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Preparation and Performance Enhancements of Low-Heat-Releasing Polyurethane Grouting Materials with Epoxy Resin and Water Glass

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Abstract: Polyurethane (PU) grouting materials possess excellent fluidity and strong injectability. However, the high heat release during the reaction process restricts its application. In this study, with the addition of water glass (WG), a prepolymer was prepared by epoxy resin reacted with isocyanate to form modified polyurethane. The effects of epoxy resin and water glass on the compressive properties, expansion rate, structure of the cell, and maximum reaction temperature of the grouting materials were also investigated. The results showed that the cell size of modified PU was smaller and more regular, the maximum reaction temperature of the modified PU was reduced to 89 °C, and the compressive strength and expansion rate went up to 0.27 MPa and 57, respectively. This investigation will expand the application of PU grouting materials in underground engineering.

Keywords: polyurethane grouting material; composite materials; polymeric composites; prepolymer; heat release

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1. Introduction

Coal is one of the most important energy sources and the collapse of roofs caused by weak rock and structural discontinuities is a challenge in the coal mining industry [1]. Grouting materials, which can connect and support the weak structures in mines, have been commonly used to reinforce broken coal and rock in mines to prevent such mine fatalities [2]. Several inorganic materials have been used as grouting materials, for example, water glass (WG) [3–5], silica sol [6], and cement because they are inexpensive, easily obtained, and non-flammable; however, they shrink easily and the short grouting length that results from poor penetration limits their application [7].

Meanwhile, there are also many kinds of organic grouting materials, such as polyurethane and epoxy resin, and organic materials burn easily. Due to their ability to penetrate small cracks and voids easily, polyurethane (PU) grouting materials have good fluidity and strong injectability, and they have played an increasingly important role in coal mining [8]. Until recently, rigid polyurethane foam (RPUF) was used as grouting material due to the advantages of easy molding, corrosion resistance and high strength compared with traditional grouting materials. However, considering the real conditions of underground engineering, the poor ventilation and high amount of gas in the working environment, the application of polyurethane in underground engineering was limited as polyurethane is highly flammable. Therefore, it was necessary to modify traditional polyurethane and decrease the reaction temperature, combining the advantages of organic materials and inorganic materials while also enhancing the strength of grouting materials as far as possible to avoid potential danger [9–11]. However, because of the high heat release during the reaction process, which can easily cause a fire in a poorly ventilated area with high amounts

of gas, the application of PU grouting materials in underground engineering has been limited [12,13]. Recently, several investigations have been performed on the modification of PU grouting materials. Hong et al. selected sodium silicate as a reactive component to form inorganic microspheres-reinforced PU composite [14]. Feng et al. used water glass to prepare polyisocyanurate-WG materials; the strength increased up to 0.16 MPa and the reaction temperature was lower than pure PU [15]. Zhang et al. composed a novel PU modified with epoxy resin via copolymerization between polyurethane prepolymer (PUP) trimer and epoxy resin (E-44) [16]. However, these studies mainly focused on improving the performance of grouting materials, and no reports have focused on reducing heat release.

Herein, WG and low-viscosity epoxy resin (NPEF-170) were simultaneously employed to reduce the heat released and improve the strength of the grouting material. The reaction temperature, mechanical properties and the microstructure of the polyurethane composite foams were studied in detail.

