Influence of filler content on adhesive properties of radiation-protective sheeting

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Abstract. It is actual now to work out new radiation protecting sheeting on the basis of a curing polymeric composition, which possesses self-glued properties, are easily mounted and dismantled and provide high tightness and low permeability. For the creation of a new self-glued radiation-protective material it is necessary to define the filler volume at which composite would be sticky enough (peel strength not less than 4 N/cm); character of a separation would be cohesive (on a material) and thus there would be no migration of softener and satisfactory resistance of fluidity. The object of investigation is a composite material, consisting of butyl rubber, industrial oil, barite and alkyl phenol-formaldehyde resin. The area of structures, which meet the requirements for a self-glued composite, is revealed. The optimal composite content is determined. The given structure has the high filler content, necessary for the content of radiating protection against gamma radiation, and also a reserve in its self-glued properties. The given structure is possible to consider as a base for the optimization of radiation-protective sheeting with the application of other fillers, such as lead, tungsten etc.

1. Introduction

One of the most important problems of ecology is a problem on recycling of radiation-active waste the final solution of which has not been found yet. The matter is that a source of the radiation waste is not only atomic power stations, but also various enterprises, research centers, military bases and medical institutions [1]. And though the most part of waste makes low radioactive dust, it can be very dangerous, too. The main problem is that radiating dust keeps its pernicious properties throughout hundreds and even thousand years as a half-life period of such element as strontium-90 is twenty six years, and, for example, plutonium-239 is twenty four thousand years.

Both radiating materials which have fulfilled the resource, and materials which have come into contact with radiation must be recycled: from capsules containing fulfilled materials (strontium, uranium, plutonium, radium, etc.) to building designs which have not been cleared at application of various types of deactivation. The volume of the last represents the greatest complexity at recycling. One of effective decisions to reduce the volume of materials which are to have an entombment after finishing their work in radiation-dangerous areas is application of radiation protecting sheeting [2]. Now used radiation protecting sheeting represent curing materials put on surfaces in the form of mastics, or sheet polymeric materials which fasten special devices. Manufacturers of such materials are ITW and LEMER PAX. Sheet materials don’t have tight joints that allow getting radiation to the
basic designs. Barite plaster FullMIX X-ray protection is known among radiation-protective materials. The disadvantage of barite plaster is that it is difficult to remove it at saturation by radionuclide.

In V. N. Gulbin's articles with co-authors [3,4] it is shown, that investigated radiation-protective polymeric composites filled nano-tungsten, can weaken essentially only low energy streams of gamma quanta.

As a result it is actual now to work out new radiation protecting sheeting on the basis of curing polymeric composition which possess self-glued properties, are easily mounted and dismantled and provide high tightness and low permeability.

Radiation protecting sheeting on the basis of curing compositions as a rule include following components: viscosity element, fillers, softeners, various modifying and technologically additives. All components separately and together can directly regulate technological, and physical and mechanical properties of a material [5].

Heavy materials are the most effective concerning ionizing radiation absorption: widely applied are lead, barium [6]. Unfortunately, materials on the basis of lead do not always possess sufficient physical and mechanical properties, and filler itself is toxic [7, 8].

Barium sulfate (BaSO₄) is ecologically pure nontoxic material widely used in radiation-protective materials [9-11]. In the work of Seon-Chil Kim with co-authors [12] results of researches on working out of the radiation-filter used in medical institutions are presented. As the main filler barium was applied into which tungsten and tourmaline, as viscosity element - synthetic rubber and silicone were added. As a result it was established, that barium application allows receiving effective highly filled radiation-protective material. However there are also disadvantages - the received covering has the sheet form, it works on a bend badly, does not possess glutinosity to various surfaces. There are also technological disadvantages - complexity of blend preparation because of high density and big maintenance of barium in the blend.

The researches showing efficiency of a composite polymer-tungsten in struggle against an ionizing radiation [13, 14] are carried out. In the work of H. M. Soylu with co-authors [15] test results of a composition on the basis of ethylene-vinyl acetate, filled with carbide tungsten are presented. It is shown, that at the greatest filling (70 %) metal-polymeric the composition possesses the best radiation-protective properties.

Fillers, added into polymer, can carry out various functions [16]. The content increasing of heavy filler in a composite polymer-metal increases radiation-protective properties, but worsens physical and mechanical properties of a system, reducing first of all durability, adhesive properties.

In R. Yu. Galimzjanova's works with co-authors influence of technological additives, modifiers [17-19] and softeners [20] on properties of composites on the basis of synthetic rubbers is studied. In work as [21] team of authors showed physical and mechanical properties of highly filled compositions on the basis of synthetic rubbers. It is established, that at filler content approximately 40 % the maximum adhesive durability to such materials as steel, duralumin, glass is observed. The further increasing in the filler content considerably reduces adhesive durability of a material.

