Short communication

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Synthesis and oil absorption of biomorphic MgAl Layered Double Oxide/acrylic ester resin by suspension polymerization

Yihan Wang[1], Qiurong Li[*1], Lifang Bo[1], Xinpei Wang[1], Tao Zhang[2], Sihua Li[1], Peng Ren[1],Gengyao Wei[1]

[1]College of Environmental and Chemical Engineering, Hebei Key Laboratory of Applied Chemistry, Yanshan University, Qinhuangdao, Hebei 066004, China

[2]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013 , Jiangsu Province, China

Abstract：

In this paper, we reported on the synthesis, characterization, and the oil-absorbing properties of biomorphic MgAl Layered Double Oxide/acrylic ester resin by combining the biological template method and suspension polymerization method. The biomorphic MgAl Layered Double Oxides (LDO) were prepared by template-directed synthesis employing cotton fibers as templates. Then, oil-absorbing LDO/acrylic ester resin composites were synthesized by suspension polymerization in the presence of functional coupling agents. The oil-absorbing properties and thermal stability of as-synthesized composites were evaluated intensively as well. The morphology and structure of polymer-matrix composites were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. Both acrylic ester resin and composite resin were used in the absorption of organics. The results indicated that oil-absorbing properties and thermal stability of polymer-matrix composites were

improved significantly due to the nanocomposites with low particle content which the physico-chemical properties were superior to the pristine polymer. The composites showed excellent stability over 5 cycles of use and regeneration without significant decrease in the oil absorption. These results suggested that the oil absorbents may potentially be useful as next-generation oil absorbent materials for the remediation of the maritime ecosystem in the wake of a massive oil spill.

Keywords Polymer-matrix composites; Biomorphic MgAl Layered Double Oxide; Absorption; Thermal properties.

1. Introduction

The modern society is facing a water pollution crisis due to the increasing release of wastewater containing oil into the environment. The root cause of the problem lies in the rapid development of industry and the frequent occurrence of oil spill accidents [1-5]. Therefore, the removal of oil spills or organic contaminants from water surface has been an active research field. Many approaches have been used for oil spill clean-ups, such as oil containment booms, mechanical extraction, chemical dispersants, membranes, bioremediation, absorbent materials, *in* situ burning etc[6-9].

Although these measures have been widely applied in research and practical applications, they still have limitations due to the technical and environmental constrain. For example, chemical dispersants and *in* situ burning of oil spills may cause the

* Corresponding author. Tel..: +86 335 8387744; Fax: +86 335 8061569.

E-mail address: liqiurong63@aliyun.com (Q. Li).

secondary pollution to the environment. Among these methods, absorption approach for oil spill clean-ups is the most promising one for effective removal of oil spills or organic contaminants from water surface.

The conventional absorption materials contain activated carbon, wool fibers, zeolites, straw, fly ash, etc. However, these traditional absorbent materials generally have some shortcomings including environmental incompatibility, low absorption capacity, poor recyclability, etc. Therefore, searching for an oil-absorbing materials with high absorption capacity, high selectivity, easy fabrication, and low cost is highly imperative [10, 11].

In recent years, oil-absorbing resin has replaced the traditional oil-absorbing materials used in pollution control[12]. Oil absorption resin is a polymer with a three-dimensional network structure and the polymer is composed of hydrophobic monomer. The preferable absorption resins should possess these properties such as fast oil absorption rate, high oil absorption capacity, high oil retention capacity, and good reusability. Among these properties, fast oil absorption rate and high oil absorption capacity are indispensible for the emergency treatment [9, 13].

Herein, the aim of this research is to reveal a novel acrylic ester resin composite. It is widely known that nanoparticle can affect polymer properties. Because of the well dispersion of the nanoparticle in the polymer matrix, the interfacial interaction between the inorganic and organic phases is important for the improvement of the performance in the composites. In addition, the introduction of chemical bonds between inorganic

and organic phases can effectively enhance the interfacial interaction, which is a key issue in preparing the compatible composites that will lead to the improved of oil-absorbing properties and thermal stability[14]. LDO is considered as inorganic nanoparticles, which can be used to modify a variety of oil absorption polymer matrices. LDO is obtained by Layered double hydroxides (LDHs), which are a class of anionic clays that have attracted great attention in the last decades due to their potential applications in anion exchangers, heterogeneous catalysts, absorbents, electro and photoactive materials, two-dimensional solid-state nano reactors, etc[15-18].