2. Material and Methods Section

2.1. Materials

Poly ((phenyl isocyanate)-co-formaldehyde) (PAPI, NCO% was 32 wt%, industrial grade) was purchased from Shandong Yantai Wanhua Chemical Group Co., Ltd. (Yantai, China). Epoxy resin (NPEF-170, industrial grade) was purchased from Guangzhou Kuibang Chemical Co., Ltd. (Kuibang, China). Water glass ($Na_2O{\cdot}nSiO_2$, modulus(n) = 2.31, industrial grade) was purchased from Wuxi Yatai Chemical Co., Ltd. (Wuxi, China). Polyether polyols (HEP-330N, the hydroxyl value was 54 mg KOH/g, industrial grade), polyether polyols (HSH-303, the hydroxyl value was 408.8 mg KOH/g, industrial grade) were purchased from Hongbaoli Group Co., Ltd. (Nanjing, China). Glycerin (Analytical Reagent) was purchased from Wuxi Yatai Chemical Co., Ltd. (Wuxi, China). Foam stabilizer AK8805 (industrial grade) was purchased from Jiangsu Meister Chemical Co., Ltd. (Nanjing, China). and Tris(dimethyl amino methyl) phenol (DMP-30, Analytical Reagent) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Dibutyltin dilaurate (DBTDL, Analytical Reagent) was purchased from Shanghai Anyu Chemical Technology Co., Ltd. (Shanghai, China).

2.2. Methods

The WG-modified polyurethane (PU-WG) was prepared by polycondensation with the WG mixed with polyol and other auxiliary chemicals as Component A, and the PAPI as Component B. On this basis, epoxy resin was added through two methods; one approach was that epoxy resin was directly added to Component A (EPU-WG), and the other was that epoxy resin and isocyanate were firstly prepared as a prepolymer as Component B (EPUP-WG). The formulas for all samples are shown in Table 1 and the schematic illustration of EPUP-WG preparation is shown in Figure 1.

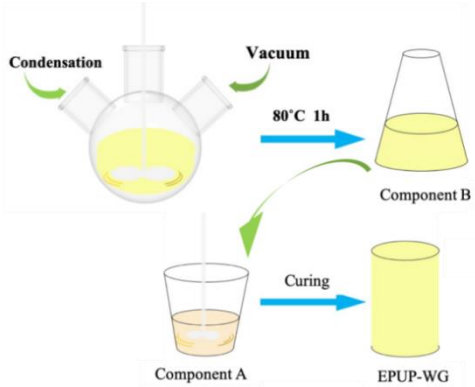

Figure 1. Schematic illustration of EPUP-WG preparation.

Table 1. Formulas of different grouting materials.

Sample	Component A										Component B
	HEP-330N (g)	**HSH-303 (g)**	**Glycerin (g)**	**AK8805 (g)**	**H_2O (g)**	**DMP-30 (g)**	**DBTDL (g)**	**WG (phr)**	**KH560 (g)**	**NPEF-170 (g)**	**PAPI (g)**
PU-WG-1	8.4	13.1	10	1.5	1.7	0.3	0.1	0	1.5	0	64.9
PU-WG-2	8.4	13.1	10	15	1.7	0.3	0.1	5	1.5	0	64.9
PU-WG-3	8.4	13.1	10	1.5	1.7	0.3	0.1	10	1.5	0	64.9
PU-WG-4	8.4	13.1	10	1.5	1.7	0.3	0.1	15	1.5	0	64.9
PU-WG-5	8.4	13.1	10	1.5	1.7	0.3	0.1	20	1.5	0	64.9
EPU-WG-1	8.4	13.1	10	1.5	1.7	0.3	0.1	0	1.5	28	64.9
EPU-WG-2	8.4	13.1	10	1.5	1.7	0.3	0.1	5	1.5	28	64.9
EPU-WG-3	8.4	13.1	10	1.5	1.7	0.3	0.1	10	1.5	28	64.9
EPU-WG-4	8.4	13.1	10	1.5	1.7	0.3	0.1	15	1.5	28	64.9
EPU-WG-5	8.4	13.1	10	1.5	1.7	0.3	0.1	20	1.5	28	64.9
	Component A									Component B	
EPUP-WG-1	8.4	10	10	1.5	1.7	0.3	0.1	0	1.5	28	64.9
EPUP-WG-2	8.4	10	10	1.5	1.7	0.3	0.1	5	1.5	28	64.9
EPUP-WG-3	8.4	10	10	1.5	1.7	0.3	0.1	10	1.5	28	64.9
EPUP-WG-4	8.4	10	10	1.5	1.7	0.3	0.1	15	1.5	28	64.9
EPUP-WG-5	8.4	10	10	1.5	1.7	0.3	0.1	20	1.5	28	64.9

