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Preparation and performance of the modified high-strength/high-modulus polyvinyl alcohol fiber/polyurethane grouting materials

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HIGHLIGHTS

- The PVA fibers were successfully modified by APTES or MDI.
- The PVA fiber modified by MDI showed more hydrophobicity and more rough surface than that of PVA fiber modified with APTES.
- The modified PVA fibers can increase the interfacial adhesion with PU matrix remarkably.
- The best overall performance of composites can be achieved when the weight fraction of modified PVA fibers is 0.1%.

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ABSTRACT

In this study, modified polyvinyl alcohol fiber (MPVA) filled polyurethane (MPVA/PU) grouting materials with high interfacial bonding strength were prepared. Firstly, the high-strength/high-modulus PVA fibers were modified by γ-aminopropyl triethoxysilane (APTES) and diphenyl-methane-diisocyanate (MDI) respectively. The chemical structure, surface morphology and hydrophilicity were characterized by FT-IR, XPS, SEM and contact angle analysis. Second, the performance of PU mixed with different dosages of modified PVA fibers as the grouting material was studied. The results showed that mechanical properties and hot air aging resistance of the MPVA/PU composite were significantly increased compared with pure PU. In particular, it also can be found that modified PVA fiber bring better interface adhesion, especially, when the dosage is 0.1%, the best overall performance of MPVA/PU can be achieved. SEM analysis demonstrated that the interface adhesion between modified PVA fiber and PU was obviously improved.

1. Introduction

Grouting material, known as a special kind of slurry, has been widely used in repairing or reinforcing the loose or broken structures including roadway, bridge and the coal mine, due to its strong adhesion, easy manipulation and high permeability into the micro fracture [1–3]. In the last few decades, various materials including water glass (WG) [4], silica sol [5], methacrylate [6], cement [7], polyurethane (PU) [2,8], as well as epoxy [9,10] have been developed as grouting materials, depending on the different actual demand of grouting. Among the above-mentioned grouting materials, PU has been attracted tremendous interest in terms of their outstanding advantages, such as light weight, low viscosity, good permeability, low thermal conductivity and good mechanical performance [2,8,11], which utilizing the rapid chemical reaction between the isocyanate and polyol compound and obtained high mechanical strength to repair or reinforce. Moreover, the PU-based grouting materials exhibit the secondary filling ability and high permeability into micro fracture due to CO_2 exerted from the reaction between isocyanates and water, thus obtained better mechanical strength for the broken matrix, which is not the case compared with other grouting materials [12].

Although the highly efficient consolidation of PU grouting materials has been achieved in recent years. It should be noted that PU grouting materials is far from optimal, such as high cost, poor barrier performance and inflammability, which limit their practical applications [13]. The strength and poor barrier performance of PU grouting material cannot fully meet the requirements of reinforcing the broken roof in the coal mine. To overcome the limitations, more attention is paid to the nanoparticles, fibers or other additives that can improve their mechanical and thermal properties

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[14–16]. For instance, clay, montmorillonite, silica nanoparticles and calcium carbonate have play important roles in improving mechanical property, abrasive resistance and thermal stability [17–22]. It should be noted that, nonetheless, the main disadvantage of the additives is agglomeration and incompatibilities with the polymeric matrix due to its high surface energy and badly consistent interface [23,24]. In most cases, it is difficult to achieve homogeneous dispersion in polymeric matrix well. Consequently, many researchers devote to explore for some other materials and search new approaches (e.g. modified the surface of the additives) to achieve PU composites with improved performance.

The high-strength/high-modulus PVA fiber, owned high crystallinity and high degree of orientation, is one of the most frequently used reinforcing material elements in cement products due to their excellent mechanical properties, good affinity and adhesion with cements, as well as low price [25–27]. Ohno developed strain hardening ductile fiber reinforced geopolymer composites by using randomly oriented short PVA fibers [28]. Chen found that the concretes with PVA fiber are beneficial in restricting the drying shrinkage, increasing the split tensile strength and restraining the initiation and development of cracks in cement pastes and concrete [29]. In view of properties of PVA fibers, the composite strategy combined the advantages of PVA fibers and PU is an important consideration in the performance improvement of PU grouting material. It is expected that the combination of PU with PVA fibers into the composite grouting material may integrate the advantages of two materials but avoid their drawbacks, produced a more effective grouting material for reinforcement. However, the existence of surface hydroxyls in the PVA fibers may result in an incompatibility with the PU matrix, which negatively affects the dispersion and interfacial adhesion of PVA fibers in PU matrix, thereby affect the mechanical properties of the resulting grouting materials [14,16].