In this paper, we describe the synthesis MgAl LDO/acrylic ester resin obtained by suspension polymerization and characterization of inorganic materials MgAl LDO using the template method. The synthesized composites exhibit excellent oil-absorbing properties, offering the combined benefit of the oil absorption capacity of porous LDO and good reusability of oil-absorbing resins, which have promising application in the emergency treatment of oil and organics.

2. Experimental

2.1. Preparation of MgAl LDO

All the chemicals are of analytical grade and used without further purification. A mixture of $Mg(NO_3)_2 \cdot 6H_2O$(0.6 mol), $Al(NO_3)_3 \cdot 9H_2O$(0.3 mol) and urea (CH_4N_2O)(2.7 mol) were first dissolved in 100 ml deionized water under continuously magnetic stirring to form a homogeneous solution. Then, 2 g of dried cotton was immersed into the above solution and treated under ultrasound for 5 h. After that, the

mixture was then transferred into a Teflon-lined autoclave. The autoclave was heated at 180 ℃ for 24 h. After cooling down naturally to room temperature, the precursor was picked out and washed with deionized water. Finally, the precursor was calcined at 500 ℃ for 4 h in the air, biomorphic MgAl LDO was obtained.

2.2 Preparation of MgAl LDO/resin composites

A certain amount of polyvinyl alcohol(PVA) was put into two-neck round bottom flask contained 30 ml of distilled water, dissolved at 90 ℃ with magnetic stirring. Under nitrogen atmosphere, a solution containing butyl acrylate, butyl methacrylate, ethyl acetate, styrene, pure benzoyl peroxide, N,N'-methylene bisacrylamide and MgAl LDO was poured into two-neck flask. Then the mixture was reacted at 85 ℃ for 6 h. After the reaction, the sample was washed with ethanol and distilled water and dried at 80 ℃.

2.3 Characterization

X-ray power diffraction (XRD) (Model D/MAX-2500/PC) equipped with Cu-Kα radiation was used to characterize the structure of synthesized LDHs and LDO. The surface morphology of samples characterized by scanning electron microscopy (SEM) was performed by Supra55 Field Emission SEM (Zeiss, Germany) at an accelerating voltage of 15 kV. Thermogravimetric (TG) and differential thermal (DTA) analyses were carried out simultaneously using a DTA-60A instrument (Shimadzu Corporation, Japan). About 10 mg of sample was weighed on an alumina crucible and isothermally heated from 30 to 800 ℃ in a static air atmosphere, and the heating rate was 10 ℃

/min.

2.4 Absorption experiment

All tests were performed at 25 ℃. The absorbent was weighed and immersed in the pure oil or organics solution for 12 h. Then, the absorbentwas took out from the solution and weighed. The sorption capacity of the absorbent was expressed in grams of the pollutant (oil or organics) absorbed by per gram of the absorbent ($g \cdot g^{-1}$):

$$Q_{eq} = \frac{(m_e - m_0)}{m_0} \quad (1)$$

Where Q_{eq} ($g \cdot g^{-1}$) was the sorption capacity of the absorbent, m_e (g) was the weight of absorbent at equilibrium, and m_0 (g) was the initial weight of the absorbent.