2.3. Characterization

Scanning electron microscopy (Hitachi SU8010, Tokyo, Japan) was used to observe the fracture morphology of the foams, and the surface of the foam was sputtered with thick gold. The viscosity of the prepolymer and epoxy resin was measured by a rotary viscometer NDJ-79 at 25 °C. The experiment was stopped when the viscosity exceeded 200 mPa·s. Each sample was measured three times, and the arithmetic average of the three measurements was taken as the test result. A digital display temperature sensor (test temperature ranging from 55 °C to 150 °C, Jiangsu Yinxin Electric Heating Appliance Co., Ltd. Xinghua, China) was used to measure the reaction temperature of the sample, and the data were recorded every 10 s. The compressive strength was determined according to AQ/T1090-2020 under ambient conditions with a universal testing machine. The reported values were the average of at least 3 specimens. The size of the sample was determined according to GB/T6342-1996. Each size was the average of at least 3 specimens and the volume was calculated by the height and the diameter of the sample. The mass of the sample was measured to the nearest 0.5%, in grams (g), and the expansion rate was calculated by the following formula:

$$n = \frac{\rho_0}{\rho}$$

where

n is the expansion rate, and the unit is times;
ρ_0 is the average density of each liquid component of the material, in grams per cubic centimeter (g/cm^3);
ρ is the apparent core density of the cured product, in grams per cubic centimeter (g/cm^3).

3. Results and Discussion

The FTIR spectra of epoxy resin, PAPI and prepolymer are shown in Figure 2a. The spectra showed that the characteristic groups of the polyurethane prepolymer were the stretching vibration peak of carbonyl at 1729 cm^{-1}, which confirmed that the epoxy resin reacted with isocyanate during the pre-polymerization, and the hydroxyl group of epoxy resin peak was at 3058 cm^{-1}. The characteristic absorption peak of PAPI(-NCO) was observed at 2240 cm^{-1}. Compared with NPEF-170, the absorption peak of prepolymer at 3058 cm^{-1} became weaker and wider after the reaction between PAPI and epoxy resin; the infrared peak of prepolymer disappeared at 2240 cm^{-1}. Therefore, the synthesis of the modified epoxy resin was accomplished by the reaction between the isocyanate and the hydroxyl group. Figure 2b shows the FTIR spectra of EPUP-WG-1, EPU-WG-1 and PU-WG-1. The spectrum showed the C=O of the isocyanate trimer peak at 1710 cm^{-1}, and

the characteristic peak of oxazolidone (OX) ring was observed at 1763 cm^{-1}. For PU-WG-1, the characteristic peak of the oxazolidone ring disappeared [17].

