Construction and Building Materials 116 (2016) 110–120

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of silane treatment on the mechanical properties of polyurethane/water glass grouting materials

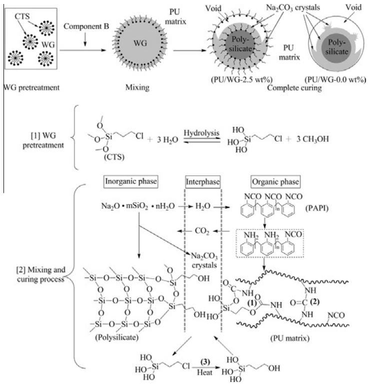
Zhenglong He [a,b], Qifeng Li [a,*], Junwei Wang [a], Ning Yin [a], Shuai Jiang [a,b], Maoqing Kang [a]

[a] *Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

HIGHLIGHTS

- The PU/WG grouting materials modified with CTS were synthesized.
- The incorporation of 2.5 wt% CTS in WG dramatically improved the mechanical properties of PU/WG hybrid materials.
- A probable mechanism of the functions of CTS in the PU/WG grouting material was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form 11 April 2016
Accepted 26 April 2016
Available online 3 May 2016

Keywords:
Polyurethane
Water glass
Grouting materials
Mechanical properties
Silane coupling agent

ABSTRACT

In this study, silane coupling agent 3-chloropropyltrimethoxysilane (CTS) was used for improving the distribution of water glass (WG) in the polyurethane (PU) matrix and increasing the crosslinking density of PU/WG grouting materials. The optimum dosage of CTS and the pretreatment time of WG were investigated. The effect of CTS on the surface property of WG and the fracture morphology of the PU/WG composites was studied by contact angle measurement and scanning electron microscopy, respectively. The effect of CTS on the mechanical properties of PU/WG grouting materials was systematically studied by compression test, fracture mechanical test, flexural test and dynamic mechanical analysis. The introduction of CTS in the PU/WG grouting materials improved the surface property of WG, the homogeneous distribution of polysilicate particles in PU matrix, the compressive property of PU/WG composites by 11.65–40.65%, the fracture toughness by 9.68%, the fracture energy by 21.33%, the flexural strength by 6.60%, the flexural modulus by 15.85%, and the dynamic mechanical properties of the composites. A possible mechanism of the functions of CTS in the PU/WG grouting materials was proposed.

1. Introduction

Throughout the history of mining industry, one of the most severe challenges is the fall of roof and rib due to the weak rock and structural discontinuities [1,2]. A widely used and time-proved technique for preventing such mine fatalities is to reinforce the broken coal and rock through grouting, which could connect and support the weak structure effectively. In the last few decades, various materials, depending on the purpose of grouting and local conditions, have been used as grouting materials, *e.g.*, water glass (WG) [3], silica sol [4], cement [5–9], polyurethane (PU) [10,11]

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* Corresponding author.
E-mail address: liqf@sxicc.ac.cn (Q. Li).

http://dx.doi.org/10.1016/j.conbuildmat.2016.04.112
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as well as epoxy [12]. Inorganic grouting materials such as cement are easy to shrink which results in unsatisfactory elasticity and reinforcing performance. Moreover, the poor penetration of inorganic materials results in a short length of grouting. While, the inflammability and high price of organic polymers, such as PU and epoxy, also limit their applications. Therefore, the composite grouting materials, such as PU/cement [13,14], epoxy/cement [12,15,16], PU/WG [17–20], have been developed to combine the advantages of inorganic and organic grouting materials. Among them, PU-based composite grouting materials exhibit unique advantages, e.g. the secondary filling ability for minor cracks and fissures due to carbon dioxide exerted from the reaction between isocyanates and water [21,22], which is not the case in the epoxy-based grouting materials. Moreover, the permeability of WG as a colloidal solution is superior to that of cement with large solid particles. These advantages make the PU/WG hybrid system an ideal grouting material for coal mine reinforcement. However, the existence of water molecules and the Si-O$^-$ and Si-OH groups in WG results in an incompatibility of WG with organic matrix, which negatively affects the size and distribution of polysilicate particles in PU matrix, thereby the mechanical properties of the resulting grouting materials.

Hence, some emulsifiers, resins or additives such as phosphate [23], vinylester [24], epoxy resin [25], and melamine/formaldehyde [26], have been used to achieve a fine water-in-oil (WG/PU) emulsion. However, to obtain the desired effect, a large amount of these emulsifiers, resins or additives are usually needed, which increases the cost significantly. Therefore, an efficient and cost-effective additive is urgently needed.