In this study, combining the advantages of the PVA fibers and PU, we proposed that the modified PVA could be reacted with the PU matrix during the preparation, forming a chemical bridge to improve the interfacial adhesion between them, thereby improve the properties of the resulting grouting materials. To obtain the desired effect, γ-aminopropyl triethoxysilane (APTES) and diphenyl-methane-diisocyanate (MDI) were selected and modified the PVA fibers, as shown in Scheme 1. The performance of PU mixed with different types and dosages of modified PVA fibers as the grouting material was studied. The possible mechanism was also proposed.

2. Experimental

2.1. Materials

High strength and high modulus PVA fiber with 6 cm length was supplied by Changzhou Tianyi Engineering Fiber Co., Ltd. 4,4′-diphenylmethane diisocyanate (MDI) was purchased from Germany Bayer Co., Ltd. Polyaryl polymethylene isocyanate (PAPI) was purchased from Wanhua Chemical Group Co., Ltd. Polyether polyol N303 was supplied by Jiangsu Haian Petrochemical Plant Co., Ltd. γ-aminopropyl triethoxysilane (APTES) was provided by Nanjing dawn Chemical Group Co., Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

2.2. Characterization

The chemical structures of the PVA fiber which was modified by APTES and MDI were analyzed by the Fourier transform infrared spectroscopy (FTIR) (NEXUS-870, Nicolet, USA), using air as background, scanning from 4000 cm^{-1} to 500 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a VG ESCALAB-MK-II spectrometer equipped with AlKa X-ray source, operated at 150 W. The morphologies of the modified PVA fibers and MPVA/PU grouting materials were performed on a scanning electron microscope (SEM) (S-4800, Hitachi, Japan) operating at 3 kV. The contact angle was measured by a contact angle measurement system (KRUSS, DSA10-Mk2, Germany). Thermo degradation was detected by Thermo Gravimetric Analyzer (Pyris-1, PE, America) under nitrogen atmosphere in temperature range from 50 °C to 600 °C at a heating rate of 10 °C /min. Tensile strength and bonding strength was recorded on a microcomputer control electronic testing machine (UTM-2000, Xinsansi, China) according to the standard of GB/T1040-2006 and GB/T7124-2008 at a speed of 20 mm/min. The notched impact strength as accomplished by using a pendulum impact testing machine (ZBC1400-1, Xinsansi, China) according to the standard of GB/T1043-2008, the notched width is 2 mm. All the samples used for mechanical performance testing were dumb-bell specimens with a dimension of 100 mm × 20 mm × 10 mm. The viscosity of the grouts was measured by rotational digital viscosimeter (NDJ-5S, Shanghai Heng Ping Scientific Instruments Co., Ltd. China) at 25 °C after mixed the component A and component B solutions in 30 min. The dumbbell-shaped specimens were placed in a thermal aging oven (BPG-9050AH, Shanghai Yiheng Co.Ltd. Inc, China) at 120 °C for 24 h, and then were kept at room temperature for 24 h before further tests.

2.3. Surface modification of the PVA fiber by APTES (APTES-PVA)

1.0 g of PVA fiber was dispersed in 150 mL ethanol and then stirred at room temperature for 30 min to obtain a well dispersed PVA fiber suspension. Given amount of the APTES was added into the PVA fiber suspension at 75 °C for 4 h under stirring. The precipitate was filtrated and washed with acetone for three times. Finally, the products were dried at 45 °C for 12 h and then kept in a desiccator for characterization. The grafting rate measured by gravimetric method is about 5.78% [30].

2.4. Surface modification of the PVA fiber by MDI (MDI-PVA)

1.0 g of PVA fiber was dispersed in 150 mL distilled methylbenzene and then stirred at room temperature for 30 min to obtain a well dispersed PVA fiber suspension. Given amount of the MDI and stannous octoate were added into the PVA fiber suspension at 85 °C for 4 h under stirring. The precipitate was filtrated and washed with acetone for three times. Finally, the products were extracted by soxhlet extraction for 4 h, and dried at 45 °C for 12 h before keeping in a desiccator for characterization. The grafting rate is about 3.92% [30].

2.5. Preparation of MPVA/PU composites

The total amount of two-component raw materials, additives and catalysts was controlled by 100 g, and the molar ratio of hydroxyl and isocyanate groups was set at 1:1. Firstly, predesignated weight fractions of the PVA fiber (0.05–0.2%) were mixed with polyether polyol N303, denoted as component A. PAPI, stannous octoate and other additives were introduced into another plastic container, denoted as component B. Subsequently, the solutions in the above two plastic containers were mixed by vigorous stirring, and then was put into the mould for 72 h to solidify under the room temperature. The rectangular specimens with different size were used for the tensile strength, bonding strength, and impact strength analysis. Each data was got by the average of the test results with five samples.