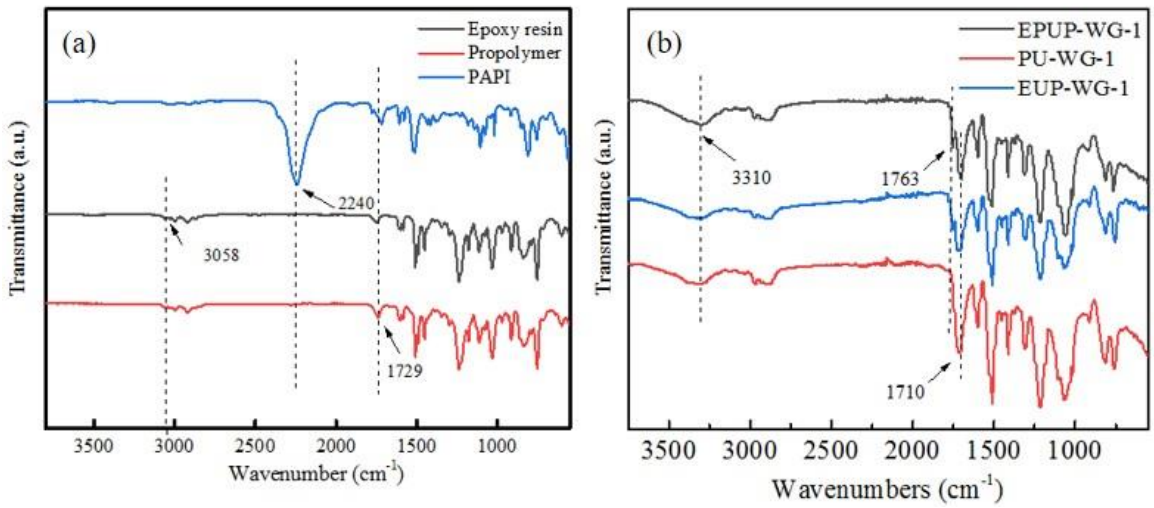

Figure 2. (**a**) FTIR spectrum of epoxy−isocyanate prepolymer, (**b**) FTIR spectrum of EPUP-WG-1, EPU-WG-1 and PU-WG-1.

The industry standard, AQ/T1090-2020 stipulated that the maximum reaction temperature (MRT) should be less than 95 °C. The reaction temperature was measured by a temperature sensor inserted into the center of the sample, and the reaction temperature reached the maximum in the 50th second for the PU-WG system (Figure 3a). For PU-WG-1, the MRT reached 124.6 °C, which was the highest among the PU-WG systems. With the addition of WG, the MRT of all systems decreased (Figure 3b), which indicated that WG reduced the MRT of the PU dramatically. One possible reason is that the generated CO_2 reacted with WG to form orthosilicic acid, and then much heat was absorbed when a dehydration reaction took place [14]. As Figure 3b shows, the MRT of the EPU-WG system was 148 °C, which was higher than the PU-WG system. This is because the addition of epoxy resin increased the content of the hydroxyl group (-OH), which could react with free isocyanate (-NCO) in the system [18]. However, due to the heat generated by the reaction of -OH in epoxy resin and -NCO was partly released in the process of the prepolymer, the MRT of EPUP-WG-1 was lower than that of EPU-WG-1. It is worth noting that the MRT of the three systems decreased significantly after 5 phr of WG was added; additionally, when the content of WG was 15 phr, the MRT of EPUP-WG system decreased further to 89 °C.

The industry standard, AQ/T1090-2020 stipulated that the compressive strength should be more than 0.01 MPa. As can be seen from Figure 3c, the addition of epoxy resin can enhance the compressive strength; the EPUP-WG-4 with 15 phr of WG and epoxy resin showed the highest compressive strength, which was 0.27 MPa. However, with the increase in WG, the compressive strength decreased dramatically in three types of grouting materials. When the content of WG reached 15 phr, the compressive strength of the system tended to be stable.

The CO_2, which was produced from the reaction between isocyanates and water, served as the forming agent. Therefore, the amount of water played a crucial role in the expansion rates [19]. As can be seen from Figure 3d, the expansion rates increased with the addition of WG and finally stayed at a stable value. This was because the addition of WG led to an increase in water in the system, and then the content of CO_2 in the system increased, while the content of -NCO was fixed. Compared with the PU-WG system, the -OH of the epoxy resin could react with -NCO to reduce the expansion rate of the EPU-WG grouting material. The -NCO, which reacts with polyols to form CO_2, was further reduced during the process of prepolymer preparation. Therefore, the expansion rate of the EPUP-WG system was the lowest when the content of WG was less than 15 phr. Since

the content of -NCO was fixed and the silicate could consume a part of the CO_2 [20], the production and consumption of CO_2 in the system reached an equilibrium value when the WG was 15 phr. At this time, the expansion rate of both the EPU-WG and EPUP-WG systems was almost 57 and did not increase with the increase in WG content.

