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Flame retardant polyurethane microporous membrane preparation and the performance testing

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Abstract. Take liquid phase separation method to prepare polyurethane microporous membrane. In the preparation of microporous membrane process phosphorus add modification flame retardant agent in order to improve the polyurethane flame retardant properties. Experiments prove that the add of flame retardant can increase the flame retardant performance of polyurethane greatly. when phosphorus add quantity of flame retardant agent for 8 % polyurethane microporous membrane flame retardant was the best effect. And microporous membrane other performance also have no obvious effect. Because of flame retardant performance was good, this kind of polyurethane can be widely used in floor synthetic leather, wall paper, decoration, etc.

Introduction

Polyurethane (English abbreviation as PU), poly amino acid esters, it was consisted of the isocyanate and polyether polyols or polyester polyols and small molecular polyols, multiple amine or water extender chain agent or crosslinking agent of the preparation of raw materials such as polymer. Through the change of raw material composition and classes, can greatly improve the product configuration and performance. Pu products from form soft, half a cent on hard and hard foam, paint coating, elastomers (polyurethane elastomer English referred to as TPU), sealed plastic, adhesives, synthetic leather coating resins, elastic fiber, etc, is widely used in the refrigerator manufacture, transportation, civil building, automobile manufacture, footwear, synthetic leather, fabric, mining machinery, electrical and mechanical equipment, aviation, petrochemical industry, medical care, agriculture, etc.

Polyurethane materials is one of the most widely used polymer materials in the world at present, global years away quantity of up to 3.5 million tons of above estimates. Polyurethane materials because of its good oil resistance, heat insulation, cold and damp resistance and stability performance advantage and become a liner, shock, heat preservatio and indispensable materials, and some industries are using polyurethane cohere agent for preparation of composite materials.

But, as other high polymer materials, without the treatment of fire-retardant, PU in the air was flammable, the oxygen index (LOI) was only 17 to 18[1]or so. So with the widely used of polyurethane materials, the flame retardant technology is also receiving more and more attention. At present, the evaluation of flame retardant's effection, widespread use of the method is the oxygen index, the density of smoke emission and vertical flame.

Adding the flame retardant to the polyurethane was the realizated method of the polyurethane flame retardant performance[1~3], usually used polyurethane type of flame retardant add more for solid and liquid containing phosphorus or halogen phosphate and phosphate. This test to add the polyurethane modified phosphorus-containing flame retardant prepare polyurethane microporous membrane to improve microporous membrane flame retardant performance, so as to get with the flame retardant performance pu microporous membrane. this kind of polyurethane can be widely used in floor synthetic leather, wall paper, decoration, etc.

Experimental

1.1 The experiment materials and equipment

a A main experimental drugs

Methyl phosphate, methyl 2 (DMMP), analyzes the pure; Glycerin, analysis the pure; With maleic anhydride and analysis pure; DMF, analysis the pure, tianjin rich yu fine chemical Co., LTD.; Butyl ketones, analysis the pure, yantai and chemical reagents Co., LTD; Pu, MP-108, yantai ethnic group.

b A main instrument

Table 1. Main test instrument

Device name	model	manufacturers
Magnetic heating blender	78-1	Guohua electric appliance Co., LTD
Precision increase force blender	JJ-1	Guohua electric appliance Co., LTD
Electric vacuum drying oven	ZK-35AB	Electric furnace factory
Constant temperature and humidity box	HWS-150	Shanghai sa even experimental equipment Co., LTD
Circulating water type multi-purpose vacuum pump	SH(B)-III	Zhengzhou the Great Wall trade Co., LTD,
Digital display constant temperature oil bath pot	HH-S	The jintan city medical instrument plant

1.2 Modified phosphorus flame retardant agent preparation

Put 0.3mol DMMP in 250 ml threeneck flask, install the blender, then put them in the 105 centigrade oil bathpan. Put 0.6 mol phosphoric acid in the threeneck flask which had 0.3mol DMMP in advance, mix them well-distributed. Mixing 5 hours in oil bath pot use blender in order to make them fully reaction. Then put 0.6 mol glycerol into the threeneck flask. Keep the temperature of the oil pan was still 105 centigrade, Mixing heat for 2 hours. Add 0.6 mol maleic anhydride (use the diminishing quantity method) at last, after 3 hours's reaction we can get the ending product, the product was the colorless transparent liquid, Low viscosity.

