Synthesis of hydrophobic fluorinated polyurethanes and their properties of resistance to cavitation and wear

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ABSTRACT

Hydrophobic fluorinated polyurethanes (FPU) without hydrophilic —CH$_2$OH groups were prepared by introducing fluorine with the method of perfluoroalkyl ethanols (TEOH-10) for modification of diphenyl-methane-diisocyanates (MDI) and regulating the dosage and time of the MDI added. The experiment of water resistance indicates that the hydrophobicity of the FPU are very strong, owing to the low surface energy of fluorocarbon chains (-CF$_2$CF$_3$) migrating to the surface of material and forming the organic fluorine membrane which was equivalent to the hydrophobic effect of the lotus leaf. Especially when the molar dosage of TEOH-10 was 0.3–0.5 theoretical quantity of MDI, the water absorption of FPU is only between 0.0146% and 0.0182%, and the high cohesive pressure of FPU maintained at 10.31 MPa–10.79 MPa after 3200 h' water soaking. The erosion wear experiment showes that the anti-erosion performance of FPU continuously improved with the increasing of fluorine content, however, the cohesive pressure of FPU continuously reduced with the increasing of fluorine content. Comprehensive consideration of water conservancy and hydropower engineering application requirements of underwater protective coating, when the molar ratio of TEOH-10 versus MDI was about 0.5, the cavitation erosion amount of FPU reduced from 2.3756×10^{-3} kg to 0.9334×10^{-3} kg, and the cohesive pressure of FPU stayed over 10 MPa, which can be used as protective coating of flow components under water.

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Cavitation was proposed and used for the first time by Forude, Barneby and Parsnos 100 years ago when they investigated what caused the performance degradation of steamer propellers. Cavitation wear occurs near the surface of the material there bubble burst. According to the calculations by Forude [1], the water hammer effect can reach the frequency of 100,000–200,000 times per second as a result of the bubble formation, growth and collapse, and the maximum pressure of the bubble collapse can reach 2200 atmospheres which make flow surface of the turbine under enormous local impact of repeated load. The partial surfaces of flow components were eroded into holes like honeycomb, and even become spongy under repeated impact load, resulting in a sharp decline in strength of materials, not up to the expected service life, a serious threat to the safe operation of turbines. Therefore, cavitation mitigation is important to ensure the normal and safe operation of turbines [2–6].

Cavitation wear is a phenomenon associated with fluid mechanics. Many researchers who have done a lot of research work in the nature of cavitation wear and the fluid characteristics. They slowed the cavitation wear of the flow components by the design of streamline contour of the blade head and the even distribution of the pressure on the back of the blade [7,8]. However, it can only avoid the generation of cavitation wear to a certain extent by designing and changing fluid properties. To minimize the hazards of cavitation wear, comprehensive measures should be combined with the optimization of materials and surface protection. In the aspect of optimizing material, alloy steel with excellent anti-cavitation performance (such as ZG0Cr16Ni5Mo, GX5CrNi13-4V1, 0Cr13Ni5Mo) are used as the material of domestic and foreign flow components so far. In terms of surface protection, it means that the surface of flow components is coated with an anti-cavitation wear of the coating material which can avoid effectively cavitation wear. It had been simple to measure the properties of cavitation-resistant by the hardness of coating; and such coatings are mostly hard chrome nickel (Cr-Ni) coating. But practice had proved that the properties of anti-cavitation of materials with high hardness were poor

because of materials with high hardness prone to fatigue failure under repeated impact of the bubble collapsing [9].

In recent years, people continue to study and perfect the fatigue mechanism of cavitation damage, and they suggested that we should first consider the material itself must have a high strength and toughness, high anti-fatigue strength and good dynamic mechanical properties when designing anti-cavitation coating material, which can absorbs and buffers the repeated impact force of the bubble collapsing, enhancing the properties of anti-cavitation [10]. And polyurethane elastomer is the most promising material in such protective coatings, it has been widely used in mining transportation, concrete mixers and other areas of dry lining anti-erosion and sediment wet anti-abrasion coating owing to its excellent performances of anti-fatigue toughness and resistance to abrasion. With the continuous improvement of the physical properties of polyurethanes and construction technology, polyurethane elastomeric coating being used as protective coating which is abrasion resistant of underwater concrete and steel are more frequently in hydraulic engineering, and it shows good performances of resistance to high temperature toughness, fatigue and cavitation wear. However, there is a drawback that hydrophilic —CH_2OH groups are easy to absorb water resulting in water resistance of polyurethanes decreasing, which seriously affect the anti-cavitation performance and service life of polyurethanes coating [11].

Currently, the main method to improve the water resistance of the polyurethanes is introducing hydrophobic structure and cross-linked structure into the polyurethane chains. The introduction of hydrophobic structure is mainly fluorine-containing segment and silicon segment [12]. Compared with the fluorine-containing segment, the silicon segment typically reduces the bonding properties of the polyurethane coating to the substrate. Even though expensive fluorine element, FPU combines the advantages of polyurethane and fluorine-containing compound, which make the FPU research still become a craze because of its high strength, fatigue resistance and high cushioning properties, water resistance, solvent resistance and chemical resistance, low surface tension and low friction coefficient.