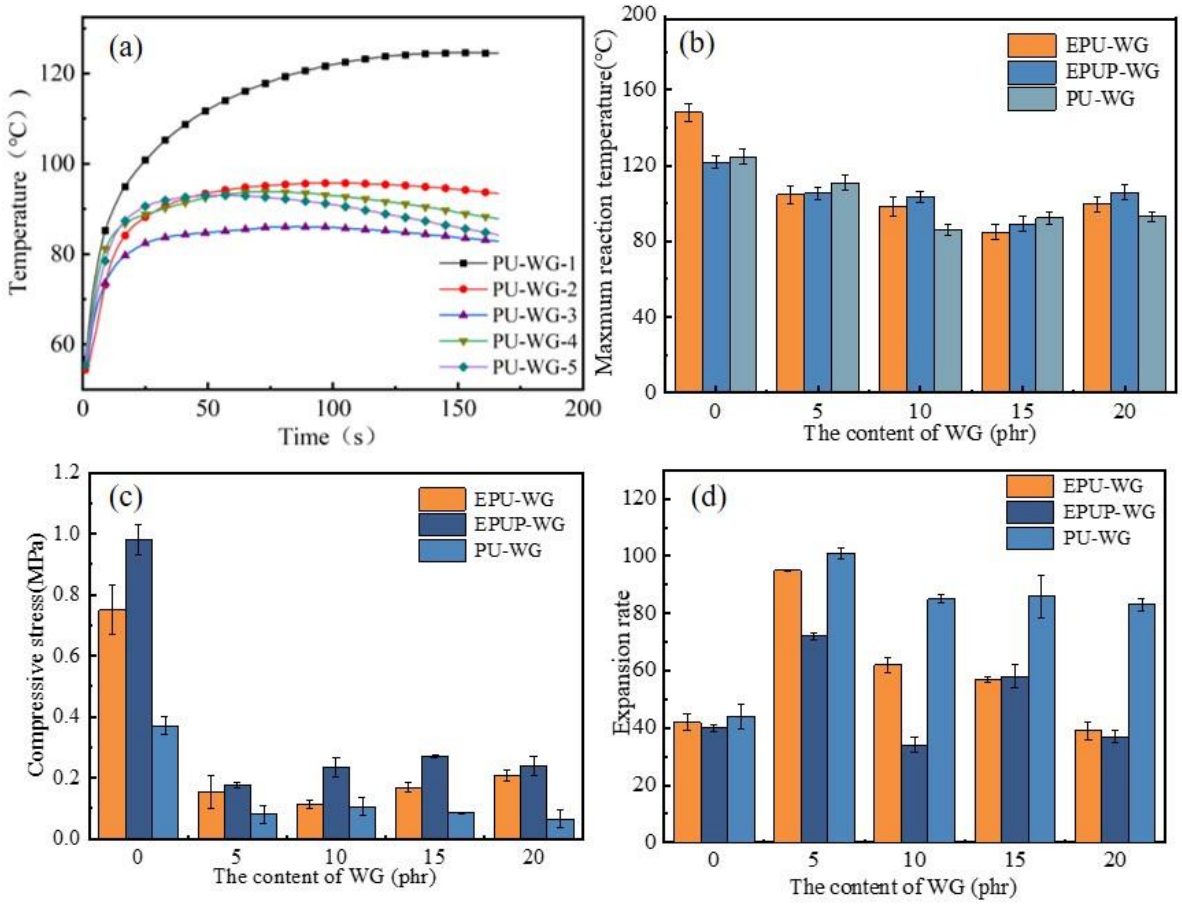

Figure 3. (**a**) The reaction temperature curves of different PU-WG, (**b**) the maximum reaction temperature, (**c**) the compressive strength, and (**d**) the expansion rate of grouting materials.

