and thickness were averaged of three points randomly selected and the median was recorded as the test result with each sample was measured five times.

2.3.2 The degradation test

The degradation performance of prepared composites was evaluated by biodegradation method and the degradation solution was configured according to QB/T 2461-1999 Industry Standard. Pieces of sample with 4.0 cm × 2.0 cm × 0.2 cm, (length × width × thickness) were randomly cut out from prepared composite material, and dried to constant weight. The fragments were placed into the prepared degradation solution, which mainly included lactic acid bacteria, yeast, rhizopus, mucor and saccharifying strains, respectively. The sample was placed in a well-ventilated natural condition and one week is regared as a degradation period. The remaining material in the process of degradation was rinsed by water, then dried to constant weight. The degradation efficiency was calculated according to [Equation \(1\)](#):

$$W_i(\%) = [(W_{i0} - W_{i1}) / W_{i0}] \times 100\% \quad (1)$$

where, W_{i0} and W_{i1} are the mass of initial fragment and fragment after degradation, respectively.

2.3.3 Antibacterial test

Small square box-shaped containers (10 cm × 8 cm × 2.5 cm, length × width × height) were made by composite material prepared. 50 mL of domestic sewage (COD = 100 mg/L) was poured into each small container and they were stored in large enough basin. The change of COD in sewage was measured every three days by potassium dichromate method.

2.3.4 Characterization methods

The cross-section morphology was observed with ZEISS ULTRA PLUS thermal field emission scanning electron (SEM). The sample was cut into sheet along the transverse direction, which was sprayed by gold in vacuum. The FT-IR spectra were measured by FTS 3000 spectrometer from DigiLAB Merlin, USA. The scanning range is 4000-5000 cm^{-1} . The XRD

patterns were tested at 40 KV and 60 mA by the D/max-2400 powder X-ray diffractometer (Cu K_{α} , Rigaku, Japan).

3 Results and discussion

3.1 Effect of synthesis conditions on properties of composite material

3.1.1 Effect of the content of palygorskite-gypsum associated ore on the mechanical properties

The mechanical properties and formability of composite were measured when optimal amount palygorskite-gypsum associated ore was added and the effect of different palygorskite-gypsum associated ore on impact strength and formability of composite is shown in Table 2. Lp-I is mainly composed of palygorskite and a small amount of quartz. The impact strength of composite is 4.4 kJ/m² and molded composite is prone to cracking when LP-I is added, indicating that quartz does not improve the mechanical properties of composite. The impact strength of composite is 0 kJ/m² and composite has no formability when LP-IV (gypsum layer) is added, indicating that gypsum does not improve the mechanical properties of composite. Although the LP-II, LP-V and LP-VI are similar in composition, the content of palygorskite decreases successively from LP-II to LP-VI. The impact strength of composite is decreases gradually when the same amount of LP-II, LP-V and LP-VI is added. In conclusion, palygorskite is beneficial to the improvement of mechanical properties of composite. The formability of the composite material is the best and the maximum impact strength is 30.8 kJ/m² when LP-II was used. Therefore, effect of the amount of LP-II on the mechanical properties of the composite was studied and the result is shown in Figure 1. As can be seen from Figure 1, the tensile strength and impact strength of the composite increase first and then decrease with the increase of LP-II content. The tensile strength increases when the content of LP-II is less than 200%. It is mainly due to that palygorskite has excellent adhesivity and it plays the role of nanostructural support in the composite as well as there are some multifunctional groups on surface of palygorskite, which leads to LP-II can be coupled with corn stalk by KH-560. However, the tensile strength is decreased when the content is more than 200%, because it was beyond the bearing range of the added binder. The prepared composites begin to crack when the amount of LP-II exceeds 250%, resulting in a rapid decrease of impact strength. The composite has excellent mechanical properties with high tensile strength about 10.3 MPa and excellent impact strength about 29.7 kJ/m² when the amount of LP-II is 200%.