1.3 Polyurethane microporous membrane preparation

Put a certain quality of pure polyurethane into around bottomed flask, then quickly add a certain quality of Butyl ketone and DMF solvent (The mass ratio of 1:1), use the solvent to dissolve polyurethane to 20%, then take a certain quality of phosphorus-containing flame retardant (the quality of the polyurethane respectively in the pure 3%, 5%, 8%, 11%, 14%, blank sample 0% that is not add flame retardants) into around bottomed flask. Use an precision electric mixer fast mixing 1 h in 60 ˚C, then Vacuum defoaming 10 min.

Prepare a glass plate in advance, then put polyurethane solution which was defoamed in the groove of glass plate. Use glass rod push the blending solution from one to the other side, Thus form a uniform, blend of solution in groove. Stand for 10 min in a certain temperature, Then put the glass tank in the configuration of the 25 ˚C 25% concentration of coagulation bath DMF, stand for 10 min or so, Nest put the glass plate in the water and wash 3 hours and then take them out, in the drying oven drying in 100 ˚C and get the ending product.

Test method and characterization

2.1 Smoke density test

YM-3 type building materials smoke density detector of Nanjing Shangyuan instrument analysis Co., LTD. According to GB/T8627-1999 "Building materials burning or decomposition of the smoke density test methods",use the most drag density time and the most drag density to test the polyurethane performance .

2.2 The oxygen index test

HC-2 C oxygen index detector of Nanjing Shangyuan instrument analysis Co., LTD. According to ASTM D 2863-77,using the method of the oxygen polyurethane need when it burning to test [4].

2.3 Vertical flame test

HC-2 C level vertical flame detector of Nanjing Shangyuan instrument analysis Co., LTD. Accornding to ALCA Method E 50,Using polyurethane vertical burning with flame combustion of time and no flame combustion time method to test[5].

2.4 Flexibility test

Using the way of nondestructive testing method to test microporous membrane softness. refer to ISO17235:2002(IULTCS/IUP36). Put A certain weight cylindrical stem At a certain speed and pressure on the polyurethane microporous membrane,use Safety clip fixed Microporous membrane well in advance,The extension of pu membranes is recorded as the flexibility of polyurethane microporous membrane.

2.5 Mechanics performance test

Mechanics performance test refer to the way of GB/T 1040-92, Cut polyurethane microporous membrane into 15 cm long, wide 1 cm. In the universal testing machine for the tensile properties of the test, take an average in each test two sample, Stretching speed was 100 mm · min-1.

2.6 Moisture permeable performance test

Moisture permeable performance test of polyurethane microporous membrane refer to the way of GB/T 12704.1-2009 textile fabric, permeability test method. Use moisture permeability cup to test. Moisture permeability cup and their accessories was shown in figure 2-1 below. Test temperature was 18 ℃, relative humidity was 90%, measuring time was 1 h, the measuring flow use airflow, use $CaCl_2$ as desiccant. Following were moisture permeable performance test formula of polyurethane microporous membrane[6~7].

$$WVTR = \frac{m_2 - m_1}{S \times (t_2 - t_1)} \times 24$$

Among:

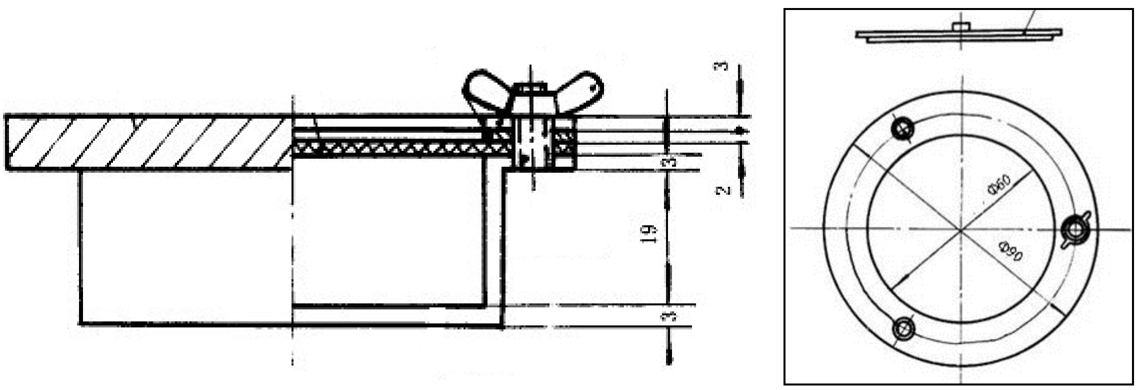
t_1------------- Test beginning time, h;

