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Surface Modification of Polyester Fiber with Perfluorooctyltrimethoxysilane

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Abstract. An excellent modified polyester fiber was prepared via chemical grafting between polyester fiber and perfluorooctyltrimethoxysilane (FAS-17), or silane coupler (KH-570), or Titanate coupler (DN-101) in isopropyl alcohol aqueous solution. Volume ratio of isopropyl alcohol in aqueous solution was 50:50, the mass concentration of FAS-17 is 2%, reacting on polyester fiber modified for 24h at 60 °C, the polyester fiber contact angle to water was 145 °, and the contact angle to peanut oil was 118°, with excellent performance of amphiphobic property. KH-570 and DN-101 modified polymer fiber to be hydrophobic properties nearly as FAS-17, but modified polyester fiber have no amphiphobic property.

1. Introduction
With the development of society and the progress of science and technology, filtering technology requirement is increasing, precision filtration and depth-type filtration and bulk leach put forward higher request to the filter and the filter materials [1]. The traditional filtration process is difficult to meet the requirements in the field of military and aerospace aviation oil, high grade lubricating oil production and oily waste water recovery technology. The modified polyester fiber has hydrophobic property, strong adsorption ability, and a property easy to back purge. And the fiber ball filter material made of polyester has large surface area because of its good fiber wire. Fiber ball filter material in the filter forms the filter layer, the filter layer hole becomes smaller and smaller along the direction of the flow, then the ideal big end up inter space distribution was formed. It was conformed that fiber ball filter layer is a good filter medium contribute to removing oil, it has a great advantage in treating sanitary sewage, polymer flooding in oil field and oil recovery, etc.

There are a lot of approach to modify fiber surface [2], such as alkali treatment, plasma treatment [3], photochemical treatment [4] and other methods, but some problems are still existed for example, vary

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degrees strength loss, short validity period, high cost, technical difficulties, hard for mass production and other issues.

Chemical grafting modification on fiber surface is simple, effective and environmentally friendly. It is a hot topic in recent years. Polyester fiber can be dissolved in sodium hydroxide solution, caused by nucleophilic substitution reaction, the hydroxyl ion and carbonyl carbon of polyester fiber react to the anionic intermediate, then continue to fracture and generate hydroxyl and carboxyl end group [5].

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{OCH_2CH_2O} \\
\text{O} & \quad \text{OCH_2CH_2O} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

Grafting modification is hydrophilic/lipophilic monomer grafting polymerization on the polyester fiber surface initiated by some suitable conditions, it changes the surface structure of the polyester, so that the materials surface is filled with many hydrophilic/lipophilic groups. The contact angle on material of water or oil become bigger, if the surface energy is lower, the hydrophobicity and oleophobicity of the materials is stronger. The ability of material surface depends on the surface morphology and the chemical composition of outer layer; it has nothing to its internal composition and molecular arrangement. Therefore, to study amphiphobic materials (90°<θ<120°), the surface chemical structure and surface morphology must be proceed from synthesis of low surface energy materials. It is found that silicone and fluoride materials have lower surface energy of all substances in nature, the surface energy of fluoride containing materials is about 0.01N/m lower than the silicone containing materials. Fluoride containing materials have a unique performance compared to other materials, so it is the first choice to prepare super hydrophobic materials.

Fluorine is the most negative element, the bond energy of the C-F can be very high, so the fluorine atom existed in fluorosilane can significantly reduce the surface energy of the surface. Fluorine silicon materials have low surface energy for its fluorine and silicon atoms, the Si-F bond energy is very high so it is hardly to be polarized, because of the existence of fluorine atoms. Fluoride silicon materials have a higher solubility in various solvents, because of the presence of silicon atoms, the modified materials have a good flexibility. Fluorine silicon material is suitable for the preparation of super hydrophobic fiber surface.

In this paper, the surface modification of polyester fibers was carried out by chemical grafting method. The effect of modification was represented in two aspects: graft ratio and contact angle. The reaction mechanism and the influencing factors were studied. The optimum reaction conditions were determined. The graft ratio is the relative ratio of the weight of the fiber before and after grafting, which reflects the effect of the grafting. Contact angle reflects the surface tension and the hydrophobicity of fiber surface.