3. Results and discussion

3.1 Synthesis and absorption mechanism

The MgAl LDO/acrylic ester resin composite with three-dimensional network structure were prepared by the method of suspension polymerization. We propose the formation mechanism of MgAl LDO/resin composite as schematically shown in Fig.1. Initially, the MgAl LDHs nanometer needles were coated on the cotton fiber. The exact microstructures of MgAl LDO was inherited from LDHs/cotton fibers by calcinated at 500 ℃, and the structures of cotton fibers have been successfully replicated. Then, the MgAl LDO nanometer needles that dispersed in mixed solution, the three-dimensional network structure was composed of hydrophobic monomer under the effect of

crosslinking agent. At the same time, MgAl LDO was involved in build of three-dimensional network of resin. After polymerization, the MgAl LDO/acrylic ester resin composite with three-dimensional network and porous structures were formed. The three-dimensional network and porous structures will provide more space as oil reservoir, and the interconnected pores can provide channels for oil diffusing into the resins rapidly. The driving force for oil absorption is mainly due to Van der Waals and capillary force interactions between the porous resin and the oil molecules.

3.2 Characterization of samples

3.2.1. SEM analysis

The SEM results were presented in Fig.2, Fig.2 A and B showed the raw cotton fiber, C and D were both the images of the LDHs/cotton. It was illustrated that the LDHs uniform and intensive grow on the cotton fiber. Fig.2 E and F show representative SEM images of the MgAl LDO, it was found that the structures of cotton fibers have been successfully replicated. The SEM images of inorganic fibers show a hollow structure(Fig.2E,2F) , which is similar to the Fig.2C,2D. Fig.2 (G, H) revealed the SEM images of raw resin and composite resin at the same magnification. It showed that the surface of the composite resin was slightly rougher than that of the raw resin. (Fig.2 H).The unique 3D hierarchical hollow structure was also favorable to efficient improved the oil-absorbing properties of composite resin.

3.2.2. XRD analysis

The XRD results of prepared samples were illustrated in Fig.3, it exhibits the

characteristic reflections of MgAl LDHs and MgAl LDO. Compared with standard card of hydrotalcite(PDF#35-0964), the reflection peaks of LDHs shifted to higher angles. This might be result from at the higher hydrothermal temperatures, the reflection peaks of LDHs became sharper and their intensities were enhanced. MgAl LDO curve exhibited that the LDHs structure was destroyed and converted to an amorphous material after calcination at 500 ℃. The reflection peaks of LDO showed formation of metal oxides MgO, there were no peaks present relating to any aluminium oxide species, as they do not crystallize at the relatively low temperature at which the calcination was carried out[19].

3.2.3 TG-DTA analysis

The weight and the thermal stability of the resin were evaluated using the thermal analysis. The TG-DTA curves of the composites were shown in Fig.4. As can be seen from TG-curve, the weight of composites decreased with increasing calcinations temperature, and then gradually approached a constant value. The curve of TG-DTA for acrylic ester resin was shown in Fig.4 A, a rapid phase of mass loss appeared at 311~394 ℃(Weight retention from 90 % to 10 %). Fig.4 B revealed the curve of TG-DTA for composite resin, its rapid phase of mass loss postponed to 321~407 ℃ (Weight retention from 90 % to 10 %), which indicated that the thermal stability of composite resin was improved. This might be result from the nanocomposites with low particle content which the physico-chemical properties were superior to the pristine polymer, their unique phase morphology and superior interfacial properties contributed to better thermal stability.

3.3 Absorption properties of composite resin

The tests of absorption on acrylic ester resin and composite resin were studied, respectively. As shown in Table 1, obviously, the absorption capacity for chloroform, carbon tetrachloride and toluene of composite resin were greater than the acrylic ester resin. There was a comparison with previous literature data of the oil absorption [5, 9, 20-23]. Compared with other literature data of synthetic sorbents, composite resin was much easier to prepare and has a better absorption performance, demonstrating its great potentials in the removal of organics. Composite resin is the polymer with three-dimensional network structure. Porous structure will provide more space as oil reservoir, and the interconnected pores can provide channels for oil diffusing into the resins rapidly. Hydrophobic modification by sodium dodecyl sulfate of MgAl LDO evenly dispersed in polymer, it has a certain supporting function for resins holes. Hence the absorption properties of composite resins are better than that of acrylic ester resin

3.4 Optimization of reaction condition

Orthogonal experimental design is a kind of design method of multiple factors level , which is based on the orthogonality, the representative tests are selected from the comprehensive tests, which have the characteristics of evenly dispersed and symmetrical comparability.