The morphologies of the fracture surfaces of the grouting materials are shown in Figure 4. Compared to the PU-WG system, the cell sizes of EPU-WG and EPUP-WG were found to be smaller and more regular. After the addition of WG, the cell size of these three systems increased, especially the cell size of EPU-WG and EPUP-WG systems, which doubled. Combined with the compressive strength of the corresponding system, it could be concluded that the increase in cell size had a negative impact on the material's properties.

The thermal stabilities of the composite foams (PU-WG-3, EPU-WG-3, EPUP-WG-3) were investigated with TGA under a nitrogen atmosphere. The corresponding curves are presented in Figure 5. The derivative thermogravimetry (DTG) curve of PU-WG-3 displayed four maximum degradation temperature, suggesting a four-stage thermal degradation process. The first stage occurred between 100–200 °C, and was attributed to the evaporation of water and other substances with a low boiling point. The second stage of degradation occurred between 200–300 °C, due to the loss of bound water and reaction water from Si-OH dehydration. Degradation occurred between 300–400 °C and was caused by the decomposition of some organic components in the PU structure. The fourth stage occurred between 400–500 °C; this stage of degradation was attributed to the decomposition of isocyanate trimers [21].

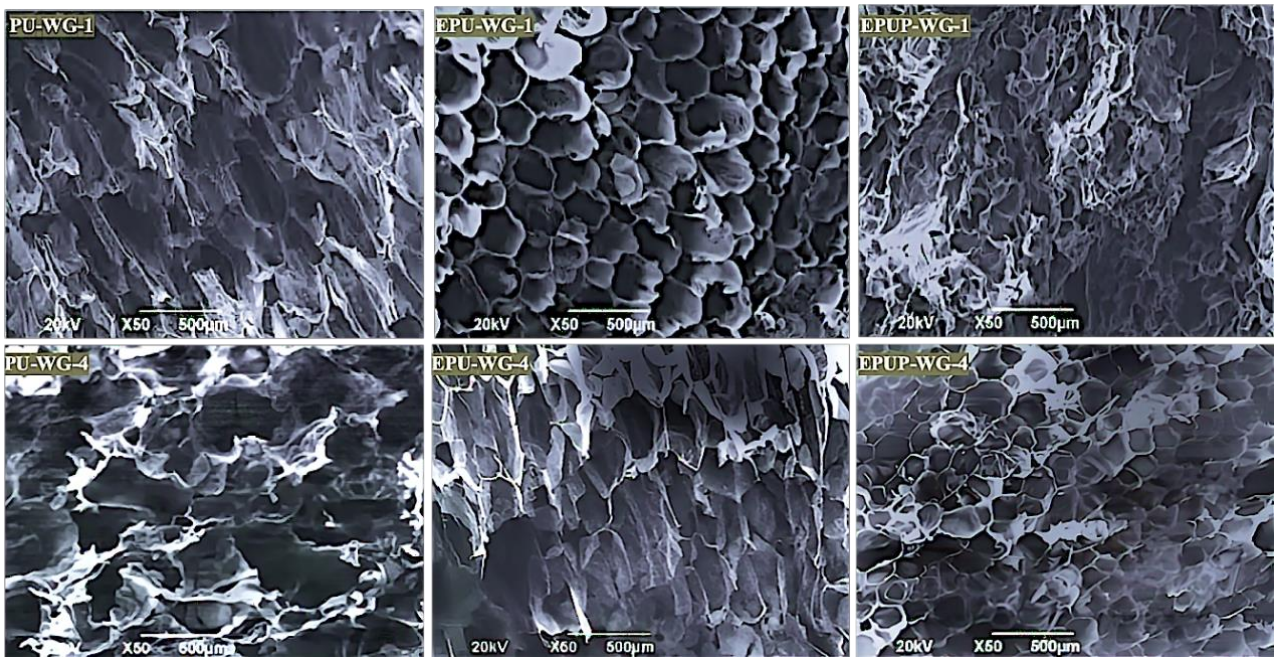

Figure 4. SEM images of fracture surfaces of grouting materials at an accelerating voltage of 20 kV and a working distance of 500 μm.

