Optimization design and application study on a high temperature resistant borated polyethylene shielding material

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Abstract. This paper carried out an optimization design and application study on a high temperature resistant borated polyethylene shielding material, according to the nuclear power plant source characteristics and special protection requirements. The composition of borated polyethylene shielding material was optimized based on the genetic algorithm and Monte Carlo methods, then it was realized by blending modification and graft copolymerization to improve the high temperature resistant, shielding and mechanical properties. Finally, comprehensive properties such as mechanical, neutron shielding, irradiation resistance and high temperature resistance experiments were verified with the ordinary borated polyethylene and polypropylene. Those just proved the optimized borated polyethylene shielding material has excellent performance comparatively, especially it could keep complete structure in a high temperature environment up to 190°C during 48 hours, meeting the requirements of radiation protection safety for nuclear power plant completely.

1. Introduction
Composite shielding materials, such as borated polyethylene, borated steel, lead-boron polyethylene and epoxy resin [1-4], were mainly used to resist and reduce the gamma ray and neutron which were harmful to workers. They were effective means to ensure the radiation safety for personnel, equipment and environment, and were widely used in nuclear power plants, nuclear power ships, radioactive laboratories and other fields.

It was required to shield neutron effectively in some part of the nuclear power plant to reduce the dose rate level and allow workers to access the containment under normal power operation conditions. The shielding material not only need to meet the normal temperature, humidity and irradiation environmental conditions, but also should consider the special situation of atmospheric temperature up to 190 °C. It was required the sample could keep the overall shielding structure stable after 48 hour test, and all other aspects of performance indicators should be within the acceptable range, and easy to repair and replace.

The ordinary borated polyethylene was a generally preferred choice for its outstanding shielding capability in the area of nuclear power plant. However, it could not work normally when the temperature environment was above 100 °C because of its low thermal deformation temperature. That limited its application in high temperature environment, especially in the loss-of-coolant accident (LOCA). Higher temperature will lead to the softening, deformation and splashing of shielding material, which will reduce the shielding effect or even lose effectiveness, causing radiation safety hazards.
Therefore, the purpose of this paper was to optimize the borated polyethylene shielding material. On the basis of better neutron shielding effect for the area of containment, it was aim to improve its high temperature resistance that could ensure the shielding structure’s completion and effectiveness under the LOCA environment, while the other capabilities of mechanics, and irradiation resistance were unchanged obviously.

2. Optimizing design of the composites

2.1. Composition ratio optimization design
Composition ratio design for borated polyethylene shielding material was a multi-objective optimization problem with constraints. As an effective random search method, genetic algorithm [5] has the characteristics of global optimization, good consistency and good convergence. It has good adaptability for solving multi-objective optimization problems with constraints. It has been widely used in many fields and achieved good results. In this work, GENOCOP III [6-7] and MCNP 5 based on Monte Carlo method were used to optimized the composition ratio for borated polyethylene shielding material.

The objective function optimized in this study was the total equivalent dose rate of neutron and gamma ray, shown in equation 1.

\[
\min f(X) = [f_n(X), f_g(X)]
\]  

In equation 1, \(f_n(X)\) was the neutron equivalent dose rate objective function, \(f_g(X)\) was the gamma ray equivalent dose rate objective function, \(X\) was the vector of the mass content of each component, \(X=[x_1,x_2,…x_p]\), while the \(x_i \ (i=1,2,…,p)\) was the mass fraction of each component in the shielding materia.

For material with multiple compositions, it need to meet the following constraints:

\[
\sum_{i=1}^{i=p} x_i = 1 \tag{2}
\]

\[
1/ \rho(X) = \sum_{i=1}^{i=p} x_i / \rho_i , \quad \rho_i \leq D \tag{3}
\]

\[
L \leq X \leq U \tag{4}
\]

Equation 2 was the normalization conditions of components; equation 3 was density of borated polyethylene shielding material, aiming to reduce the scope of optimization and increase the success rate of genetic algorithm, while \(D\) was density range of shielding material; equation 4 was interval constraint, \(L\) and \(U\) were the upper and lower limits of each component.

In the specific use area of nuclear power plant, the fast neutron flux rate was \(1.6\times10^5 n/cm^2\cdot s\), thermal neutron flux rate was \(1.4\times10^6 n/cm^2\cdot s\), total neutron dose rate was \(23 Gy/h\), and the gamma ray dose rate was \(2 Gy/h\). Considering the source characteristics with higher thermal neutron fraction, we set polyethylene composition in the range of \(0.5 \sim 0.9\), and boron carbide in the range of \(0.1 \sim 0.5\).

