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Flexible and stretchable polyurethane/waterglass grouting material

Zhengpeng Yang, Xuefeng Zhang, Xuan Liu, Xuemao Guan, Chunjing Zhang *, Yutao Niu

Institute of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China

HIGHLIGHTS

- Flexible and stretchable polyurethane/waterglass grouting material was prepared via a facile and effective strategy.
- The grouting material showed a large elongation of up to 137%.
- A probable formation mechanism of grouting material was proposed.
- The grouting material exhibited favorable thermostability and repairment performance.

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ABSTRACT

Flexibility and stretchability are of ever increasing importance in constructing high-performance grouting materials. Herein, a facile, effective and cost-efficient strategy to make organic-inorganic hybrid chemical grouting material in a "flexible and stretchable" way was based on polymerization of carbon double bond and excellent synergistic interactions among *N*-Methylol acrylamide, butenediol, waterglass and prepolymer. Upon the optimal percentages of waterglass (44%), *N*-Methylol acrylamide (3.5%), butenediol (1.5%), Alkylphenol polyoxyethylene (OP-9, 0.5%), 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (0.35%), 2,2-dimorpholinodiethylether (DMDEE, 0.15%) and prepolymer (50%), the obtained polyurethane/waterglass grouting material with three-dimensional interpenetrating network structure displayed an excellent flexibility, satisfactory compressive strength of 13.4 MPa at 50% compression state, and relatively large elongation of up to 60% with a stable stretching for 200 times. The grouting material was mainly composed of amorphous polyurethane and crystalline polysilicic acid/$NaHCO_3$/Na_2CO_3 composite, and its probable formation mechanism was proposed. Additionally, the grouting material possessed favorable thermal stability and repairment performance for roadway cracks. This work may open a simple and convenient avenue for the preparation of organic-inorganic hybrid chemical grouting material with flexibility and stretchability.

1. Introduction

Grouting, known as a technology for repairing and strengthening, has been widely adopted in recent years to reinforce the loose or broken matrixes [1–3]. Currently, Flexibility and stretchability are of practical importance in constructing high-strength, strong-permeability grouting materials owing to the requirement of construction (etc. mine, roadbed, bridge).

The chemical grouting materials have been widely explored for a variety of applications to include roadway, bridge, defense and underground engineering due to their strong adhesion, easy manipulation and high permeability into the micro fracture of broken matrix [4,5]. To realize the high-performance grouting reinforcement, various chemical grouting materials such as polyurethane [6,7], waterglass [8,9], epoxy resin [10], acrylamide [11], methacrylate [12], acrylate [13] and lignin [14] have been developed. Among the aforementioned chemical grouting materials, polyurethane and waterglass have been attracting tremendous attentions for years in terms of their extraordinary properties. More specifically, polyurethane possesses light weight, low viscosity, good permeability, low thermal conductivity and high mechanical performance [15–17], while the waterglass shows high thermal stability, low cost and nontoxic nature [18,19]. The highly efficient consolidation of polyurethane and waterglass grouting materials has been achieved, nevertheless, they show some drawbacks, such as high cost, flammability, poor barrier property and thermal stability of polyurethane [20,21], and poor curing controllability and low mechanical properties of waterglass [22], which limit their practical applications. Therefore, finding a facile, effective and cost-efficient

* Corresponding author.
E-mail address: chunjingzhang2013@163.com (C. Zhang).

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way to achieve polyurethane or waterglass grouting materials with improved performance is highly desirable.

The composite strategy is an important consideration in the performance improvement of materials. In view of respective properties of polyurethane and waterglass, it is expected that the combination of polyurethane with waterglass into the organic-inorganic hybrid grouting material may integrate the advantages of two materials but avoid their drawbacks, producing a more effective and economic grouting material for reinforcement. Recently, the waterglass-modified polyurethane grouting materials with flame resistance, low cost, high thermal stability and mechanical properties have been developed, and presented a satisfactory performance towards grouting reinforcement [23,24]. Our group also reported the protocol of the synthesis of silicate/polyurethaneurea composites based on dipropylene glycol dibenzoate, the obtained composites exhibited high thermal stability and fascinating mechanical performance [25]. However, most of these polyurethane/waterglass composite grouting materials are fragile and stiff, which cannot meet all of the requirements in many practical applications, particularly in these strengthening engineering fields with large load disturbance and temperature fluctuation. Up to date, few attempts have been successfully made to achieve flexible and stretchable polyurethane/waterglass composite grouting material although we are aware of its lower cost and practical importance for reinforcement. Thus, Searching for some new materials and methods is urgently demanded to meet the rapid growing demand of flexibility and stretchability in practical applications.