t_2------------- Test ending time, h;

m_1------------- At the beginning of the test moisture vapor transmission cup quality ,g;

m_2------------- At the end of the test moisture vapor transmission cup quality , g;

S-------------The area of moisture permeability cup edge, m^2;



Graph 2–1 Moisture permeability cup and their accessories

2.7 Polyurethane microporous membrane SEM

After metal spraying in the polyurethane microporous membrane section. Observe polyurethane microporous membrane microstructure with HITACH S-450 type scanning electron microscopy.

The experimental results and discussion

3.1 The density of smoke emission test results

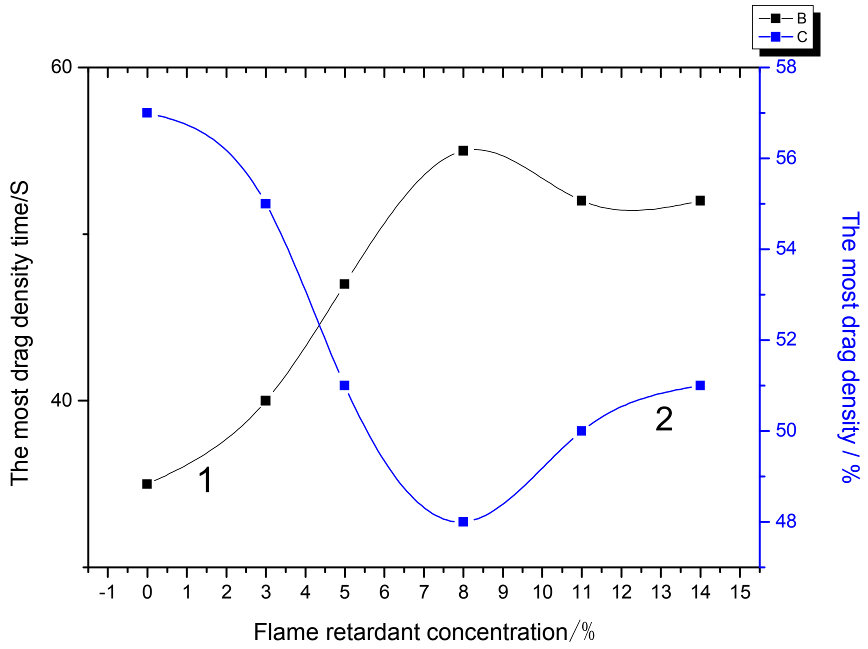


Figure 3–1 The concentration of flame retardant to the microporous membrane smoke density effect

3.2 The oxygen index test results

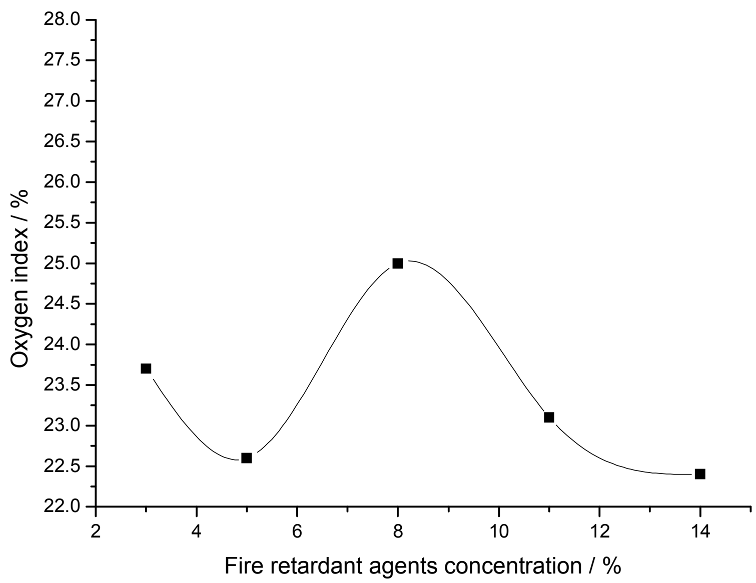


Figure 3–2 The concentration of flame retardant to the microporous membrane Oxygen index effect