The optimization design process of material composition ratio was shown in Figure 1. Firstly, the mass ratio was initialized, and the material density and element composition intervals were taken as constraints, the appropriate genetic parameters were selected, and then the GENOCOP III program was ready to run; secondly, according to the preliminary calculation results of each component, the density and calculation model were edited into MCNP input file, which was used to calculate the neutron and gamma equivalent dose rate after passing through the shielding material, and to obtain the total dose equivalent rate; each sub objective value was calculated separately, and the corresponding weight factor weighted sum was combined to feed back the output results to GENOCOP III. If the design objective was not met, the ratio, calculation and comparison will be redesigned until the optimization result meeting the conditions was reached. The optimized design result was that the boron mass ratio was 31.43%, carbon mass ratio was 60%, hydrogen mass ratio was 8.57%, then the density of the borated polyethylene shield material was about 1.25 g/cm³.
2.2. Composites modification

Modification referred to the use of physical, chemical and mechanical methods to improve the original properties of material, so as to meet different uses. The modification methods of polyethylene can be divided into physical and chemical methods. Physical modification mainly included filling and blending modification; chemical modification mainly included graft and block copolymerization. Through the research on the modification of polyethylene [8-9], we decided to choose the methods of blending modification and graft copolymerization to improve the high temperature resistant, shielding and mechanical properties of borated polyethylene shielding material.

The purpose of blending modification was to improve material’s high temperature resistance, and keep its shielding capability unchanged based on the result from chapter 2.1. Blending modification was to add one or several kinds of polymers to create new capabilities, while the molecular structure was unchanged in processing and molding. It was usually to use polypropylene, polycarbonate,
polyamide in the blending modification since their high thermal deformation temperature, tenacity, impact strength and so on, but they also had poor compatibility with inorganic nonmetal and weaker shielding capability. However, in order to not affect the shielding effect of borated polyethylene shielding material, ultra-high molecular weight polyethylene (UHMW-PE) with the same hydrogen content as ordinary high density polyethylene (HDPE) was selected finally. It has high melt strength and was not sensitive to thermal shear. Therefore, this property could be used to modify ordinary polyethylene. During mixing, the existing shear force could separate the macromolecular chains of the material and form free radicals, some block and graft copolymerization phenomena will occur at the same time. The HDPE was suspended in the liquid phase of the blend material, high temperature resistance capability were mainly reflected in: the modified borated polyethylene will be in a gel state in high temperature condition, and no softening and deformation will occur without external force. However, a certain proportion of UHMW-PE will be added considering softening deformation and machinability for the borated polyethylene shielding material.

The purpose of graft copolymerization was to improve the mixing uniformity and mechanical properties of borated polyethylene shielding material. Due to the non-polar structure of polyethylene molecular chain, the lack of affinity with inorganic fillers and poor compatibility with other polar polymers will lead to a significant decrease in aspect of tensile strength, elongation at break and so on, especially when the polyethylene need to mix with about 40% boron carbide in this paper. Therefore, we carried out a method of melt grafting of maleic anhydride(MAH) onto polyethylene. We used the twin-screw extruder as continuous reactor, and set the temperature in several intervals from 150°C to 210°C. It could plasticize, melt, disperse, mix, graft and transport the mixture of UHMW-PE, HDPE, MAH, peroxide and other additives, and then the extrudate was cooled, dried, cut in particles and ground into powder. Finally, we used the powder mixed with boron carbide in a hot-pressing machine to make different plates of borated polyethylene shielding material, which owning better mixing uniformity and bond strength. The graft copolymerization of polyethylene with MAH was a free radical reaction shown in Figure 2.

![Figure 2. Graft copolymerization of polyethylene with MAH.](image)

Table 1. Composition and amount of modified borated polyethylene shielding material.

|          | HDPE    | UHMW-PE | boron carbide | MAH     | peroxide | additives |
|----------|---------|---------|---------------|---------|----------|-----------|
|          | 550g~650g | 350g~450g | 666g          | 6g~10g  | 0.5g~1.5g | ~3g       |

3. Comprehensive verification of environmental test
The mechanical, neutron shielding, irradiation resistance and high temperature resistance properties of the modified high temperature resistant borated polyethylene shielding material were comprehensively
verified. The comparison and analysis were also carried out with the ordinary borated polyethylene and polypropylene with a higher melting temperature (about 170℃).

3.1. Mechanical property

Mechanical property test was carried out, including tensile strength, flexural strength and impact toughness (shown in Figure 3). The test results were shown in Table 2.

The test results showed that the mechanical properties of the high temperature resistant borated polyethylene shielding material meet the requirements of technical index, and the mechanical tensile strength and impact resistant of it were better due to effective modification above mentioned.

The preparation of test samples and test methods referred to the national standards such as GB/T 1040.2, GB/T 9341 and GB/T 1043.1.

