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Effect of dosage of expandable graphite, dimethyl methylphosphonate, triethanolamine, and isocyanate on fluidity, mechanical, and flame retardant properties of polyurethane materials in coal reinforcement

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ABSTRACT

In this study, orthogonal experiments were conducted to investigate the influence of expandable graphite (EG), dimethyl methylphosphonate (DMMP), triethanolamine (TEA), and isocyanate content on the compressive and bonding strengths, oxygen index, and fluidity of rigid polyurethane foam (RPUF). The results revealed that EG significantly increased the oxygen index of RPUF, enlarged the diameter of foam cells, and decreased the cell-closed content in foam; thus, leading to a pressure drop in RPUF. However, excessive EG was capable of reducing the fluidity of polyurethane slurry. TEA exhibited significant influence on the compressive strength of RPUF, which dropped initially, and then increased. DMMP had a remarkable effect on the flame retardant property and compressive strength of RPUF. Compressive strength of RPUF initially displayed an increase followed by a decrease with increasing dosage of DMMP, and achieved the maximum value at DMMP dosage of 4%. DMMP could effectively reduce the diameter of RPUF cells leading to an increase in the percentage of close area in foam. DMMP displayed the flame-retardation effects mainly in the gas phase leading to a significant enhancement in the oxygen index of RPUF. Moreover, the compressive strength and bonding strength of RPUF decrease significantly with the increase of isocyanate content due to the increased blowing efficiency by the CO_2. The oxygen index and flowing length of foam increased with the increase in isocyanate dosage.

1. Introduction

Based on the formulation and basic chemical mix, the polyurethanes can be divided into rigid, soft, integral, and compact. Rigid polyurethane foam (RPUF) is a cost-effective and energy-saving material displaying certain advantages such as excellent mechanical properties, good bonding performance, well-sealed, anticorrosion and excellent abrasion resistance [1]. RPUF is extensively employed in a wide range of applications including: military aviation refrigerators and freezers, construction, the petrochemical industry, coal mining, and transportation [2]. Bayer AG corporation and Essen mining research center in Germany were the first to utilize RPUF in the coal industry [3]. Subsequently, France, the United States, and China employed RPUF for coal reinforcement [4]. However, due to the flammability of RPUF, its application in spontaneously combustible coal seams and gassy mines is severely limited. Therefore, improvement in the flame retardant property of RPUF is highly desirable.

To improve the flame retardant property of RPUF, phosphorus-based, nitrogen-based, and intumescent flame retardants have been widely used [5–14]. Molinda et al. studied the influence of low viscosity phosphoric acid tris (2-chloro-1-methylethyl) ester, tris (2-carboxyethyl) phosphine (TCEP), dimethyl methylphosphonate (DMMP), FR708, and FR609 on the flame retardant property of RPUF, and the results showed that DMMP (10%) demonstrated the best flame retardant effect when a single flame retardant was added. Moreover, the most significant mixed flame retardent effect (LOI = 28.6, where LOI is limiting oxygen effect) was exhibited by TCEP (2%), DMMP (3%), and FR708 (1%) [15]. Spinks reported on Chemthane7001-FR launched by the Cellular Company, as a new flame retardant for RPUF, demonstrating that the flame retardant could meet the coal mine standard at the Chemthane7001-FR dosage of 8% [16]. Yuan et al. studied the combined effects of heat insulation, gas insulation, and adsorption of expanded layers and used a special functional flame retardant with phosphorus and

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nitrogen as the major flame retardant elements to inhibit the combustion of polyurethane foam for which the oxygen index was up to 30% [17]. Modesti found that the introduction of perssad with higher heat-resistance, such as increasing isocyanate content or using excessive isocyanate content to obtain carbamidos, could effectively improve the flame retardant property of materials [18]. Expandable graphite (EG) is a novel flame retardant; at high temperatures, the rapid expansion of EG prevents continuous burning, and the materials generated cover the surface of base materials, thus isolating heat radiation and oxygen contact. Moreover, acid radicals between interlayers are released during expansion, facilitating the carbonization of base materials. Thus, EG achieves good flame retardant effects from various aspects [19]. Although the influence of flame retardants on RPUF has been extensively studied, these studies mainly focused on the low-density RPUF (mainly for insulation), while the high-density RPUF (mainly for coal reinforcement) have rarely been investigated. For better penetration of RPUF into the fractures in coal for good reinforcement, RPUF should have excellent fluidity and bonding strength. Therefore, the preparation of an effective mixture by optimization and its influence on the RPUF fluidity should be considered and investigated.

In this study, EG and DMMP were selected as the flame retardants, and the impact of EG, DMMP, isocyanate content, and triethanolamine (TEA) dosage on the oxygen index, compressive strength, and fluidity of RPUF was examined by orthogonal experiments to obtain the optimal combination for RPUF displaying best performance in mechanical properties, flame retardant property, and fluidity.

