Original Article

Preparation and Properties of the Fast-Curing γ-Ray-Shielding Materials Based on Polyurethane

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Abstract
In this study, fast-curing shielding materials were prepared with a two-component polyurethane matrix and a filler material of PbO through a one-step, laboratory-scale method. With an increase in the filler content, viscosity increased. However, the two components showed a small difference. Curing time decreased as the filler content increased. The minimum tack-free time of 27 s was obtained at a filler content of 70 wt%. Tensile strength and compressive strength initially increased and then decreased as the filler content increased. Even when the filler content reached 60 wt%, mechanical properties were still greater than those of the matrix. Cohesional strength decreased as the filler content increased. However, cohesional strength was still greater than 100 kPa at a filler content of 60 wt%. The γ-ray-shielding properties increased with the increase in the filler content, and composite thickness could be increased to improve the shielding performance when the energy of γ-rays was high. When the filler content was 60 wt%, the composite showed excellent comprehensive properties.

1. Introduction
With the rapid development of nuclear technology, nuclear irradiation safety becomes more and more important. The harsh application environment of nuclear technology has promoted the development of new shielding materials that can protect workers from radiation damage. Emerging trends in shielding materials include the preparation of light shielding materials with a foam metal as a matrix [1,2], synthesis of flexible X-ray-shielding materials for irradiation-shielding garments [3], development of borated Ceramicrete coatings with irradiation-shielding functions [4], and so on.

Application and development of nuclear energy bring huge benefits to human beings, but the complex environment of nuclear power plants also causes difficulties in shielding protection. During the maintenance of a nuclear power plant, pipe failures often result in radioactive water and gas seeping out from cracks. In pipe failures, maintenance workers generally

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wrap the cracks with a lead blanket or lead sheath, or segregate the pipe with lead bricks before replacing it. However, traditional lead shielding materials are heavy without service flexibility [5,6] and cannot adhere tightly to the pipe surface. Radioactive water and gas are still likely to leak and expose maintenance workers to harmful radiation. In this study, we developed a type of fast-curing shielding material based on polyurethane (PU). Workers can conduct spraying operations at a long distance, in which shielding materials adhere to and wrap the pipe by quickly forming a fully sealed layer, thus guaranteeing the safety of workers. The research on fast-curing shielding materials has mainly been derived from the actual needs of nuclear power plants, but there is little literature or reports in relevant fields. Therefore, this study may be significant in protecting maintenance workers, especially in harsh irradiation environments.

PUs are generated via mixing and crosslinking of polyols and isocyanates with catalysts, surfactants, and blowing agents [7]. The main reaction is given as follows:

\[
R-\text{NCO} + R^3-\text{OH} = R-\text{NHCOO}R^3
\]

Active catalysts allow a rapid reaction of the PU system at room temperature. In addition, the active NCO in the system reacts with absorbed water and oxides on the surface of different materials to form hydrogen bonds. Therefore, PU possesses excellent adhesion properties [8,9]. In addition, the two components of the PU spray have low viscosity and show good filling capacities of filler materials with good fluidity. These performances show that the two-component PU is suitable for the matrix of the new fast-curing shielding material.

Owing to its economic and practical advantages, PbO was used as the shielding filler in this study and was integrated into two components of PU, and then the composites were prepared by a one-step, laboratory-scale method. Experimental results showed that PbO, as alkaline oxide fillers, could accelerate the reaction rate of the PU system. Moreover, PbO fillers could improve the γ-ray-shielding properties of PU composites.

2. Materials and methods

2.1. Materials

The following materials were used to prepare shielding materials: polyether 403 (770–800 mg KOH/g, 35,000–45,000 mPa s; Changzhou Mid-Asia Chemical Company Limited, China), polyether 4110 (450–450 mg KOH/g, 2,500–3,000 mPa s; Lianyungang Maijia Chemical Company Limited, China), polyether 204 (270–290 mg KOH/g, 60–80 mPa s; Shandong Longhua Chemical Technology Company Limited, China), surfactant (simethicone; Nanjing Xinye Polymer Technology Company Limited, China), compound catalysts (pentamethyldiethylenetriamine and cyclohexyl amine; Nanjing Xinye Polymer Technology Company Limited, China), blowing agent (distilled water), polymethylene diisocyanate (PM200, 150–250 mPa s, NCO: 30.5–32%; Yantai Wanhua Chemical Group Company Limited, China), and fillers (PbO: 9.53 g/cm³, 5–15 μm; Shanghai Zhanyun Chemical Company Limited, China).