In figure 3–2, Curve 1 being the most drag density time and flame retardant concentration relation curves, Curve 2 being The most drag density and flame retardant concentration relation curves. From the graph we can see with phosphorus-containing flame retardant additives increases, polyurethane microporous membrane to the density of the present time to spend time first increases, then decreases trends, The most drag density was also first increases, then decreases trend. When the flame retardant density was 8%, The most drag density time was longer than the others and the most drag density was also smaller than the others. From the density of smoke emission testing we can see when phosphorus add quantity of flame retardant agent for 8 % polyurethane microporous membrane flame retardant was the best effect.Figure 3-2 is microporous membrane oxygen index and flame retardant concentration of relation curves. Not add flame retardant polyurethane microporous membrane can ignite in the air, the oxygen index of less than 21, so it was not in listed in the figure, from the figure we can see after phosphorus flame retardant agent processing microporous membrane, the oxygen index increased obviously, it also explained that when add flame retardant, the polyurethane has flame retardant performance in a certain extent. And, as the phosphorus flame retardant agent adding amount increase, the oxygen index of microporous membrane trends first increases, then decreases, the oxygen index reached the maximum when added 8%, was 25.0,And then to increase the amount of flame retardants, the oxygen index will decrease, This was also the similar with the density of smoke emission curve. Analysis of the possible reasons were: when phosphorus-containing flame retardant burned, it will generate gather phosphoric acid and partial phosphoric acid, And the generation of partial phosphoric acid and gather phosphoric acid has certain dehydration effect, lead to the surface of protected polyurethane carbonized because of dehydration. And assembling partial phosphoric acid is kind of not easy volatile compounds, Chemical stability, thus form a layer of not easy volatile protective film, Generated carbonized layers reduces the fuel and the gas phase of smoke content produce. But,Because the carbonized layers only prevent produce flame and hot compounds are further oxidation, and those who have not been oxidation compounds will escape into the gas phase, being catched by free radicals which were released by dimethyl phosphate, Oxidation under control so promote the formation of smoke. So both aspects of the joint action, make the The most drag density of polyurethane tends to increased first and then decreases.

3.3 Vertical flame test results

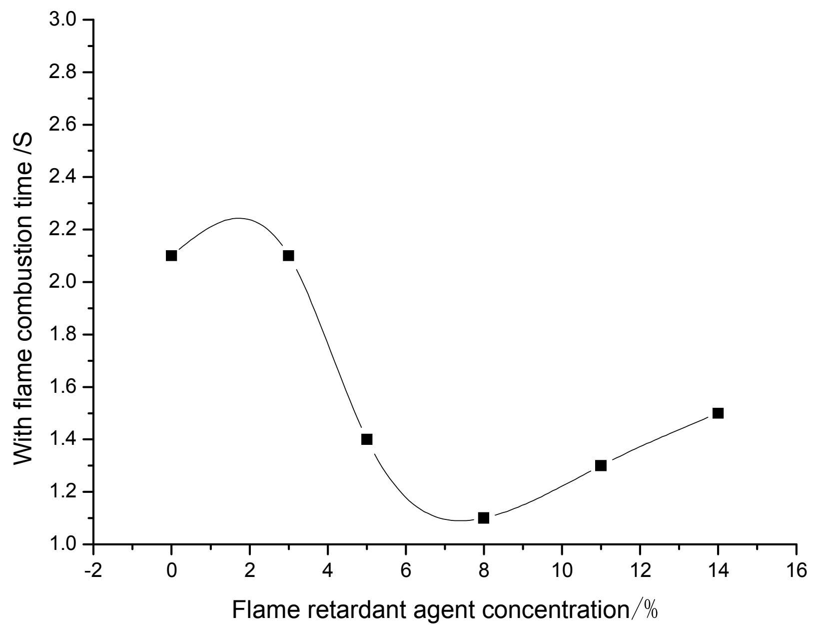


Figure 3–3 The concentration of flame retardant to the microporous membrane Vertical flame test results

Figure 3–2 was the microporous membrane with flame combustion time and flame retardant concentration of relation curves. Because of polyurethane microporous membrane time are no flame burning for 0, it did not listed in the picture. In the curve, it is known that the when different amount of phosphorus flame retardant agent was added to the polyurethane burns, With flame combustion time first increases and then decreases, when flame retardant additives was 8% the combustion time was the shortest. And with the increase of flame retardant additives, microporous membrane burning length also presents the first decrease and then increase.