![Mechanical property test](image)

(a) tensile strength  (b) flexural strength  (c) impact toughness

**Figure 3.** Mechanical property test.

**Table 2.** Mechanical property test results.

| Test items       | Technical index | High temperature resistant borated polyethylene | Ordinary borated polyethylene | Borated polypropylene |
|------------------|-----------------|-----------------------------------------------|-------------------------------|------------------------|
| Tensile strength(MPa) | ≥9.0            | 17.5                                          | 15.5                          | 12.6                   |
| Flexural strength(MPa)    | ≥9.0            | 23.55                                         | 31.8                          | 28.2                   |
| Impact toughness (MPa)    | ≥3.0            | 15                                            | 3.5                           | 1.5                    |

3.2. Neutron shielding property

The neutron shielding property test, including fast neutron shielding coefficient and thermal neutron shielding rate, was carried out (shown in Figure 4). $^{241}$Am-$^9$Be neutron source was used for the fast neutron shielding coefficient test (the radiation source strength was about 5Ci, and the maximum neutron flux was about $1 \times 10^7 n/s$). In the thermal neutron shielding rate test, the $^{241}$Am-$^9$Be neutron source was moderated to thermal neutron radiation field by using about 7cm thick polyethylene. During the measurement, the centers of neutron source, moderator, sample to be measured and neutron dose equivalent detector were on the same central axwax, and the sample completely covered the sensitive area of detector. The test results were shown in Table 3.

The test results showed that the neutron shielding property of the high temperature resistant borated polyethylene shielding material could meet the requirements of the technical index, and was close to the ordinary borated polyethylene shielding material in the aspect of fast neutron shielding ability.
Figure 4. Neutron shielding property test.

Table 3. Neutron shielding property test results.

| Test items                  | Technical index | Test results                                      |
|-----------------------------|-----------------|---------------------------------------------------|
|                             |                 | High temperature resistant borated polyethylene | Ordinary borated polyethylene | Borated polypropylene |
| Fast neutron shielding      | ≥2.0(40mm thickness) | 2.13 | 2.38 | 2.03 |
| coefficient                |                  |       |      |      |
| Thermal neutron shielding   | ≥98%(20mm thickness) | 99.64% | 99.64% | 99.64% |
| rate(%)                    |                  |       |      |      |

3.3. Irradiation resistance property
The irradiation test of the high temperature resistant borated polyethylene shielding material was carried out on a reactor. After receiving the irradiation with cumulative neutron flux of about $1.75 \times 10^{15}$n / cm$^2$ and gamma dose of about $3.5 \times 10^5$Gy, its appearance was still smooth, flat and no crack, its weight change was not more than 1%, its change of mechanical properties were acceptable.

The photos before and after irradiation test were shown in Figure 5.

Figure 5. Photos before and after irradiation test.

3.4. High temperature resistance property
The high temperature resistance properties test was carried out in a LOCA equipment after irradiation test (seen in Figure 6). During the whole test progress, the atmosphere temperature ranged from 40 °C
to 190℃, and the test time was not less than 48 hours. The test condition parameters were shown in Figure 7. The shape of three samples after test were shown in Figure 8. The appearance and weight of the three samples after test were compared shown in Table 4.

The test results showed that the high temperature resistant borated polyethylene shielding material could maintain a complete shielding structure without softening, collapse, significant deformation and weight loss after the high temperature test. Due to the thermal expansion and cold contraction, the size of the composite shielding material just has a certain amount of deformation, whose length and width direction shrunk 5 mm to 6 mm, and the thickness expanded about 3 mm. This showed that the high temperature resistant borated polyethylene shielding material has excellent high temperature resistance property, does not stick with structural parts, and was easy to unload and replaced. In contrast, there was a significant plasticizing flow in the ordinary borated polyethylene, who softened and deformed most seriously. Although the borated polypropylene with higher melting temperature maintained the basic shielding structure, it still appeared obvious deformation and flowing phenomenon, which could not be removed from the steel structure.
**Figure 8.** Shape of three samples after test.

**Table 4.** High temperature test results.

| Test items | Technical index | High temperature resistant borated polyethylene | Ordinary borated polyethylene | Borated polypropylene |
|------------|-----------------|--------------------------------------------------|-------------------------------|-----------------------|
| Appearance | The shielding structure should remain intact without softening, collapse and obvious deformation | The shielding structure remained intact without softening, collapse and obvious deformation | Softening and collapse completely | The shielding structure was basically maintained, but the deformation was serious |
| Weight(%)  | The change was not more than 4% before the test | -0.04% | 0.89% | 0.10% |

**4. Conclusions**

In this paper, according to the source characteristics and protection requirements of the nuclear power plant, a kind of high temperature resistant borated polyethylene shielding material was studied. Firstly, the composition ratio was optimized by using genetic algorithm and Monte Carlo method, which could play a better shielding effect. Secondly, UHMW-PE was added by blending modification method to keep the structure of shield material no softening and deformed without external force since its high melt strength and was not sensitive to thermal shear, it also could ensure the shielding effect and machinability do not decline. And a method of melt grafting of MAH onto polyethylene was used, which could improve the mixing uniformity and mechanical properties significantly for the high boron ratio condition. Finally, its mechanical, neutron shielding, irradiation resistance and high temperature resistance properties were comprehensively verified during the high temperature resistant borated polyethylene, ordinary borated polyethylene and polypropylene. The results showed that the high temperature resistant borated polyethylene has excellent performance, especially in the high temperature environment up to 190°C, it could keep the shielding structure intact and effective, ensure a safety use in the containment area of nuclear power plant.

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