In the experiment, the molecular formula of the fluorine silicon is C8F17(CH2)3Si(OMe)3, and the chemical bonding was formed between the hydrolysate of fluorine silicon and the -OH exposed on the substrate. Reaction mechanism is:

\[
C_8F_{17}(CH_2)_3Si(OMe)_3 + 3H_2O \rightarrow C_8F_{17}(CH_2)_3Si(OH)_3 + Me(OH)_3
\]
2. Experimental
Measurement  SEM (Magellan TM 400L XHR), contact angle measuring device (Shanghai Fang Rui, JYC-4), electronic balance (SHIMADAZU)

Reagent  polyester fiber filter ball, isopropanol, acetic acid, caustic soda (AR), perfluorooctyltrimethoxysilane (FAS-17, made in our laboratory), KH-570 (AR), DN-101 (AR), peanut oil (commercially available)

Hydrolysis of FAS-17  1g FAS-17 was placed in a conical flask with isopropanol and distilled water, the mole ratio of FAS-17 and distilled water is 1:3, then 100μL acetic acid was added as the catalyst, standing 24h at room temperature. Remove the solvent and the hydrolysis of FAS-17 was obtained.

Reaction between FAS-17 and polyester fiber  The polyester fiber ball is placed in the 500mL four-neck boiling flask, and the 200mL distilled water was added and boiling 2h to remove the oil. Be dried 12h in the oven at the temperature of 80°C to constant weight. The constant weight of the polyester fiber ball was described as m1.

200mL isopropanol, FAS-17 hydrolysate and treated polyester fiber ball was added in another 500mL four-hole boiling flask. Reacting at 60°C in a certain time, 100mL×2 of isopropanol was used to wash the polyester fiber ball, take the ball out and put it in oven at the temperature of 80°C for drying 12h to constant weight, The constant weight of the polyester fiber ball was described as m2. Graft ratio = (m2-m1)/m1.

After the modification, the polyester fiber ball was disassembled to fine fiber wires, aluminum plates were placed above and below the wires, and 10kg weight of heavy stuff was placed above the upper aluminum plate for 24h to form a thin slice. The surface contact angle of the slice was measured at five different points; the final data is the average of five points.

3. Results and discussion

Influence of polyester fiber ball quality to modification effect  The concentration of silane coupling agent FAS-17 was unchanged (c=1.9%), different quality of fiber balls were treated at 60°C, and the results were shown in table 1.

| Table 1. The graft ratio and the contact angle of the treated fiber wires at 60°C |
|-----------------------------------------------|
| Time(h) | m1(g) | m2(g) | Graft ratio (%) | Contact angle(°) |
|-------|------|------|-----------------|-----------------|
| 1     | 0.113| 0.126| 11.50           | 137             |
| 2     | 0.164| 0.184| 12.20           | 137             |
| 5     | 0.124| 0.143| 15.32           | 138             |
| 9     | 0.117| 0.139| 18.80           | 141             |
| 13    | 0.162| 0.195| 20.37           | 144             |
| 24    | 0.158| 0.194| 22.78           | 145             |
| 30    | 0.136| 0.168| 23.53           | 145             |

From table 1, it can be seen that under the condition of constant temperature and the certain concentration of coupling agent, the grafting rate increases with time, and the influence of the fiber ball size is not obvious.

In order to easily discuss the relationship between the graft ratio, time (t) and concentration (c), k was introduced, k= (c×t)/m1. If the graft ratio was proportional to the t and c, and reciprocal to the m1,
the k value should have a positive correlation with the graft ratio of the fiber. Experimental results are shown in table 2.

Table 2. The data of fiber ball treated with caustic soda and FAS-17hydrolysate

| Time(h) | m1(g) | m2(g) | Graft ratio (%) | Contact angle(°) | k |
|---------|-------|-------|----------------|-----------------|---|
| 5       | 0.193 | 0.216 | 11.92          | 129             | 0.284 |
| 9       | 0.123 | 0.139 | 13.01          | 132             | 0.804 |
| 13      | 0.112 | 0.127 | 13.40          | 134             | 1.276 |
| 18      | 0.127 | 0.145 | 14.17          | 136             | 1.559 |
| 24      | 0.109 | 0.126 | 15.60          | 138             | 2.422 |
| 30      | 0.119 | 0.138 | 16.00          | 140             | 2.773 |
| 34      | 0.122 | 0.142 | 16.40          | 140             | 3.065 |

After surface modification, the contact angle changes with the increasing graft ratio. The grafting ratio increased, the contact angle increased to a certain value, and it could be obtained by the most reasonable grafting rate. The maximum contact angle can reach 145°, meanwhile the minimum grafting ratio is 23%.

Influence of FAS-17 coupling agent concentration to the modification effect  In order to study the effect of silane coupling agent concentration on grafting ratio, the same mass of polyester fiber was taken, and the concentration of the silane coupling agent was changed. Changed the coupling agent dose, the grafting ratio of different concentrations can be obtained, as shown in table 3.