Table 2 Effect of palygorskite-gypsum associated ore of each layer on impact strength and formability of composite

Item	Seam					
	LP-I	LP-II	LP-III	LP-IV	LP-V	LP-VI
Impact Strength (kJ/m ²)	4.4	18.8	5.5	0	14.1	10.9
Molding rate	Cracked	Molding	Cracked	No-molding	Molding	Molding

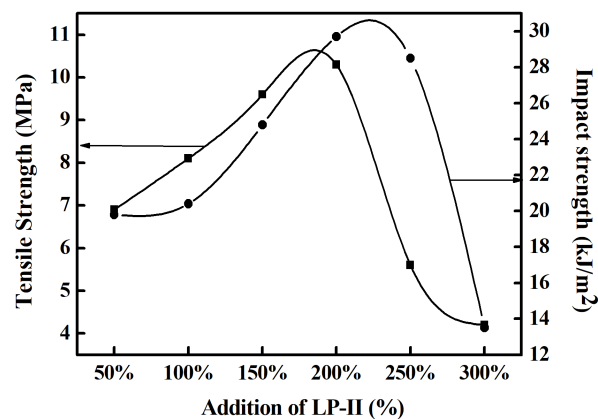


Figure 1 The effect of the addition content of LP-II on tensile strength and impact strength of composite

3.1.2 Effect of the ratio of modified starch adhesive to pretreated corn stalk on mechanical properties

The tensile strength and impact strength of composite material prepared with different mass ratios of modified starch adhesive and pretreated corn stalk were measured and the results are shown in Figure 2. The maximum tensile strength is 8.6 MPa and impact strength is 18.7 kJ/m² when the ratio of modified starch to ammoniated corn stalk is 25 : 1, while the maximum impact strength is 19.6 kJ/m² at that of 20 : 1. With the increase of the amount of modified starch, the impact strength does not significantly change, so the optimal ratio was selected to be 25 : 1.

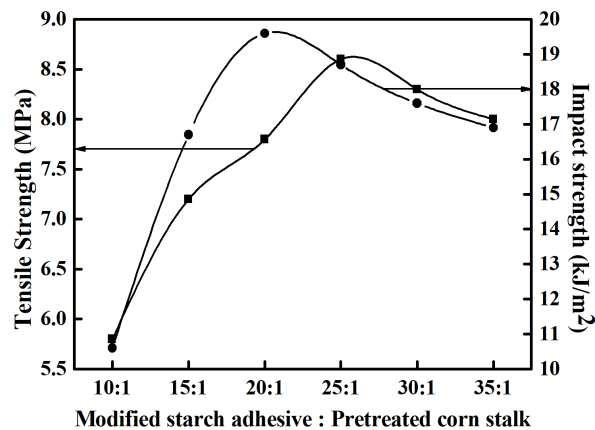


Figure 2 Effect of the ratio of modified starch adhesive to pretreated corn stalk on mechanical properties of composite

3.1.3 Effect of glycerin content on mechanical properties

In order to facilitate the study, the pretreated corn stalk mass was used as the matrix to investigate the effect of synthesis condition on the mechanical properties of composite materials. Glycerin, as a plasticizer, could affect the mechanical properties of the material. As shown in Figure 3, the tensile strength decreases gradually as the amount of glycerin increases. However, compressive strength of composite shows the shape of a volcano as the amount of glycerin increases. The synthesized composite has a maximum compressive strength of 8.4 MPa and the tensile strength of 8.7 MPa when the amount of glycerol is 70.0%.

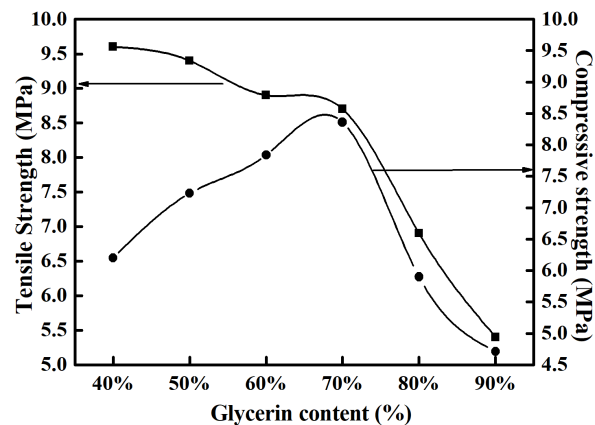


Figure 3 Effect of glycerin content on tensile strength and compressive strength of composite