In order to select the optimization factor of reaction, several preliminary experiments were carried out. The best condition of the reaction was selected from the orthogonal tests. Four independent variables: dispersant, crosslinker, initiator and MgAl LDO were

chosen, each at three levels. The investigated variables and their test levels were listed in Table 2. Reference to the experimental design theory, the orthogonal array L_9 (3^4) was selected to arrange the test program. The tetrachloromethane absorbency of the composite resin was a criterion of each test. The test results are listed in Table 3.

The order of influence of each variable on the tetrachloromethane absorbency appears to be C > B >D> A. Thus, the amount of initiator has the greatest influence and the dispersant has the smallest influence. The optimum level of each variable is A-1, B-2, C-3, D-2. Therefore, the optimum reaction conditions were as follows: dispersant 3 %, crosslinker 3 %, initiator 1.2 %, MgAl LDO 3 %. The photographs comparison between pre-oil absorption and after oil absorption has shown in Fig.5. The composite resin was immersed in an oil/water mixture. Pre-oil absorption resin was shown in Fig.5(B1). It was observed to float on the oil layer due to their hydrophobicity and oleophilicity (Fig.5A). The composite resin absorbed oil rapidly through the rapid swelling. Fig.5B showed that much of the oil on the water surface had been absorbed by the composite resin,which would be removed easily.

3.5 Reusability and oil retension capacity of composite resin

The practical application of resin was its recyclability and oil retension capacity. According to the obtained results, the oil-absorption and oil retension capacity of the resin for tetrachloromethane was shown in Fig.6. Compared with acrylate resin, the oil absorbency of the composite resin was improved obviously, and the oil-absorption capability of the resin differs slightly even after 5 oil absorption cycles, which

demonstrated the stability of this oil absorption resin (Fig.6 A). In this study, absorbed oil can be removed from resin by the vacuum drying, the milder procedure without severe disruption of the porous materials. This implies that the absorption properties of composite resins are not affected, this is the reason that the oil-absorption capability of the resin is still stable. The oil retention capacity of composite resin was shown in Fig.6 B. Composite resin and several kinds of natural absorption oil materials were chosen to be observed their weight retension. The composite resin, sponge, cotton and wood chips were weighed and immersed in the CCl_4 solution for 3 h, respectively. Then, the absorbents were taken out from the solution and weighed for pre-set time intervals. Obviously, oil retention capacity of the composite resin was better than that of other natural absorption oil materials.

The excellent structural stability and high absorption capability of resin after regeneration endow the material to be an ideal candidate to separate a variety of organic liquids from water.

4. Conclusions

MgAl LDO was successfully introduced into the resin composite to significantly improve the absorption capacity and thermal stability. SEM and TG-DTA confirmed that the improvement of properties of MgAl LDO/acrylic ester resin composite was mainly attributed to the synergistic effect of MgAl LDO and resin. The composite resin also exhibited an excellent reusability and oil retention capacity. This work not only provides a simple approach to fabricate biomimetic material by the bio-template, but

also synthesizes inorganic material and oil absorption resin composite for removing organics from waste water.

Acknowledgments

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absorbency, J. Appl. Polym. Sci. 101 (2006) 1248-1251.