Table 3. Influence of FAS-17 coupling agent concentration to the modification effect (60°C)

| Concentration (%) | m1(g) | m2(g) | Graft ratio (%) | Contact angle(°) |
|-------------------|-------|-------|----------------|-----------------|
| 1.1               | 0.331 | 0.331 | 0              | 0               |
| 1.4               | 0.285 | 0.295 | 3.51           | 125             |
| 1.7               | 0.293 | 0.329 | 12.28          | 130             |
| 1.9               | 0.341 | 0.419 | 22.87          | 145             |
| 2.0               | 0.235 | 0.296 | 25.95          | 144             |
| 2.1               | 0.254 | 0.333 | 31.10          | 145             |
| 2.2               | 0.221 | 0.293 | 32.57          | 145             |
| 2.5               | 0.271 | 0.408 | 50.55          | 144             |
| 2.8               | 0.265 | 0.472 | 84.37          | 146             |
| 3.1               | 0.275 | 0.706 | 156.72         | 145             |

The grafting ratio increased with the increase of the concentration of the silane coupling agent, but the grafting ratio increased rapidly when the concentration over 2%, and the grafting ratio was over 100% at the concentration of 3.1%, the reason for this may be that the silane coupling agent with hydroxyl at the end is very high, which is easy to combine with the surface of the fiber, and the grafting ratio increases with the increase of concentration. But the number of hydroxyl groups of the coupling agent is not determined, and the number of hydroxyl groups that can be combined with the fiber is not determined. With the increase of concentration, the coupling agent is similar to the self coupling reaction, and the coupling of the coupling agent to the surface of the fiber.

The experimental results showed that the saturation grafting ratio of polyester fiber is 23%, and the contact angle is 145°. The water contact angle of the modified fiber did not increase significantly with the increasing grafting ratio, so it is not necessary to pursue higher grafting rate. After different
concentrations of modification with FAS-17, the images of the liquid drop on the fiber surface were shown in figure 1.

![Image](a)Water drop, c=1.4%  (b)Water drop, c=1.9%  (c)Peanut oil, c=1.9%

**Figure 1.** After modification of FAS-17, the image of the liquid drop on fiber surface

**Other coupling agents**  Two other kinds of coupling agent, silane coupling agent KH-570 and titanate coupling agent DN-101 were chosen to replace FAS-17 and reacted with polyester fiber under the same conditions.

**Reaction of KH-570 and DN-101**  Titanate coupling agent formula can be expressed as RO-Ti (OX-R’Y’n), it is the tetravalent titanium as the center, organic groups linked to the surface of filter material, making the nonpolarity of filter surface enhanced, which is conducive to the treatment of oily wastewater. In short, it is a multifunctional and agile additive. Compared with traditional silane coupling agent, titanate coupling agent is suitable for a wide range, and have a low price.

Titanate coupling agent DN-101 molecular formula is C_{55}H_{111}O_9Ti. The modification mechanism of polyester fiber filter surface can be described as: the alkoxy of DN-101 molecule is easy to be hydrolyzed and reacts with the polyester fiber surface hydroxyl groups to form chemical bonds, then the filter surface covered with a layer of DN-101 molecular. And at the other end of the titanate coupling agent molecule, there are three organic macromolecular chain structural units, so oleophilicity and hydrophobicity of the fiber ball filter surface have a great improvement. After modification, the grafting ratio is 1.16%, and the water contact angle of the filter material can reach 141°.

After modification of KH-570 and DN-101, the images of water drops on the fiber surface were shown in figure 2.

![Image](KH-570) (DN-101)

**Figure 2.** The image of the water drops on fiber surface (modification with KH-570 or DN-101)

**4. Conclusions**  
Isopropanol / H_2O as the solvents, anhydrous acetic acid as the catalyst, perfluorinatedoctylsilane coupling agent FAS-17 can be fully hydrolyzed at room temperature. Studies have shown that perfluorinatedoctylsilane coupling agent FAS-17 is beneficial to gain the hydro-oleophobicity for polyester fiber filter ball. At the optimized conditions of fiber ball modification, the water contact angle of polyester fiber filter ball can reached 145°, and the peanut oil contact angle was 118°.

Several other kinds of coupling agents were used in the same conditions, KH-570 and DN-101 modification can achieved the same hydrophobicity as FAS-17 for polyester fiber ball. These can be used for the filtration of oily wastewater processing, but cannot achieve the same amphiphobic effect
compared with FAS-17. Therefore perfluorinatedoctylsilane coupling agent FAS-17 is one more ideal surface modification agent in the field of polymer flooding in oilfield, depth-type filtration of military and aerospace aviation oil, etc.

5. References
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