3.1.4 Effect of the ratio of initiator to coupling agent on the mechanical properties

To activate the hydroxyl groups of corn starch and corn straw, APS was used as the initiator. Also, to couple the organic biomass with inorganic associated minerals, KH560 was used as coupling agent (molecular formula of KH-560 silane coupling agent is shown in scheme S2). KH-560 is an epoxy functional group silane which is widely used as bonding accelerator in sulfides, ethyl carbamate, epoxy, acrylic acid fillers, sealants and adhesives. The effect of the ratio of APS to KH-560 on the tensile strength and compressive strength of the composites is shown in Figure 4. Lower content of APS makes fewer free radical active points, resulting

in lower monomer polymerization efficiency, shorter polymer chain length, and lower tensile strength and compressive strength. However, the coupling reaction is weakened as decreasing the coupling points in polygorskite in the composite. Therefore, the optimum ratio of initiator to coupling agent was observed to be 5 : 1.

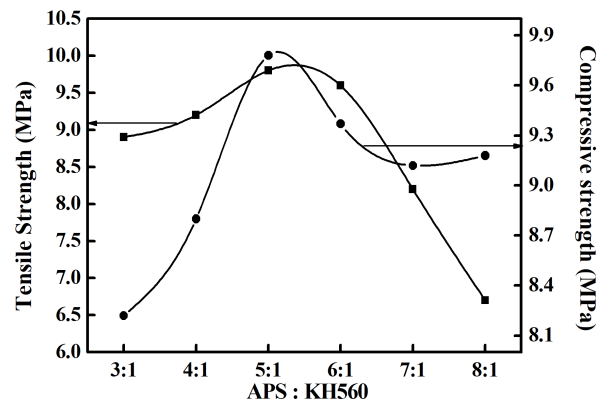


Figure 4 Effect of the ratio of initiator (APS) and coupling agent (KH560) on tensile strength and compressive strength of composite

3.1.5 Effect of biomass particle size and linseed gum content on leakage resistance performance of composite

The effect of the particle size of biomass and the amount of linseed gum on the leakage resistance performance of composite is shown in Figure 5. There is excellent leakage resistance performance when the particle size of the biomass is above 80 mesh. The leakage resistance performance of composite could be improved when linseed gum as a waterproof adhesive is added, which is attributed to the dense structure and good adhesion of linseed gum to block the microporosity of the composite. The composites do not incur leakage after continuous monitoring for 30 d when the content of linseed gum is 1.5-2.0 wt%. However, it is easy to crack during the drying process when the content of linseed gum is further increased. Thus, the particle size of biomass with 80-100 and the content of 1.5-2.0 wt% linseed gum was selected.

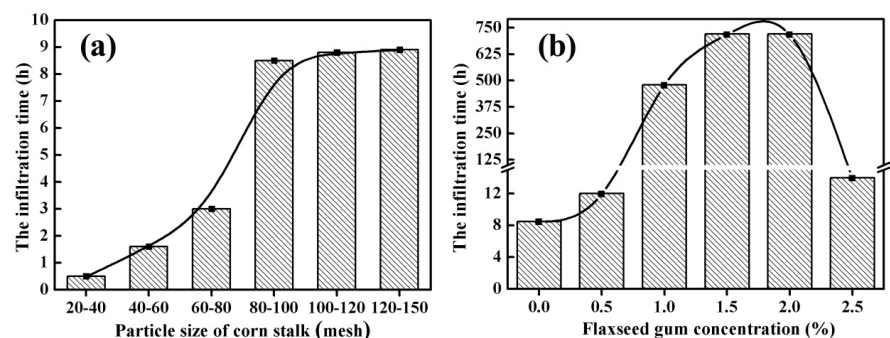


Figure 5 The effect of (a) the particle size of biomass and (b) linseed gum content on the leakage resistance of composite material

3.2 Characterization

3.2.1 SEM analysis

The SEM images of corn starch, modified corn stalk, palygorskite-gypsum associated ore of LP-II and prepared composite materials are shown in Figure 6. As can be seen from Figure 6a, corn starch granules have an irregular block and spherical structure and distribution of particle size is not uniform. The substances of bio-wax, soluble sugar and crude protein are removed and the rests are cellulose and hemi-cellulose when corn stalk is treated by chemical method, which results in bundles and partial sticking of corn stalk together. The morphology of LP-II is rod-shaped with a single crystal length of 30-250 nm. Most of palygorskite crystals are attached to lamellar plaster and shows lower apparent density. The prepared composite is with dense apparent structure and without pores. The structure of corn starch and biomass cellulose could not be observed and the lamellar materials are wrapped, indicating a good compatibility between biomass and palygorskite.