Figure Captions

Fig.1 Schematic illustration of the fabrication of composite resin

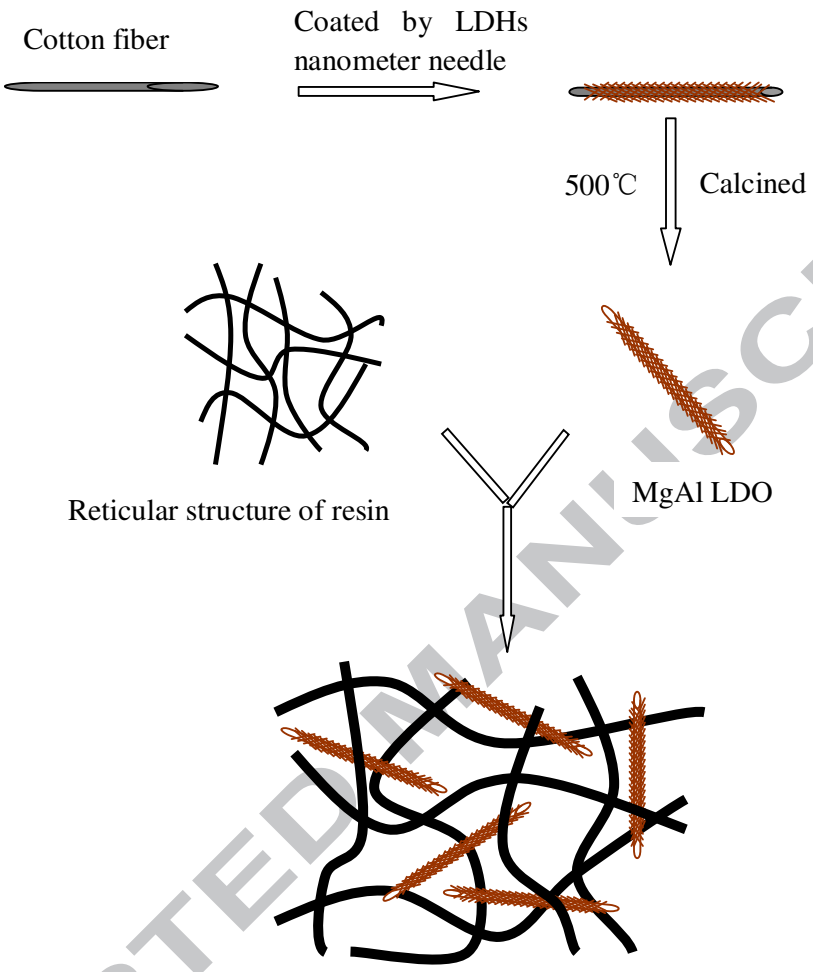
Fig.2 SEM images of cotton fibers（A,B）;before calcined（C,D）and after calcined（E,F）; acrylic ester resin(G) and composite resin(H)

Fig.3 XRD patterns of the different samples

Fig.4 TG-DTA curves for acrylic ester resin (A) and composite resin (B)

Fig.5. Removal of toluene from water surface by the composite resin, the toluene was labeled by Sudan Ⅱ for clarity(B1, pre-oil absorption;B2, after oil absorption)