According to structural characteristics of polyurethane, fluorine element can be introduced into polyisocyanate, polyol compound, chain extender agents and capping agents. There is no doubt that each method has advantages and disadvantages. Hollander and others [13] prepared a FPU with a fluorine-containing isocyanate ($C_6F_4(OCN)_2$), which had high strength but poor flexibility; Turri and others [14] prepared a FPU with fluorine-containing polyether glycols (ZDOL) and isophorone diisocyanate (IPDI), which had a low surface tension and acid resistance, but the dynamic mechanical properties of materials dropped because of internal micro-phase separation imperfect; Tang and others [15] prepared a FPU by using fluorinated capping agent, which has the advantage of low surface energy and water resistance, but it has little effect on the polyurethane-modified because the amount of fluorine introduced as the end-capper is very low. In order to meet requirements that the anti-cavitation material must have water resistance, toughness, fatigue resistance and excellent dynamic mechanical properties and many other performances, this paper firstly introduced fluorine element using the method that perfluoroalkyl ethanols are merged into diphenyl-methane-diisocyanates (MDI), which not only avoid the drawbacks of poor material flexibility caused by the fluorine-containing isocyanate halide, but also improve the water resistance of polyurethane by controlling the mode of MDI was added during the reaction in order that the hydrophilic —CH_2OH groups are completely replaced by hydrophobic —$COOCH_3$ groups. At last, comprehensive consideration of the fluorine-containing polyurethane as an underwater anti-cavitation coating, this paper determined the optimum amount of perfluoroalkyl ethanols through contact angle measurements, water absorption test, adhesion test, the friction coefficient test and cavitation-resistant materials experiments.

1. Experimental

1.1. Materials

Diphenyl-methane-diisocyanates (MDI), chemically pure, 95%(GC&T). Polytetramethylene ether glycol (PTMEG), its molecular weight is 1000, vacuum dehydration for 2 h at 80 °C before used. Perfluoroalkyl ethanols (TEOH-10), chemically pure, 98%(GC&T). Triethylene glycol (TEG), chemically pure, 99%(GC&T). The solvent used in the experiment have N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), tetrahydrofuran (THF) and butanone. These solvents are chemically pure.

1.2. Preparation of fluorined polyurethanes (FPU)

In this paper, the three-step method is used for the synthesis of fluorined polyurethanes, as shown in Fig. 1. The theoretical amount of MDI was dissolved in DMF before the experiment, and the solution was placed in another beaker A, beaker B and beaker C according to the proportion of 80%, 10% and 10%, which can control the timing and amount of MDI added during the reaction.

The first step is the synthesis of F-MDI whose one end is perfluorinated chain segment. The second step is adding polytetramethylene ether glycol (PTMEG) to synthesize polyurethanes prepolymer. The third step is expanding the chain and cross-linking reaction by the addition of a chain extender TEG, and then seal the end by the addition of methanol.

1.2.1. Synthesis of F-MDI
Firstly, the MDI solution in the beaker A was poured into the four-mouth flask equipped with a stirrer, a thermometer, a constant pressure funnel and under the protection of nitrogen. Then the TEOH-10 was dissolved in the DMF and added into the four-mouth flask with a constant pressure funnel at the dropping speed of 2–4d/s and the temperature of 60 °C. At the same time, the mixing speed was kept at a certain value, thus it can avoid the concentration of TEOH-10 in the partial reaction area too high. Otherwise, the TEOH-10 would react with both —NCO groups of MDI ends and next polymerization reaction of F-MDI and PTMEG would not happen. After the dropping process was finished, this reaction lasted 2 h at the temperature of 50 °C.

1.2.2. Synthesis of prepolymers
The temperature of reaction system was increased to 60 °C after the previous reaction was finished. The PTMEG was added into the four-mouth flask and stirred for 1 h. Then the MDI in the beaker B was poured into the four-mouth flask and stirred for half an hour to make sure the mass fraction of the —NCO groups in the free state was about 0.43 wt%. The fluorinated polyurethane prepolymers were synthesized in this process and the PTMEG plays the role of the soft segment.

1.2.3. Chain extension and sealing reaction
The TEG was added into the prepolymer and this reaction was kept for 2 h at the temperature of 75 °C. Then the MDI in the beaker C was poured into the four-mouth flask, and this reaction was kept for half an hour in order that one side of the molecular chain end with —NCO. After that, the end was sealed by the addition of methanol and was mixed for 2 min to make methanol mixed evenly. At last, the reaction material was poured on the alloy steel sheet whose material was 0Cr13Ni5Mo and its surface was coated with 100 μm epoxy dual component base adhesive, then