Silane coupling agents possess bifunctional groups, which show promising properties as additives in WG/polymer grouting materials. The bifunctional groups can react with inorganic fillers and polymer matrix, respectively, thereby forming a chemical bridge to improve the interfacial adhesion between them. Additionally, it can also improve the compatibility between the inorganic fillers and the polymer matrix, which is beneficial for the uniform distribution of fillers in polymer matrix. Generally, chloropropyl, epoxy, and amino-terminated silanes are used in PU system [27]. However, amine functional groups, like the alkoxy groups and epoxy groups, can also be anchored to the WG surface [28]. In this case, the bifunctional groups at both ends of the coupling agents anchor on the surface of WG, therefore no obvious change of the surface tension and no coupling functions were discovered. Moreover, after mixing the two components, the viscosity of the hybrid system increased dramatically due to the high reactivity of amine functional silanes with –NCO groups in the PU matrix. Therefore, 3-chloropropyltrimethoxysilane (CTS), with chloropropyl functional group, was selected as a model silane coupling agent in this work.

In this study, the effect of CTS on the mechanical properties (compressive, fracture, flexural and dynamic mechanical properties) of PU/WG grouting materials during the curing process was investigated based on the optimum dosage and pretreatment time of CTS. A possible mechanism of the functions of CTS in the PU/WG grouting materials was proposed.

2. Experiments

2.1. Materials

PU/WG grouting material used in this study is a bi-component inorganic-organic hybrid system. The composition of the PU/WG grouting material is listed in Table 1.

2.2. The optimization of CTS dosage and pretreatment time

In order to obtain the optimum CTS dosage and WG pretreatment time, a series of related optimization experiments were designed. The two optimized parameters (CTS dosage and WG pretreatment time) were analyzed by measuring the compressive strength of the PU/WG test specimens, which were prepared by using different contents of CTS in WG by weight (0.0%, 0.5%, 1.5%, 2.5%, and 3.0%) and different pretreatment time of WG (0 min, 15 min, 30 min, 45 min, and 60 min). The pretreatment was carried out by using a two blade paddle mixer at 300 rpm. Before the compression test, the specimens were cured at 23 ± 1 °C for 3 days.

2.3. Preparation of PU/WG specimens

The preparation of the PU/WG specimens is schematically shown in Fig. 1. First, glycerol and cyclohexylamine (used as the curing initiator) were added to the pre-prepared WG emulsion in a plastic cup and homogenized at 300 rpm for 5 min, denoted as component A (see Fig. 2-left). Component B (see Fig. 2-right), consisting of PAPI, GE-220, DOP (used as plasticizer), and CP-52 (used as filler), was also homogenized in the same way. After that, components A and B were mixed and

Table 1
Composition of the PU/WG grouting materials.

	Ingredient	Amount (g)	Properties
Component A	WG	100 ± 0.1	SiO_2/Na_2O molar ratio: 2.09–2.21 Baume (20 °C, Be′): 50.0–51.0 Na_2O (%) $\geqslant$ 14.00 SiO_2 (%) $\geqslant$ 29.50 Viscosity (mPa s): 600
	CTS	0–1.05 ± 0.02	
	Glycerol	1.5 ± 0.02	
	Cyclohexylamine	0.4 ± 0.02	
Component B	Polymethylene polyphenylene isocyanate (PAPI)	90 ± 0.1	NCO content (%): 30.5–32.0 Viscosity (25 °C, mPa s): 150–250 Density (25 °C, g/cm^3): 1.22–1.25 Acidity (HCl) (%) $\leqslant$ 0.05
	The polyether polyol (GE-220)	10 ± 0.1	Molecular weight (g/mol): 2000 Hydroxyl value (mg KOH/g): 54.5–57.5 Acid value (mg KOH/g) $\leqslant$ 0.08 Viscosity (25 °C, mPa s): 300–500 Moisture (%) $\leqslant$ 0.05
	Chlorinated paraffin-52 (CP-52)	13 ± 0.2	Chlorine content (%): 50–54 Density (50 °C, g/cm^3): 1.23–1.27 Viscosity (50 °C, mPa s) $\leqslant$ 300
	Dioctyl phthalate (DOP)	8 ± 0.1	Purity (%) $\geqslant$ 99 Density (20 °C, g/cm^3): 0.982–0.988, Moisture (%) $\leqslant$ 0.15