Fig.6 The reusability (A) and oil retention capacity(B) of the composite resin



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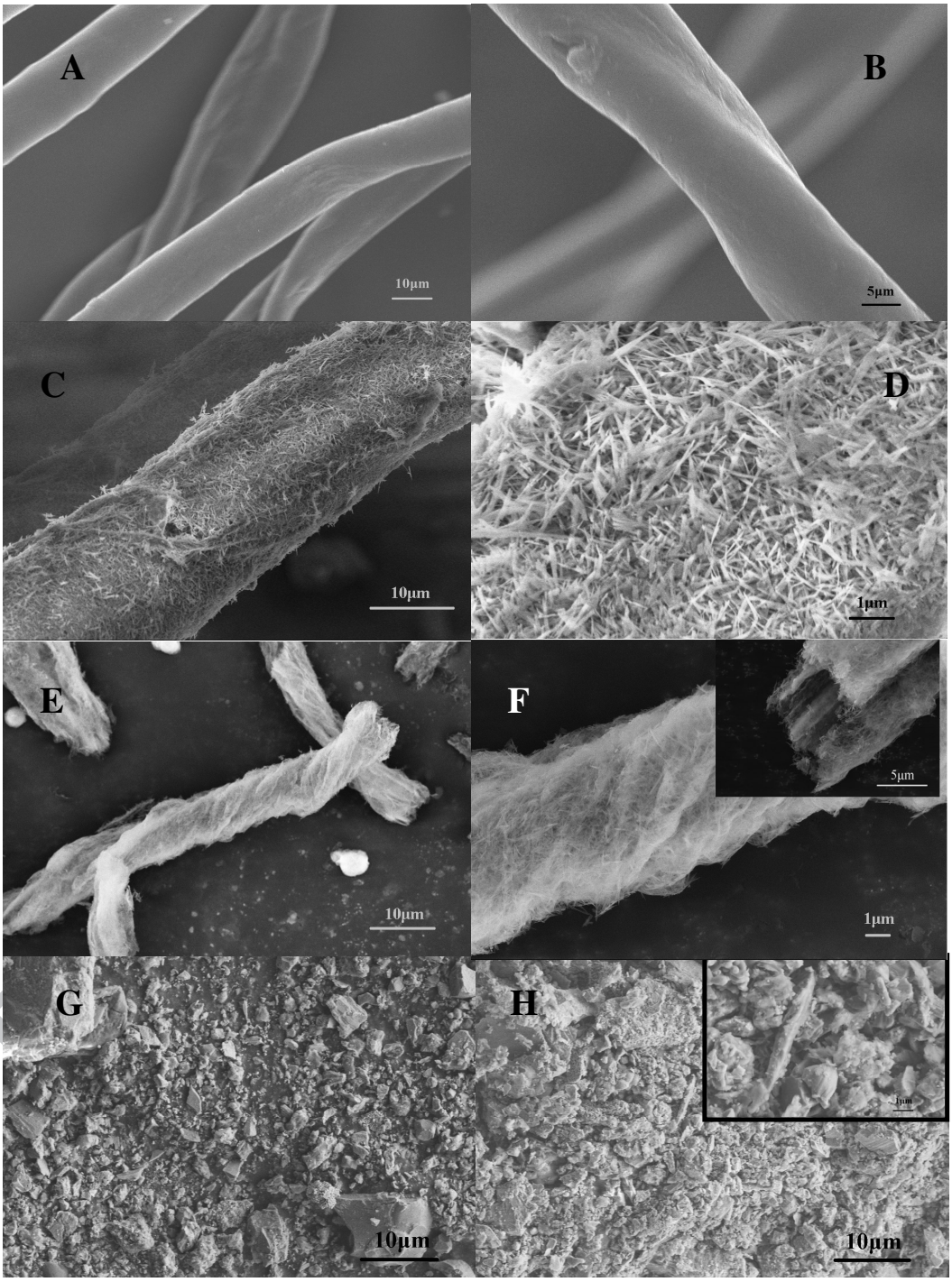


Fig.2 SEM images of cotton fibers（A,B）;before calcined（C,D）and after calcined（E,F）; acrylic ester resin(G) and composite resin(H)