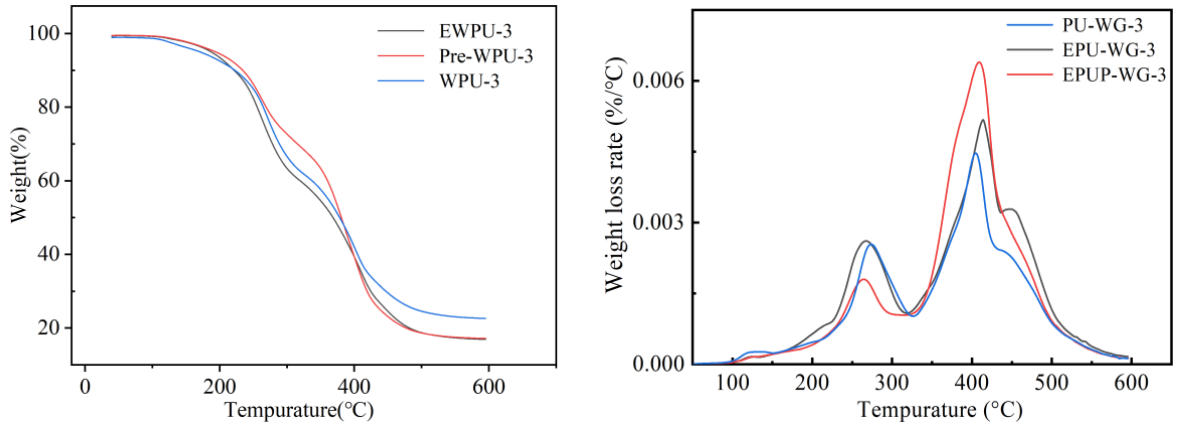

Figure 5. TG (**left**) and DTA (**right**) curves of three kinds of grouting materials.

The derivative thermogravimetry (DTG) curve of EPU-WG-3 showed three obvious stages in the thermal degradation process. The first stage was between 100–300 °C, which showed the volatilization of water and other substances with a low boiling point. The second stage was between 300–400 °C, which was mainly caused by the elimination reaction of the terminal groups (hydroxyl groups, amino groups) of the modified epoxy resin cured structure. The third stage occurred between 450–500 °C, and was caused by the degradation of the main chain of the epoxy resin. Nevertheless, the derivative thermogravimetry (DTG) curve of EPUP-WG-3 exhibited two obvious stages in the thermal degradation process; the first stage (100–300°C) was attributed to the evaporation of the remaining oligomer and residual moisture in the composite foam. In the second stage, the thermogravimetric loss between 450–500 °C was caused by the degradation of the main chain of the epoxy resin.

As shown in Table 2, EPUP-WG-3 had the highest $T_{5\%}$ and $T_{50\%}$ values among the samples, with values of 194.06 and 380.7 °C, respectively. The results showed that the EPUP-WG grouting materials with a rigid OX ring had higher thermal stability.

Table 2. Temperature for specific weight loss.

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
PU-WG-3	170.77	378.4
EPU-WG-3	187.52	368.1
EPUP-WG-3	194.06	380.7

4. Conclusions

In this study, WG and epoxy resin were selected as reactive components to reduce the heat release and improve the performance of polyurethane grouting materials. When the content of WG was 15 phr and the epoxy resin was added in the form of a prepolymer, the general properties of the material were the best, the reaction temperature decreased to 89 °C, the compressive strength was up to 0.27 MPa, the expansion rate was 57, and the cell size was smaller and more regular. TG curves showed that the thermal stability of the EPUP-WG composite deteriorated and the residue rate clearly increased compared with PU-WG and EPU-WG. Finally, possible reaction equations and the formation mechanism of the special structure were proposed. The modified polyurethane can be used for grouting, especially in rigorous underground coal mining; this provides further opportunities to apply polyurethane grouting materials in underground engineering.

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