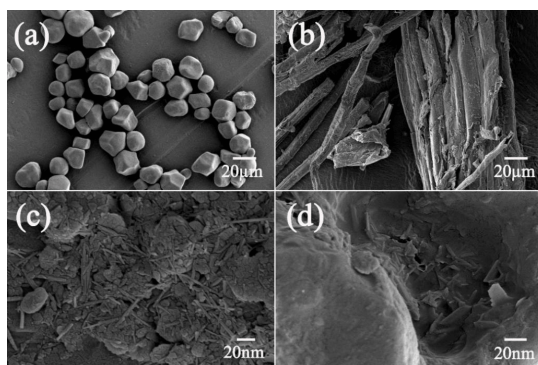


Figure 6 SEM images of (a) corn starch; (b) corn stalk after chemical treatment; (c) LP-II; (d) composite material

3.2.2 FT-IR analysis

The FT-IR spectra of corn stalks, corn stalks after removal, chemically treated corn stalks, corn starch, LP-II and composite are shown in the [Figure 7](#). The bands at 3393 cm^{-1} and 2900 cm^{-1} are attributed to the bending vibrations of the O-H and C-H in [Figure 7a](#), respectively. However, these absorption bands are weakened in [Figure 7b](#) and [Figure 7c](#). The strength of C-H vibration absorption band at 896 cm^{-1} increases in [Figure 7b](#), indicating that the type I ultrafine cellulose or micro-nano cellulose are present in the corn stalks after removing impurity [12]. The low-intensity shoulder band at 1159 cm^{-1} are attributed to the vibration of C-O-C and the absorption band at 1107 cm^{-1} and 1060 cm^{-1} are caused by the stretching vibration of C-O [13, 14], which still exists in [Figure 7b](#) and [Figure 7c](#). The absorption band at 1717 cm^{-1} is the stretching vibration of C = O in *p*-coumaric acid, ferulic and uronic acid, which are the main components of hemi-cellulose and lignin in corn stalk [15]. The band at 1531 cm^{-1} represents the stretching C = C in lignin, and the above absorption band almost disappears in [Figure 7b](#) and [Figure 7c](#). In [Figure 7c](#), the absorption band at 1621 cm^{-1} , 1661 cm^{-1} are attributed to the vibration of N-H and the stretching vibration of C-O in the amide group, respectively. These results shows that the lignin, biological wax and hemi-cellulose in corn stalk are removed basically by oxidative ammonolysis. Compared with [Figure 7c](#), the flexural vibration of O-H, C-H and N-H appears in [Figure 7d](#), which indicates that corn stalk after chemically treated participates in the reaction. The broader bands at 3430 cm^{-1} and 2929 cm^{-1} are attributed to the stretching vibration of -OH and C-H in [Figure 7d](#) and [Figure 7f](#). Compared with [Figure 7d](#), the stretching vibration of -C = O at 1624 cm^{-1} and the characteristic band of the starch structure at $1200\text{-}1029\text{ cm}^{-1}$ are weakened in the [Figure 7f](#), indicating that corn starch is involved in the reaction [16]. The absorption band at 3611 cm^{-1} in the [Figure 7e](#) is caused by the stretching vibration of hydroxyl in the octahedral sheets and bonded to different metal cations (Mg^{2+} , Fe^{3+}) in lattice [17]. The vibration bands at 3551 cm^{-1} and 3409 cm^{-1} are caused by coordination water in the channel and physically adsorbed water (zeolite water), respectively [18]. These bands in the [Figure 7f](#) coincides with the stretching vibration of -OH in [Figure 7c](#) and [Figure 7d](#). The vibration bands of Si-O-Si at 1028 cm^{-1} and 520 cm^{-1} are weakened in [Figure 7f](#), due to the dilution of the mineral phase in the composite. The band of carbonate ion at 1456 cm^{-1} also appears in [Figure 7f](#), which shows that carbonate is present in the minerals.