In this work, a flexible and stretchable polyurethane/waterglass grouting material was prepared successfully via a simple and effective strategy. The microstructure, composition and property of the resultant grouting material were explored in detail, and its possible formation mechanism was proposed.

2. Experimental

2.1. Materials

The prepolymer (16.7 wt% NCO, 420 mPa·s) was purchased from Shanghai Hecheng Polymer Science and Technology Co., Ltd. Waterglass ($Na_2O{\cdot}nSiO_2{\cdot}mH_2O$, modulus 2.3) was supplied by Zhengzhou Jiankete Engineering Materials Co., Ltd. *N*-Methylol acrylamide was purchased from Tianjin Tianfu Chemical Industry Co., Ltd. Butenediol was supplied by Zhejiang Jinjinle Chemical Industry Co., Ltd. Initiator (2,2′-azobis[2-(2-imidazolin-2-yl)propane]) was purchased from Shanghai Hengyuan Biological Technology Co., Ltd. Emulgator (OP-9, 93 mg KOH/g) was obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd. Catalyst (DMDEE) was supplied by Shanghai Rongrong Chemical Co., Ltd. All other chemicals were of analytical grade and purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. The main parameters of the above materials were tabulated in Table 1.

Table 1
The main parameters of materials.

Ingredient	Index
Prepolymer	NCO content (%): 16.7, Viscosity (25 °C, mPa·s): 420
Waterglass	Modulus: 2.3
N-Methylol acrylamide	Purity (%) ⩾98
Butenediol	Viscosity (20 °C, mPa·s): 21.8, Purity (%) ⩾99
2,2′-azobis[2-(2-imidazolin-2-yl) propane]	Molecular weight: 323, Purity (%) ⩾98
OP-9	Hydroxyl number (mg KOH/g): 93
DMDEE	Amine value (mmol/g): 7.9–8.1, Purity (%) ⩾99

2.2. Preparation of grouting material

The preparation of grouting material was performed according to our method with some modification [25]. Specifically, waterglass, *N*-Methylol acrylamide, butenediol, emulgator, initiator and catalyst with weight ratio of 88:7:3:1:0.7:0.3 were added into a plastic cup and homogenized at 300 rpm for 5–10 min, denoted as component A. The prepolymer was introduced into another plastic container, denoted as component B. Subsequently, the equal solutions in above two plastic containers were mixed for 30 s by vigorous stirring (500 rpm), and then a fully cured specimen for tests was achieved under the room temperature. The detailed preparation information of grouting material was illustrated in Table 2.

2.3. Characterization

Scanning electron micrograph (SEM) was performed on a Hitachi S-4800 field emission scanning electron microscope (Hitachi Ltd., Tokyo, Japan) working at 15 kV. IR spectra were recorded using Fourier transform infrared spectroscopy (FTIR: Thermo Nicolet, WI. USA). Raman spectra were conducted on a Renishaw RM3000 Raman spectrometer (InVia, Renishaw Co., UK). X-ray diffraction (XRD) was carried out on a Bruker-AXS D8 X-ray diffractometer using Cu Kα radiation. The thermo gravimetric data were obtained between 28 and 800 °C with the DSC-TGA Q600 thermal analyzer system at a heating rate of 5 °C/min, under air atmosphere.

2.4. Mechanical measurements

All the tensile and compressive strength measurements were carried out on a universal testing machine (Model WDW-20, Jinan Hengruijin Instrument Equipment Co., Ltd, China) at room temperature. The tensile tests were done according to the standard of GB/T1040.2-2006 with sample dimensions of $25 \times 5 \times 2$ mm^3, and the compressive tests were performed according to the standard of GB/T1041-92 with sample dimensions of $40 \times 40 \times 40$ mm^3.

3. Results and discussion

The route of design and fabrication of the flexible and stretchable polyurethane/waterglass grouting material was schematically shown in Fig. 1. *N*-Methylol acrylamide, butenediol, initiator, emulgator and catalyst were added to waterglass under continuous stirring to form a homogenous solution, denoted as component A. The colorless prepolymer was used as component B. After facile mixing of components A and B, a stable milky solution was formed. The as-prepared uniform mixture was directed transformed into rectangular or square specimens via a room-temperature-curing process. Thus, the cured polyurethane/waterglass grouting material with flexibility and stretchability was finally fabricated.

The obtained polyurethane/waterglass grouting material exhibited the intriguing flexibility and good resistance to deformation as shown Fig. 2a. Bending had no damage to the grouting material

Table 2
The detailed preparation information of grouting material.

	Ingredient	Percentage (%)
Component A	Waterglass	44
	N-Methylol acrylamide	3.5
	Butenediol	1.5
	OP-9	0.5
	2,2′-azobis[2-(2-imidazolin-2-yl)propane]	0.35
	DMDEE	0.15
Component B	Prepolymer	50