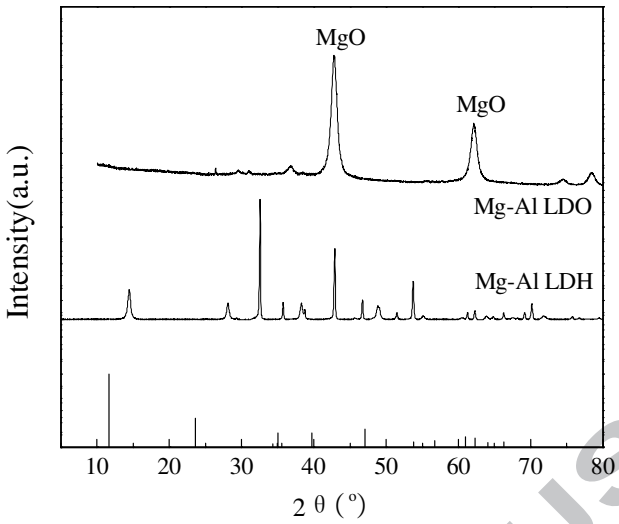


Fig.3 XRD patterns of the different samples

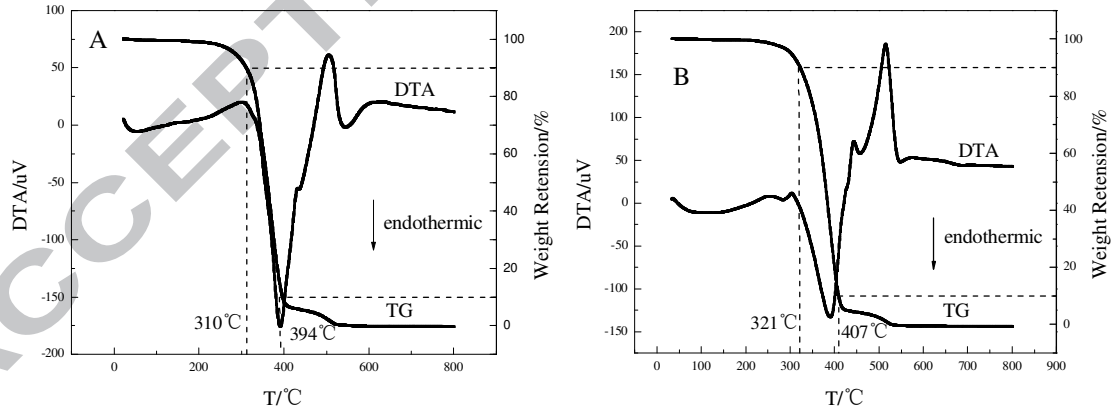


Fig.4 TG-DTA curves for acrylic ester resin (A) and composite resin (B)

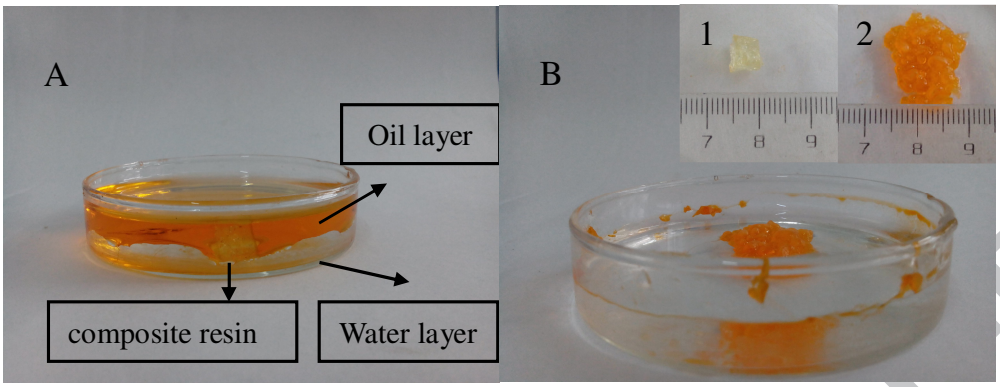


Fig.5. Removal of toluene from water surface by the composite resin, the toluene was labeled by Sudan II for clarity(B1, pre-oil absorption;B2, after oil absorption)

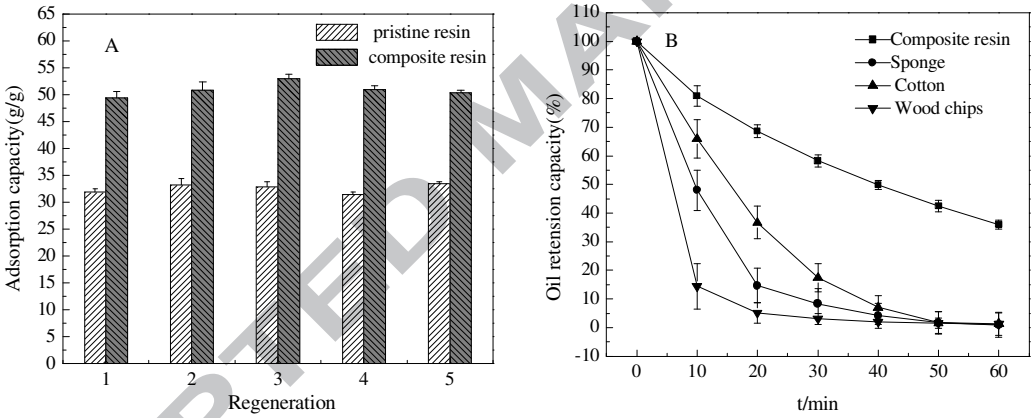


Fig.6 The reusability (A) and oil retention capacity(B) of the composite resin

Table 1 Comparison of oil sorption capacities from this study and other literature data