2.2. Preparation of composite samples

Component A of PU consisted of polyether polyols, surfactant, catalysts, and a blowing agent. According to the designed different ratios of parts, Component A was prepared by vigorous stirring in a vacuum mixer. The weight of Component B containing polymethylene diisocyanate was calculated according to the composition of Component A. The weight ratio of Component A to B was 1:1, and the isocyanate index was 105. Table 1 shows the components used in the preparation of two-component PU.

The fillers were dried in a vacuum drying oven at 120°C for 1 hour and then cooled at room temperature. Fillers with the same weight were respectively added into Components A and B, and were blended homogeneously in a vacuum mixer (ZKJ-3, Shanghai Truelab Lab-Sci Company Limited, China) at 6.2 × g for 30 minutes. The vacuum allowed us to rule out the influence of air on the result of the experiment. Next, the components along with PbO were placed into an ultrasonic dispersing apparatus (KH-100B, Kunshan Hechuang Company Limited, China) under 24 KHz for further dispersion about 30 minutes. Table 2 shows the components used in the preparation of a fast-curing shielding material. Lastly, the composites were prepared through a one-step, laboratory-scale method. Two components with PbO fillers at a mass ratio of 1:1 were blended using a mixer at 17 × g for 5 s. The resulting reaction mixture was poured into a metal mold with the dimensions of 10 cm × 10 cm × 5 cm. Then, the composites were seasoned at room temperature for 24 hours.

2.3. Characterization

2.3.1. Viscosity test

Viscosities of Components A and B with different filler contents were measured using a rotational viscometer (NDJ-1, Shanghai Precision Scientific Instrument Company Limited, China).

2.3.2. Curing time

The foam curing process mainly involves three time parameters [10,11]. First, the cream time was the beginning point of the foam rise. Second, the gel time was the starting point of a stable polymer network formation. Third, the tack-free time

| Table 1 – Weight percentage of raw material for two-component polyurethane. |
|-----------------------------|--------------------------|
| Material                  | Weight percentage |
| Polyl 403                  | 10                       |
| Polyl 4110                 | 20                       |
| Polyl 204                  | 70                       |
| Simethicone                | 1.5                      |
| Compound catalysts         | 2.5                      |
| Water                      | 1                        |
| PMDI, polymethylene diisocyanate. | 105                  |
was the time when the outer surface of the foam lost its stickiness as a result of crosslinking, and the PU foam could be removed from the mold. Time parameters were recorded by a stopwatch.

2.3.3. Morphological observations
Morphological features of new fast-curing composites were observed under a scanning electron microscope (SEM, JSM-7500; JEOL, Japan). Surfaces of the samples should be smooth and clean, and were sputter coated with gold for observation. The foam structure and distribution of the fillers were observed to evaluate the performance of the composites.

2.3.4. Mechanical properties
Tensile strength and compressive strength of the composite were tested using an electronic universal testing machine (WANCE ETM-D, Shenzhen Wance Equipment Company Limited, China). Tensile samples were prepared according to ASTM (American Society for Testing and Materials) D 3574 [12] and tested at a rate of 5 mm/min. Compression specimens were prepared according to ASTM D 1621 [13] and tested at a rate of 5 mm/min.

2.3.5. Cohesional strength
New shielding materials were designed for preventing radiation pollution caused by the leakage of metal pipeline. Thus, the fixtures in this test were prepared using Q235 steel (Fig. 1A). According to the test method in JC/T 998-2006 [14], the fixtures (upper and lower) were fixed in parallel at a distance of 1.5 cm on a board. Then the mixture of Components A and B was deposited between the two fixed fixtures. After the mixture foaming and curing at room temperature, the extra material beyond fixtures was removed and the test samples were obtained (Fig. 1B). The samples were tested using a universal testing machine at a tensile rate of 2 mm/min. The tensile force and cross-sectional area of the sample were recorded, and the cohesional strength \( f_b \) was calculated according to the following formula:

\[
    f_b = \frac{F}{A}
\]

where \( F \) is the tensile force (N) and \( A \) the cross-sectional area of the sample (m²).

2.3.6. \( \gamma \)-ray-shielding measurements
Under different irradiation point sources [PU-238 (43 keV and 99 keV), Cs-137 (662 keV), and Co-60 (1.17 MeV)], shielding performances of the composite samples with different filler contents were measured using an NaI detector (ORTEC, America). The thickness of the composites were 2 cm, 4 cm, 6 cm, 8 cm and 10 cm. A schematic diagram of the apparatus is shown in Fig. 2.

3. Results and discussion

3.1. Viscosity test
The two components of PU were liquid at room temperature. When the fillers were added into the components, a new solid–liquid phase system was formed. The fillers affected the liquidity of the system. Viscosities of the two components

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Proportion of fast-curing shielding material.</th>
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<tr>
<td>Sample no.</td>
<td>Polyurethane (A and B)/wt%</td>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>90</td>
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Fig. 1 – Cohesional strength test. (A) Fixtures of cohesional strength test. (B) Samples of cohesional strength test.