2. Experimental

2.1. Materials

The flame retardant EG (100 Mesh) was purchased from Qingdao Huateng Graphite Technology Co., Ltd. DMMP (industrial grade) was purchased from Yantai Yida Polyurethane Co., Ltd., China. PM-200 (NCO = 30.5%), average functionality of 2.8, and viscosity of 600 mPa s at 25 °C was used. The polyether polyols-4110 had a hydroxyl value of 410–460, with viscosity of 3500 mPa s at 25 °C. The polyether polyols-403 had a hydroxyl value of 750–780, with viscosity of 40,000 mPa s. *N*,*N*-Dimethylcyclohexylamine (DMCHA) and Tris-2,3,6-(dimethylaminomethyl) phenol (DMP-30) were employed as the catalysts, the blowing agent was distilled water, TEA was the crosslinking agent and polysiloxane-polyether copolymer (AK-8805) was used as the surfactant. All the above mentioned reagents were purchased from Yantai Wanhua Co., Ltd. The diameter of the commercially available gravel was around 15–20 mm.

2.2. Preparation of RPUF

An orthogonal test was employed to obtain optimal combination for RPUF displaying best performance in mechanical properties, flame retardant property, and fluidity based on the following four factors: (i) EG, (ii) DMMP, (iii) isocyanate content, and (iv) TEA. The indicators were as follows: (i) compressive strength, (ii) bonding strength, (iii) limited oxygen index and (iv) flowing length. Various factors and levels of the orthogonal test are shown in Table 1.

The Polyurethane reinforcement material was composed of two materials, A and B. Material A was isocyanate (PM-200), and B was a mixture of polyether polyol and other additives. The composition of the reaction mixtures applied for polyurethane reinforcement material are shown in Table 2.

Table 1
Orthogonal factors levels (%).

Levels	EG	TEA	DMMP	PM-200
1	3	2	1	150
2	6	4	2	200
3	9	6	3	250
4	12	8	4	300
5	15	10	5	350

Note: Ratio of the raw materials is based on polyether polyol.

To determine the compressive and bonding strengths of polyurethane foam, two types of foam were prepared for the experiment. First, the polyurethane foam was prepared by directly mixing the reinforced materials A and B in a mold (130 mm × 130 mm × 130 mm, no gravel), which was used to test the compressive strength; and the second was prepared by completely mixing materials A and B in a mold with gravel (130 mm × 130 mm × 130 mm), simulating the process of reinforcing coal by polyurethane to determine the bonding strength between the material and gravels. The specific process is as follows: first, the polyether polyols, surfactant, flame retardants, blowing agent, crosslinking agent, and catalysts were completely mixed to prepare material B. Subsequently, materials A and B were mixed thoroughly by agitator at high speed for 20 s, and the mixed slurry was poured into a mold with gravel to let the slurry penetrate into the cracks between gravel pieces. After about 3 min, the mixed slurry started to foam in the cracks between the gravel pieces, leading to an expansion in volume followed by sodification due to the effect of catalysts. Finally, all the as-prepared polyurethane foams were aged for 24 h at 70 °C.

2.3. Performance test

Oxygen index test: The oxygen index of the samples was measured by a SH5706A Type oxygen index tester according to ASTMD2863, and the sample size was 121 mm × 10 mm × 10 mm.

Mechanical properties test: The compressive and bonding strengths of foams were measured by WDW-20E Type microcomputer-controlled electron universal testing machine according to ASTMD1621-94; the sample size was 100 mm × 100 mm × 100 mm.

Fluidity test: Thoroughly mixed slurry of polyurethane (30 mL, the recipe is listed in Table 2) was added into a small funnel and connected to a plastic hose (length = 100 cm, diameter = 1 cm). Subsequently, the flow length of the mixed slurry of polyurethane after solidification in the hose was measured, and was characterized as the fluidity of the slurry.

Microstructure test: The microstructure of reinforced polyurethane materials was observed by a Quanta 250 scanning electron microscope (FEI Company, USA). Samples were cut into pieces (10 mm × 10 mm × 2 mm) from the polyurethane materials and coated with golf on the surface. The diameter of polyurethane foam cells was analyzed by Image J Software, and the closed cell content was determined by Ultrapychometer.

3. Results and discussion

Table 3 shows that the degree of influence of different added reagents on the compressive strength of RPUF is in the following order: isocyanate content > EG > TEA > DMMP. However, DMMP displayed maximum effect on the bonding strength of RPUF and the order is as follows: DMMP > isocyanate content > TEA > EG. The degree of influence on the flame retardant properties of RPUF is: EG > DMMP > isocyanate content > TEA. TEA exhibited maximum effect on the fluidity of RPUF and the order is follows: TEA > isocyanate content > EG > DMMP. Therefore, in this study, a