3.4 Softness test results

Table 3.4 Different content of flame retardant polyurethane microporous membrane softness influence

Flame retardant additives /%	0	3	5	8	11	14
Softness /mm	5.87	7.45	8.16	7.73	8.06	7.69

Table 3.4 was different content of flame retardant to the polyurethane microporous membrane softness influence. Look from whole, after joining flame retardant, Polyurethane microporous membrane softness generally all increase, when phosphorus flame retardant agent content of 5%, 11%,the softness is large, we can see that phosphorus-containing flame retardant can improve the feel of Pu synthetic leather slightly.

3.5 Mechanical properties test and analysis

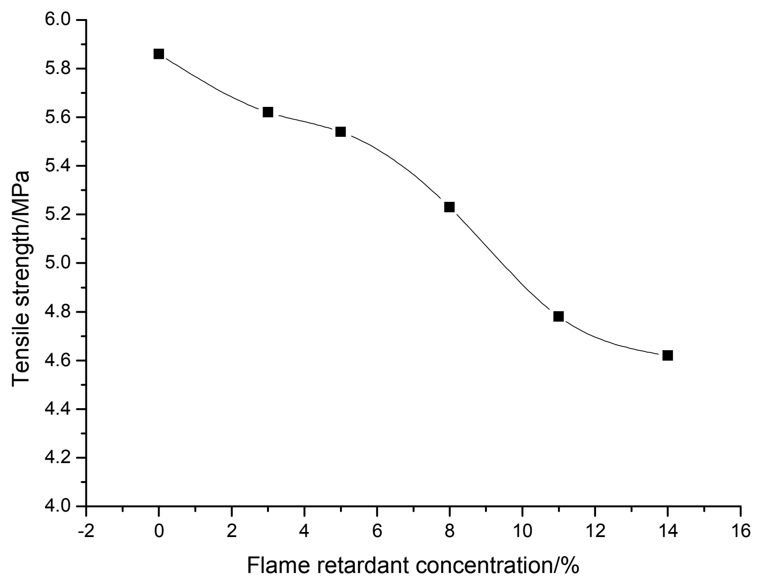


Figure 3–5 Phosphorus concentration of flame retardant agent polyurethane microporous membrane mechanics performance impact

Table 3.4 was different content of flame retardant to the polyurethane microporous membrane Mechanical properties influence. As can be seen from the graph, after adding phosphorus-containing flame retardants, The tensile strength of the microporous membrane was lower than blank samples, and with the increase of flame retardant,The tensile strength of the microporous membrane was a trend of gradual decrease. The reasons may be: on the one hand flame retardants and polyurethane macromolecular chain did not form strong interaction, Molecular inter-atomic forces was weak, which leaded to microporous membrane overall mechanical properties drop; On the other hand the formation of initial modulus is due to the forces produced in the space curly state of polyurethane macromolecules. Adding phosphorus flame retardant agent destroyed the forces between polyurethane macromolecular chain, cause microporous membrane overall mechanical properties of decline.