Fig. 2 – Schematic diagram of the apparatus used to measure the \( \gamma \)-ray-shielding properties of PbO/PU composites. PU, polyurethane.
Fig. 3 – Viscosities of Components A and B with different filler contents.

Fig. 5 – Curing time of polyurethane system with different filler contents.

with different filler contents were measured to characterize the liquidity of the system (Fig. 3). Viscosities of Components A and B increased as the filler content increased. The initial viscosity of Component A was higher than that of Component B. However, Component B showed a faster increase in viscosity than Component A. The difference might be interpreted as follows. Hydroxyl on the surface of PbO powder reacted with isocyanate, thus making the chain movement of Component B more complex than that of Component A. Fig. 4 shows the reaction between PbO particles and isocyanate. When the filler content exceeded 60 wt%, although Components A and B showed different rates of increase in viscosity, viscosities of Components A and B increased quickly and their liquidity became poor. For the same filler content, Components A and B showed no significant difference in viscosity. Fillers of the same amount were added into Components A and B in order to ensure good shielding performance.

3.2. Curing time

In order to reduce the irradiation time of workers and ensure a normal and orderly process of maintenance, the shielding composite should have fast-curing properties. The cream time, gel time, and tack-free time were recorded to evaluate the curing properties of the PbO/PU composites (Fig. 5). The two-component PU had fast-curing properties at room temperature with a cream time of 6 s, gel time of 33 s, and tack-free time of 49 s. When PbO was added, the cream time, gel time, and tack-free time decreased as the filler content increased. The minimum cream time (5 s), gel time (17 s), and tack-free time (27 s) were obtained at a filler content of 70 wt%. This phenomenon might be interpreted as follows: PbO was an alkaline oxide and influenced the pH of the system. The catalysts used in this study were amine catalysts, and the alkaline environment might have improved their activity. The experimental results showed that when PbO fillers were added into two-component PU, curing properties of the composites were significantly improved.

3.3. Morphological observations

Surfaces of the PbO/PU composite after cutting were investigated to observe the microstructure of the foam and the distribution of PbO fillers using an SEM. Figs. 6A–6H and 7 show the SEM micrographs of the PbO/PU composites. The images at the top right corner in Figs. 6A–6H are enlarged views of the areas that have been marked by red solid-line circles. Fig. 7 shows the distribution of PbO particles in the foam structure obtained at a filler content of 30 wt%. As the filler content increased, the cell size of composites decreased and the density of cells increased (Figs. 6A–6H). The change might be ascribed to the nucleation effect of particles. PbO particles promoted the nucleation process and served as nucleation sites in the foam matrix. The particles were heavier than PU, and they hindered the expansion process of gas and reduced the cell size. As shown in the enlarged views, the fillers mainly exist at the intersections of the cell wall, which are called plateau borders [15]. The number of particles in the plateau borders increases as the filler content increases. Some big holes with many particles were observed at the bottom when the filler content reached 70 wt%. This might be interpreted as follows: the foam structure could not bear the weight of excessive fillers. Owing to the drainage effect [16] during the foam process, the fillers were mainly embedded in the plateau.
borders and firmly bonded with the matrix (Fig. 7). The PbO fillers reduced the cell size and increased the cell density of composites. Fillers showed good distribution and excellent bonding in the plateau borders of PU, but the distribution became poor when the filler content exceeded 50 wt%.

3.4. Mechanical properties

Mechanical properties of the PbO/PU composites generally determine the service conditions of the materials. Mechanical properties of the PU-based $\gamma$-ray-shielding materials with different filler contents at room temperature are shown in Fig. 8. Tensile strength and compressive strength of the composites are shown in Figs. 8A and 8B, respectively. The tensile strength and compressive strength increased initially and then decreased as the filler content increased. When the filler content reached 30 wt%, the tensile strength and compressive strength, respectively, reached their maximum values of 521 kPa and 185 kPa. The change was caused by the reinforcement effects of PbO fillers. Filler particles were
inserted into plateau borders, which improved the strength of the foam structure. When the filler content exceeded 60 wt%, the tensile strength and compressive strength decreased rapidly. The tensile strength and compressive strength were lower than those of the matrix as the filler content reached 70 wt%. This phenomenon could be attributed to the collapse of foam caused by excessive fillers. When the filler content was very high, consumption of isocyanate in the reaction with hydroxyl on the surface of PbO particles increased and the effective content of isocyanate reacting with polyols decreased, thus decreasing the mechanical properties of the composites. In this study, as the filler content increased, mechanical properties of PbO/PU shielding materials reached their maximum values at a filler content of 30 wt% and then decreased. Properties of the composite materials were lower than those of the matrix when the filler content reached 70 wt%.