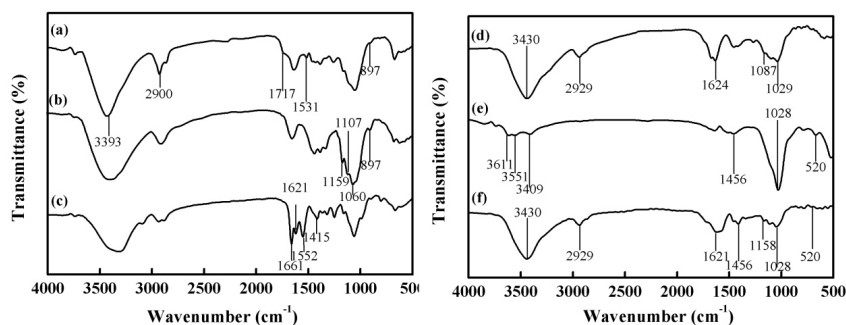


Figure 7 FT-IR spectra of (a) corn stalk; (b) corn stalk after removal; (c) corn stalk after chemical treatment; (d) corn starch; (e) LP-II; (f) composite material

3.2.3 Thermogravimetric analysis

The TG/DTG curves of LP-II, corn starch/corn stalk and composite are shown in Figure 8. The weight loss LP-II, corn starch/corn stalk and composite are 13%, 67% and 60% at 800°C respectively. The maximum decomposition temperature are at 646°C, 393°C and 435°C for LP-II, corn starch/corn stalk and composite, respectively. The weight loss of LP-II is attributed to the adsorbed water and channel water of gypsum and palygorskite from room temperature to 350°C and thermal decomposition of gypsum at 82.8°C. The weight loss at 350-500°C is attributed to removal of crystal water from palygorskite. The weight loss about 5% from 550°C to 700°C is due to the removal of structure water [19] and the decomposition of associated minerals, such as gypsum, dolomite, limestone, *etc.* [20–22]. The weight loss of corn starch/corn stalk is attributed to free water removed and decomposition of poor thermal stability substance of hemi-cellulose, ligninin completely extracted compounds (sugar, amino acid and protein) in biomass materials from room temperature to 190°C [23]. The weight loss of corn starch/corn stalk at 190-360°C is attributed to the decomposition of small molecules polymers. The thermal decomposition occurs rapidly in the range of 360°C to 490°C, which is due to the molecular chain of macromolecular organic compounds is broken [24]. The weight loss rate of the composite was lower than that of corn starch/corn straw, The peak of the composite moved to a higher temperature than that of corn starch/corn straw, indicating that adding LP-II into the composite was beneficial to the thermal stability of the composite.

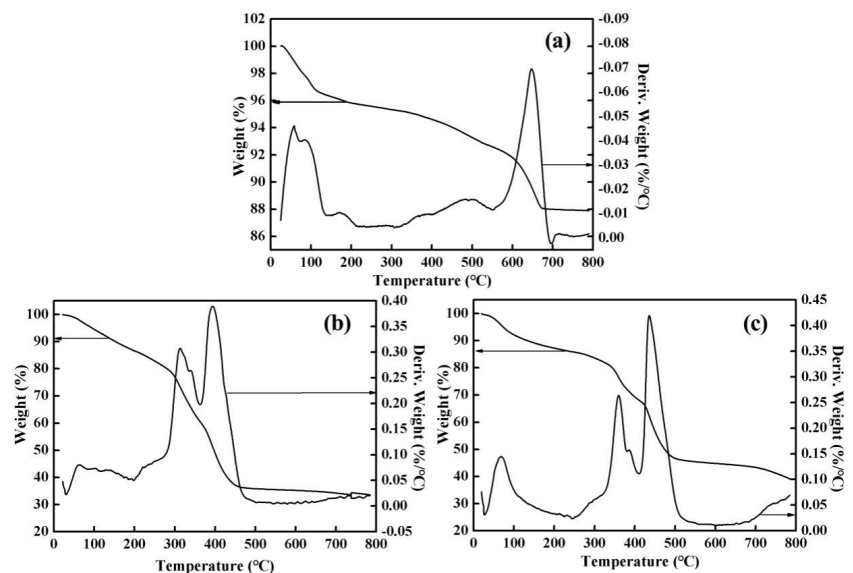


Figure 8 TG/DTG curves of (a) LP-II; (b) Corn starch/Corn stalk; (c) Composite material