Adsorbent	Adsorption radio ($g \cdot g^{-1}$)			
	Chloroform	Carbon tetrachloride	Toluene	Reference
Superhydrophobic/superoleophilic cotton	45	—	30	[5]
Hierarchical porous resins	26.10	—	17.10	[9]
Ternary polyacrylate copolymer resin	21	24	13	[20]
Magnetic graphene foam	20	—	19	[21]
Carbon-nanotube-based organogels	47	31	22	[22]
Methacrylate–lauryl methacrylate fiber	34.7	—	15	[23]
Pristine resin	29.24	27.32	21.38	This study
Composite resin	41.70	38.47	24.23	This study

Table 2 Investigated variables and their levels

Levels of each variables	A dispersant (wt.%)	B crosslinker (wt.%)	C initiator (wt.%)	D Mg-Al LDO(wt.%)
1	3	2	0.8	2
2	5	3	1.0	3
3	7	4	1.2	4

Table 3 Orthogonal experimental arrangement and test result

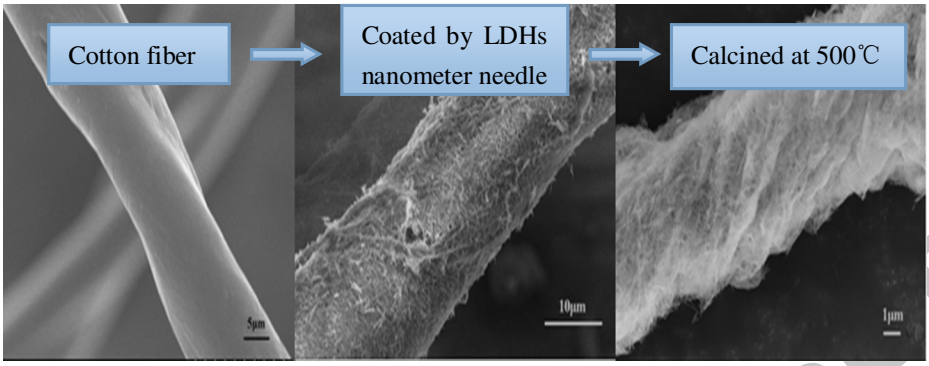
Experiment number	A	B	C	D	Absorbency (g/g)
1	1	1	1	1	2.69
2	1	2	2	2	27.53
3	1	3	3	3	33.51
4	2	1	2	3	13.77
5	2	2	3	1	29.97
6	2	3	1	2	15.98
7	3	1	3	2	24.93
8	3	2	1	3	15.37
9	3	3	2	1	18.63
K_1	63.73	41.39	30.04	51.29	—
K_2	59.72	72.87	59.93	68.44	—
K_3	58.93	68.12	88.41	62.65	—
k_1	21.24	13.80	10.01	17.10	—
k_2	19.91	24.29	19.98	22.81	—
k_3	19.64	22.71	29.47	20.88	—
R	1.60	10.49	19.46	5.71	—
Order			C > B >D> A		
Optimal level	A1	B2	C3	D2	
Optimal combination			A1B2C3D2		

K_1~K_3: Estimates value of the level 1~ 3

k_1~k_3: General average of level 1~3

R: Range (The influence of variables on the results)

Graphical abstract



Highlights

- Biomorphic inorganics/ resin composites are a novel composites.
- The structures of cotton fibers have been successfully replicated by MgAl LDO.
- The oil absorbency and thermal stability of the composite resin were improved.