The presented results confirm possibility of creation self-glued radiation-protective sheeting on the basis of curing polymeric composition with given physical and mechanical properties. For creation of a new self-glued radiation-protective material it is necessary to define filler volume at which composite would be sticky enough (peel strength not less than 4 N/cm); character of a separation would be cohesive (on a material) and thus there would be no migration of softener and satisfactory resistance of fluidity.

2. Materials and Methods

2.1. Materials
As a basis for a polymeric composite material butyl rubber BK-1675H TU 38,303103-93 (SIBUR, Russia) is used. Softener - industrial oil I-40 GOST 20799-880 (RussNeft, Russia). As a filler
microbarite Mibari (GeoKOM, Russia) is used. As an agent of stickiness alkyl phenol-formaldehyde resin SP-1045 ("SI Group", France) is used.

Compositions and brands of the studied composites are given in Table 1.

| Table 1. Compositions and brands of the studied composites. |
|-----------------------------------------------------------|
|               | Volume fraction, % | Mass fraction, g |               |               |
|               | BK-1675H I-40 Mibari SP-1045 | BK-1675H |               |               |
| B14B30        | 42 28 30           | 19.4 12.9 67.7  |               |               |
| B14B40        | 36 24 40           | 14.1 9.4 76.5   |               |               |
| B14B50        | 30 20 50           | 10.2 6.8 83.0   |               |               |
| B15B40        | 30 30 40           | 11.7 11.7 76.5  |               |               |
| B15B50        | 25 25 50           | 8.5 8.5 83.0    |               |               |
| B15B60        | 20 20 60           | 6.0 6.0 88.0    |               |               |
| B16B40        | 24 36 40           | 9.4 14.1 76.5   |               |               |
| B16B50        | 20 30 50           | 6.8 10.2 83.0   |               |               |
| B16B60        | 16 24 60           | 4.8 7.2 88.0    |               |               |
| B15B60S1.5    | 19.4 19.4 58.1 3.1 | 6.0 6.0 88.0 1.5 |               |               |
| B15B60S3      | 18.8 18.8 56.3 6.1 | 6.0 6.0 88.0 3  |               |               |
| B15B60S4.5    | 18.2 18.2 54.7 8.9 | 6.0 6.0 88.0 4.5|               |               |
| B16B60S1.5    | 19.4 19.4 58.1 3.1 | 4.8 7.2 88.0 1.5|               |               |
| B16B60S3      | 18.8 18.8 56.3 6.1 | 4.8 7.2 88.0 3  |               |               |
| B16B60S4.5    | 18.2 18.2 54.7 8.9 | 4.8 7.2 88.0 4.5|               |               |

In the blends marked B14 a ratio of butyl rubber/softener in a polymeric blend - 60/40; B15 - 50/50; B16 - 40/60.

Relative density was applied to recalculation of volume fractions in the density the components, making for BK-1675H - 0.92 g/cm³; I-40 - 0.90 g/cm³; Mibari - 4.45 g/cm³; SP-1045 - 1.40 g/cm³.

Composite mixtures were made with the help of a batch laboratory mixer with tangential rotors. The polymer was initially stirred at a temperature of 120°C at a speed of 44 rpm for 20 minutes. Further, the polymer was mixed with a plasticizer, then filler and modifier were added, then it was rolled on a rolling mill machine till a material had a uniform thickness.

2.2. Methods
Adhesion strength with metal is determined by GOST 24025. Peel strength with metal is determined by GOST 21981. Densities, penetration, resistance of fluidity and plasticizer migration are determined by GOST 25945.

3. Results and Discussion
3.1. Composition without agent of stickiness
Butyl rubber possesses low stickiness and for adhesion maintenance to metal it is necessary to add plasticizer. As it has been found out earlier [22], addition of industrial oil as softener to the volume content of 40% conducts to increase adhesive durability, and then it starts to decrease. The filled compositions at the oil content in a polymeric blend of 40% show the highest values adhesion
strength and peel strength to metal (figure 1), however at the filler content over 40 % on volume adhesive character of rupture (composite-metal boundary fracture or fracture between net and composite, figure 3 see) in this connection, for formation of composites with bigger filler share the softener content in a polymeric mix is necessary to increase is observed. The increase in the maintenance of softener leads to decrease adhesion strength and peel strength to metal (figure 1) irrespective of filler quantity, increases penetration and slightly reduces composite density (figure 2).

**Figure 1.** Adhesion strength and peel strength from metal at different volume content of oil in polymer bland, %. Continuous line - adhesion strength; Dashed line - peel strength.