3.2.4 XRD analysis

The XRD patterns of palygorskite, LP-II, corn straw, corn starch and composite are shown in Figure 9. The physical phases of the raw associated ore (LP-II) mainly include $2\theta = 8.51^\circ$, 19.60° , 35.10° of palygorskite, 11.63° of gypsum, 26.87° of quartz, 31.16° of dolomite, 29.59° of calcite and 25.99° of wollastonite, which is consistent with those reported in literature [25,26]. These results indicates that the mineral composition of the associated ore is very complex. The characteristic diffraction peak ($2\theta = 8.51^\circ$, $d(110) = 1.05$ nm) of palygorskite is used as the basis for quantitative analysis of palygorskite content in raw ore (Xu *et al.* 2002) and the content of palygorskite in LP-II is 21.44 wt.%. The main components of corn stalk are cellulose and hemi-cellulose. The crystal phase of cellulose mainly include typ I, II, III and IV. The peaks of cellulose I appear at $2\theta = 14.8^\circ$, 16.3° and 22.7° , respectively. It can be seen from the Figure 9b and Figure 9c that the obtained products are mainly cellulose I when impurities of corn stalk are removed and are treated by oxidative ammonolysis [27]. The mechanical properties of composite are enhanced by adding modified corn stalk [28]. The natural corn starch has two sharp diffraction peaks of A-type crystal patterns [29]. As starch is oxidized, gelatinized and cross-linked as well as corn stalk is subjected to removal impurity, the oxidative ammonolysis and coupling reactions in the process of preparing composite would destroy the hydrogen bonds in organic molecules and the regularity of molecular chain. Compared with Figure 9a, the characteristic peaks of palygorskite could also be seen in the Figure 9e, indicating that the

palygorskite crystal structure had barely changed during the preparation process of composite and palygorskite is beneficial to the improvement of mechanical properties of composite.

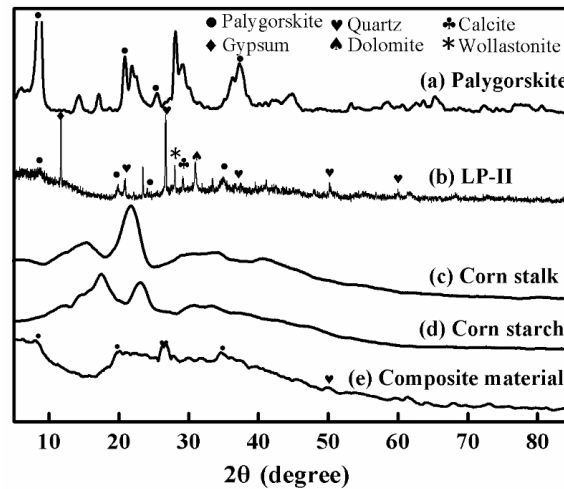


Figure 9 The XRD curves of (a) Palygorskite; (b) LP-II; (c) Corn stalk; (d) Corn starch; (e) Composite material

3.2.5 Biodegradability of composite material

There are many methods for evaluating degradability, such as mould method, soil burial method and enzymatic degradation method. Palygorskite-gypsum associated ore has excellent adsorption properties and slow-releasing properties for nitrogen fertilizer. Therefore, palygorskite-gypsum associated ore could be used as a fertilizer with supplement to inorganic mineral elements in the field. Corn starch and biomass are biological materials that can be completely degraded. The composite with inorganic minerals and biological materials as raw materials are biodegradable and environmentally friendly, but the degradation process is complex including a series of biochemical changes, such as the hydrolysis of microorganisms and catalysis of biological enzymes. The variation with time of the degradation efficiency of composite material is shown in Figure 10. The degradation rate of the composite reached 52.7% after 42 d, it is mainly due to the decomposition of organic matter in the composite.