3.5. Cohesional strength

The environment of nuclear power plants during maintenance is complex. Leaked radioactive water might lead to external exposure, and the escaped radioactive gas might result in serious internal exposure if the gas was inhaled accidentally. Therefore, it is important for shielding materials to have good adhesion performance on the surface to prevent the spread of radioactive water and gas. Fig. 9 shows the results of the cohesional strength test between composites and the surface of steel. The two-component PU showed good adhesion performance. With the increase in the filler content, cohesional strength of composites decreased. When the filler content exceeded 50 wt%, the cohesional strength decreased rapidly. However, the cohesional strength of the composite was still > 100 kPa when the filler content reached 60 wt%. According to JC/T 998-2006, this shielding material had excellent adhesion performance. This is due to the fact that the active NCO of PU could react with absorbed water and oxide on the surface of metal to form hydrogen bonds to firmly connect composites with the surface. When the fillers were added into PU, the hydroxyl on the surface of particles would consume the isocyanate, and the effective content of isocyanate that could react with absorbed water and oxide decreased. Therefore, the cohesional strength decreased. In this investigation, PbO/PU shielding materials showed good cohesional strength on the surface of steel. Although the cohesional strength decreased as the filler content increased, the cohesional strength was 125 kPa when the filler content reached 60 wt%.

3.6. γ-ray-shielding properties

The γ-ray-shielding properties of the PbO/PU composites prepared at filler contents were measured. The γ-ray transmission factor $I/I_0$ was used to assess the γ-ray-shielding properties, with $I_0$ and $I$ being the intensities of the incident γ-ray beam and the γ-ray beam transmitted through the thickness direction of the sample composites, respectively. Fig. 10 shows the γ-ray flux attenuation properties of the composites with different thicknesses at different energy levels. The PbO/PU shielding materials had excellent γ-ray-shielding
properties under the irradiation of a PU-238 point source with energy levels of 43 keV and 99 keV (Figs. 10A and 10B). Transmittance decreased as the filler content and thickness of the composite increased. When the filler content was 70 wt% and thickness was 10 cm, the composite had the minimum γ-ray transmittance. The two minimum γ-ray transmittances at the energy levels of 43 keV and 99 keV were 1.9% and 6.52%, respectively. Figs. 10C and 10D show similar test results obtained under the irradiation of Cs-137 and Co-60 point sources, respectively. However, the γ-ray-shielding properties became poor because the transmittance increased as the irradiation energy increased. The minimum γ-ray transmittances at the energy levels of 662 keV and 1.17 MeV were, respectively, 85% and 90% because the penetrating power of γ-ray photons increased as the energy of the point source increased. This finding indicated that the PbO/PU composites had excellent γ-ray-shielding properties under low and middle irradiation energy. In engineering applications, thickness can be increased to improve the shielding properties of the composites when the energy of γ-rays is high.

4. Conclusion

A new fast-curing shielding composite based on two-component PU was fabricated with PbO as the filler through a one-step, laboratory-scale method. Moreover, we explored the effects of the filler contents on the viscosities of the two components of PU, curing time in the reaction process, mechanical properties, cohesional strength on the surface of
steel, and γ-ray-shielding properties of the composites. Viscosities of the two components increased with the increase in the filler content. However, the two components showed a small difference. Therefore, fillers with the same weight were added into Components A and B in order to ensure good shielding properties. PbO fillers, such as alkaline oxide, may improve the activities of amine catalysts, and the curing time was shortened with the increase in the PbO content. The mechanical properties increased initially and then decreased as the filler content increased. When the filler content reached 60 wt%, the mechanical properties were still greater than those of the matrix. Cohesional strength decreased with the increase in filler content, but the composite still had excellent adhesion on the surface when the filler content reached 60 wt%. The PbO/PU composites had excellent γ-ray-shielding properties under low and middle irradiation energy levels, and the thickness could be increased to improve the shielding properties under high irradiation energy. The results showed that, when the filler content was 60 wt%, the PbO/PU shielding composites had better shielding performance and shorter curing time, and the mechanical properties were still greater than those of the matrix; as a result, the composites could adhere to the surface well. Thus, the PbO/PU shielding composites had excellent comprehensive performance at the filler content of 60 wt%.

Therefore, the fast-curing γ-ray-shielding composites, which were prepared successfully in this study, featured excellent shielding performance, cohesional strength, and mechanical properties. The new shielding materials had extensive potential applications in the maintenance of nuclear plants and may be of great significance in preventing workers from radiation damage.

Conflicts of interest
All authors have no conflicts of interest to declare.

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