**Figure 2.** Penetration and density at different volume content of oil in polymer bland, %. Continuous line - penetration; Dashed line - density.

Increasing of barite in percentage content, as well as other fillers [21,23], at first they raise adhesion strength (figure 1) and peel strength to metal (figure 2), but since a volume fraction of filling of 40 % durability starts to decrease irrespective of the softener maintenance. Also with share increasing of filler penetration decreases (figure 3) and the composite density (figure 4) raises. At the maximum filler share the composite density makes 60 % on volume about 2,9 g/sm3 and penetration makes about 3,3 mm, and the difference of these values depending on the softener maintenance is insignificant.
All samples were tested on resistance of fluidity, however softener migration is found out in samples with the softener content in a polymeric blend of 50 and 60 % and with filler content in a composite to 50 % on volume. 

Having united all data of tests for the scheme (fig.5) for optimization of a composite structure to begin with we will reject areas where the composite mismatches technical requirements, namely:

- Area A, with plasticizer migration;
- Area B, with low peel strength (low, then 4 N/cm);
- Area C, with adhesion fracture (composite-metal boundary fracture or fracture between net and composite)

![Figure 3. Optimization of bland.](image)

As a result the area was formed, any structure of a composite from which corresponds to technical requirements. From drawing it is seen, that at the volume content of barite of 60 % any of structures does not answer technical requirements. The structure with the maximum filler content, meeting these requirements, will be the following: a ratio butyl rubber/oil in a polymeric blend 52/48, the volume content of barite - 56 %. However this structure does not have safety factor at possible technological variations and thereupon there is a technical necessity to use in the blend content special agents of stickiness in which various resin have been characterized from a positive side.

3.2. Composition with agent of stickiness

In various sources researches of adhesive durability of composites depending on the content of various resin are resulted. For composites on a basis of butyl rubber the best agent of stickiness is alkyl phenol-formaldehyde resin [19]. It is necessary to notice, that in the literature, as a rule, the certain weight of resin is added to some structure of a composite then the new composition is investigated. It is also accepted in this article. Thus it is considered, that heavy filler is used in research of radiation-protective compositions, the composite density is very high too, and thereupon it is recommended to consider, what volume in a composite will be occupied by this or that weight of resin. In the given article as initial blends structures with the greatest filler content with marks B15B50 and B16B60 in which consistently added 1.5, 3 and 4.5 g SP-1045 on 100 g of a composite are accepted. In volume fractions it will make accordingly 3, 6 and 9 %. Results of experiments by definition adhesion strength and peel strength to metal are shown on fig. 6 and 7 accordingly.
Figure 4. Adhesion strength and peel strength from metal at different content of SP-1045 in a composite, %. Continuous line - adhesion strength; Dashed line - peel strength.

As it is seen from drawings, resin considerably raises adhesive durability of composites, thus cohesive character of a separation is observed. To a mass fraction of 3 % durability grows almost linearly, further growth of durability not so such considerable and if to continue to increase the resin content in a composite, it will gradually start to turn to plastic, i.e. stickiness quickly enough will disappear, cohesive character of a separation will turn in adhesive and durability will decrease. Thereupon it is possible to consider as the optimum maintenance of resin 3 g on 100 g a composite (at its density of 2,9 g/cm3) or 6 % on volume. It is thus observed cohesive character of destruction, and durability with a stock exceeds value 4 N/cm even at 60 % of the filler content in the initial blend. Though to be exact, resin addition in the described technology has lowered the percentage volume content of barite to 56 % (see the left bottom part of table 1).

4. Summary
Properties of composites consisting from various percentage ratio butyl rubber-oil-barite are investigated. The area of structures which meet the requirements for a self-glued composite is revealed: durability on a separation not lower than 4 N/cm, cohesive character of a separation, absence of softener migration, satisfactory resistance of fluidity. It is shown, that structure with the maximum content of barite meeting these requirements, will be the following: a ratio butyl rubber/oil in a polymeric blend 52/48, volume content of barite - 56 %. However this structure does not have safety factor at possible technological variations and thereupon there is a technical necessity to use resin in the blend content.

Structures with maximum content of barite with addition into them alkyl phenol-formaldehyde resin are investigated. It is established, that it is possible to consider as optimum quantity of resin 3 g on 100 g a composite (at its density of 2,9 g/cm³) or 6 % on volume. At the given content of resin the structure in which ratio butyl rubber/oil in a polymeric blend 50/50, the volume content of barite – 60 % (or 88 % by mass) has shown cohesive character of a separation and durability 5 H/m. The given structure has the high filler content, necessary for content of radiating protection against gamma radiation, and also a reserve in its self-glued properties. The given structure is possible to consider as a base for optimization of radiation-protective sheeting with application of other fillers, such as lead, tungsten etc.

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