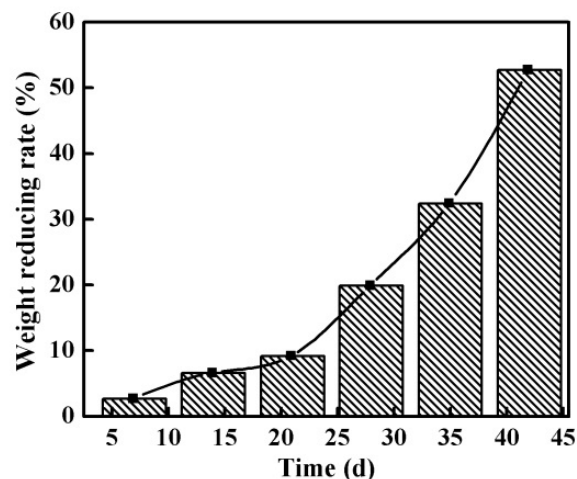


Figure 10 The degradation efficiency of composite material varies with time

3.2.6 Antibacterial property of composite material

The COD concentration of sewage with time is shown in Figure 11. The COD concentration of sewage in the container prepared by composite material decreases from 100 mg/L to 95 mg/L on the third day, which may be caused by the adsorption by palygorskite. The COD concentration could not increase rapidly and it is only 150 mg/L after 18 days. However, the COD concentration of sewage in the beaker increases rapidly and it is 150 mg/L on the third day and 472 mg/L on the 18th day. It is indicated that the composite has not only excellent adsorption property, but also a good antibacterial property.

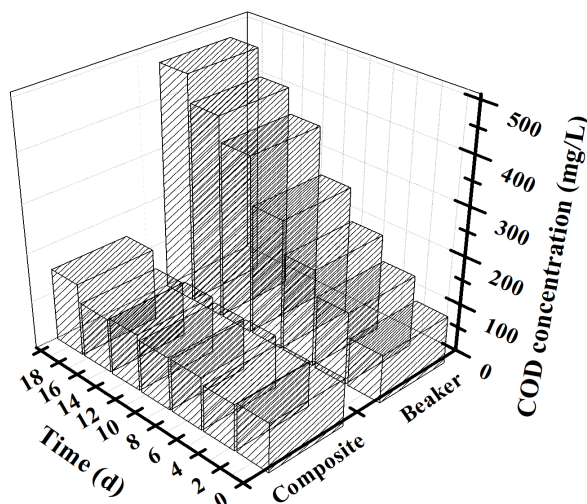


Figure 11 The COD concentration of sewage in different container varies with time

3.2.7 Application of composite materials

The processing samples from composite material are shown in Figure 12. The composite material was used to replace part of the plastic products in production and life, because of its good mechanical properties, anti-leakage performance, antibacterial performance, degradation performance, thermal stability and thermal resistance. The small sink, beaker cup holders, flower pot, heat insulation pad, egg tray and ancient buildings fire storage tank could be prepared from the composite material.

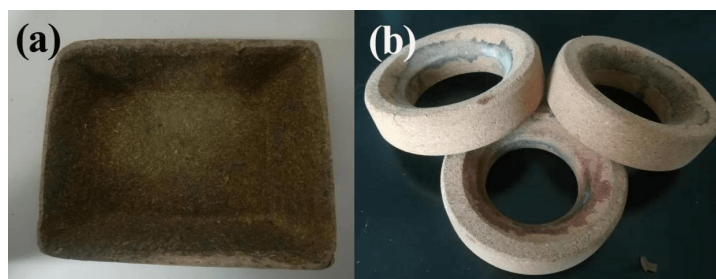


Figure 12 Small sink (a) and beaker cup holders (b) made of composite materials

4 Conclusion

The composite materials were prepared with modified corn starch, corn stalk, palygorskite-gypsum associated ore as raw materials, glycerin as plasticizer, ammonium persulfate as initiator, KH-560 as organosilane coupling agent and linseed gum as adhesion promoter. The optimal weight ratio of synthetic degradable composite was modified starch : ammoniated corn stalks : glycerin : ammonium persulfate : KH560 : LP-II : linseed gum = 86.52 : 3.46 : 2.42 : 0.52 : 0.11 : 6.92 : 0.05. The composite showed excellent mechanical properties that the tensile strength was 22.5 MPa and the impact strength was 24.7 kJ/m² when the added amount of the LP-II was 6.92 wt%. The anti-leakage performance of the composite had no leakage occurred during 30 d when the content of linseed gum was 1.5 wt%. The mechanical properties and hydrophobicity of the composite were improved when organosilane coupling agent of KH-560 was coupled with biomass and associated ore. The composite material had excellent antibacterial property and thermal stability. The degradation rate of composite reached 52.7% when the degradation time was 42 d.

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