3.6 Moisture permeable performance test results

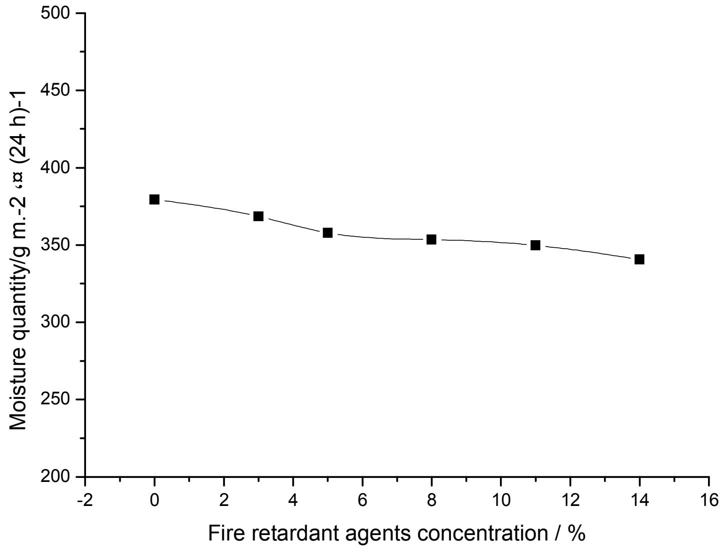
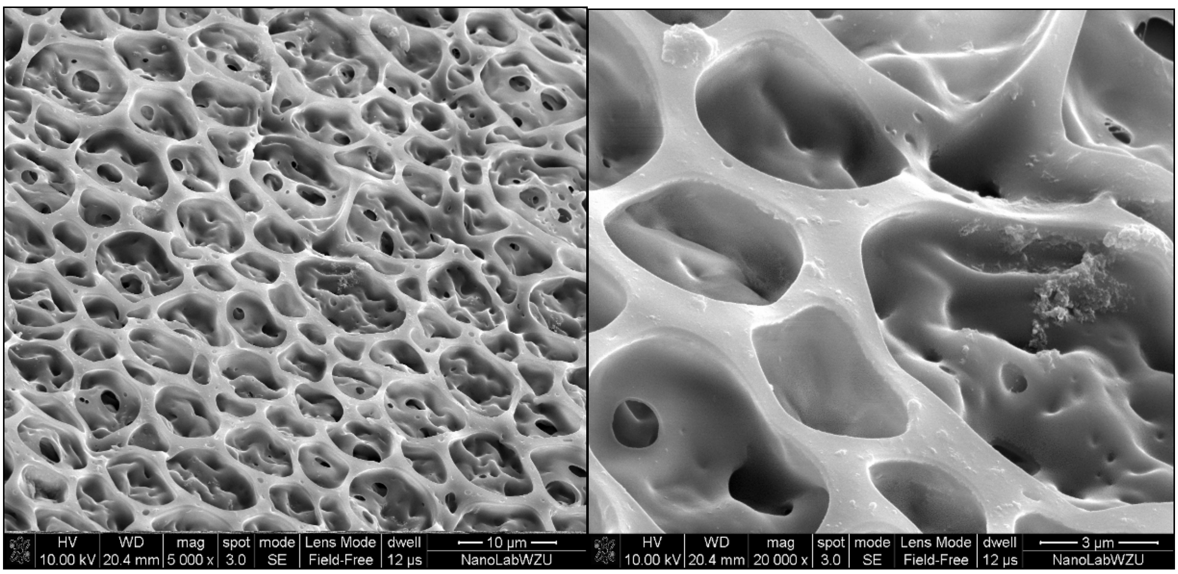


Figure 3–6 The concentration of flame retardant to the microporous membrane moisture quantity test results

Table 3.4 was different content of flame retardant to the polyurethane microporous membrane moisture quantity influence. As can be seen from the graph, adding phosphorus flame retardant agent had some effect on moisture quantity of polyurethane microporous membrane, but the impact is not big, the reason maybe flame retardant agents uniformity dissolved in pu solution, the process of forming porous did not change the pore structure and size in the later. But the adding of flame retardant agents increase the thickness of polyurethane microporous membrane slightly so the moisture quantity of polyurethane microporous membrane became lower.

3.7 Polyurethane microporous membrane SEM



Graph 3–7 When phosphorus flame retardant agent 8% polyurethane microporous membrane SEM section graph

Graph 3–7 was the chart that when phosphorus flame retardant agent was 8% polyurethane microporous membrane SEM section graph. From the graph we can see, Polyurethane microporous membrane was three-dimensional network structure which formed by the cell shape relization the structure. when phosphorus flame retardant agent was 8% we can see the microporous size of polyurethane microporous membrane were between 3~6 μm.

Summary

Comprehensive comparison we can see, the adding of phosphorus-containing flame retardant can improved the flame retardant performance of polyurethane significantly. When adding flame retardant additives for pure PU of quality score of 8%, Polyurethane microporous membrane flame retardant performance was the most ideal. The adding of phosphorus-containing flame retardant also didn't reduce microporous membrane other performance.

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