CHARACTERIZATION OF ASPHALTIC/ELASTOMERIC MATRICES PROCESSED BY MICROWAVE ENERGY FOR IMMOBILIZATION OF RADIOACTIVE WASTE

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The asphaltic/elastomeric matrices used in this work were compounded by bitumen and production leftovers of ethylene vinyl acetate (EVA). They were employed to embed radioactive waste (ion exchange resin) after irradiation by using a microwave device (2,450MHz), at IPEN-CNEN/SP. They were carried out varying the irradiation time and power. The temperature during the processes was controlled by a thermocouple. In order to get the most homogenous matrix formulation, the following process parameters were analysed: irradiation time, microwave power, bitumen/resin/rubber percentages, penetration, fire and flash points of the samples. The characterization results of the samples (before and after irradiation) were obtained according to Associação Brasileira de Normas Técnicas (ABNT-NBR). The purpose was to improve the chemical and physical properties of matrices and then reduce any possible dispersion of the radioactive waste in the environment during the stages of intermediate storage, transportation and final disposal.

Introduction

Researches and developments in nuclear area have generated radioactive wastes in a variety of physical and chemical forms, including gases, liquids and solids, and have a wide range of levels of radioactivity. The management of those wastes is a matter of serious concern and a lot of immobilization process have been used for their safer storage.

Immobilization of wastes is intended to prevent or restrict the unintended dispersal of radionuclides into the environment from a storage or disposal facility. The continuous improvement of waste immobilization conditions, in more stable form, would be able to keep its insulation during its entire decay and to protect both human life and the environment from harmful radiation effects. The storage of those residues depends on the composition, activity level and disposal options for the final product. It also must be done by applying chemically stable materials as immobilization matrices in order to avoid as much leaching and dispersal of compounds as possible.

The matrices considered for immobilization are cementitious materials, bitumens, other organic and inorganic polymers, the products of high-temperature incineration and melting, phosphate ceramics, glasses and glass ceramics, among others.

Bitumen and other polymers have been widely used to embed low level radioactive waste (LLW) - not exceeding 4GBq/t alpha or 12GBq/t beta-gamma activity - and intermediate level radioactive waste (ILW) - waste whose radioactivity levels exceed the upper boundaries for LLW, but which does not require heating to be taken into account in the design of storage or disposal facilities. Bitumen is a complex mixture of heavy aliphatic and aromatic hydrocarbons whose properties make it a potentially good immobilization matrix. It is usually obtained from asphaltic crude oil after separation of light fractions and also contains small amounts of sulphur, nitrogen and oxygen. This material has some advantages, like: good leach resistance, all the water in the waste is removed by the process, resulting in good waste loadings structural stability, plasticity with the aggregate, impermeability, stable blend and easy application. It encapsulates waste in a viscous, self-sealing, low-permeability, neutral, amorphous solid waste form with good long-term durability LLW and ILW (mainly liquid and wet wastes). Moreover, it has a common practice in industrial routine in Belgium and France, besides a relatively low cost.

Other categories of polymers that can be employed as immobilization matrices for radioactive wastes are plastics and vulcanized rubbers. When these materials are discarded after being used or in production leftovers, they also cause a lot of trouble to the environment where they remain for many years, before they are naturally decomposed. The reasons for their use is that they: encapsulate waste in a variety of hard, low permeability, amorphous to semi-crystalline solid waste forms with good long-term durability (best suited to beta-gamma emitting wastes). They are also commonly applied in industrial routine, with low relative cost in the United States of America. [1, 2]

In general, in those immobilization process the mixture of polymeric matrix and radioactive waste is made in an extruder, where the materials are heated (although the equipment might be contaminated). Next, the mixture is poured in barrels for final storage where it becomes solid as it gets cold. This is the most usual method because it brings excellent results.[3]

In this work, the possibility of reusing polymeric materials was analysed, particularly with production leftovers of vulcanized rubber (EVA - ethylene vinyl acetate) as a component of bitumen matrices for immobilization of radioactive waste. This material was utilized as aglomerate agent in the immobilization matrices of radioactive waste.
The radioactive waste employed for preliminary texts of materials compatibility was used ion exchange resin (insoluble matrix in which ions are easily trapped and released).
The preparation of matrices and generation of homogeneous blends of those materials were made by using microwave radiation. The advantages of using this type of electromagnetic energy for treatment or immobilization of hazardous components are the rapid and selective heating and the environmentally clean process with low pollutant emission. Other features are: ability to treat wastes in-situ; improved safety, including reductions in human exposure to potentially hazardous chemicals or materials for processing and disposing; energy saving; easy, rapid and flexible control process that can also be made remote etc. The microwave heating occurs when the electromagnetic waves penetrate the material, usually polar molecules, and release energy as heat. [4, 5]
Therefore, the objective of this work was to show the results of the characterizations of the studies carried out to determine the ratio of bitumen/resin/rubber irradiated with microwave energy, suitable for incorporating ion exchange resin, similar to that one contaminated by radioactive waste in a stable matrix. This would provide not only an environmentally sound strategy, but could also result in a significant potential return on investment.

Experimental

Samples Preparation

Several samples were prepared in order to better define the proportion of materials that should be used in the immobilization of radioactive waste (contaminated ion exchange resin) with bitumen and rubber.
The percentage of bitumen incorporated in the blend resin/rubber was determined by means of preparation of sets of samples, varying the bitumen amount from 40.0%wt to 50.0%wt; resin, from 45.0%wt to 50.0%wt and rubber, from 0.0%wt to 15.0%wt. They were weighed in a scale model LC2 (*Marte Balança e Equipamentos*), 400g of total mass: bitumen – oxidated asphalt VIT – 90, Viapol; rubber - EVA (shoe sole leftover, Grendene®) and inactive (non contaminated by radiation) ion exchange resin - Amberlite® – IRN 217 (type anionic-cationic, with sphere diameter of 0,3mm-0,2%, formulated especially to nuclear application – primary circuit water chemical treatment in the research reactor at IPEN, IEA-R1. [6]

Samples Irradiation
All the samples were irradiated in a microwave device (power of 1,000W and frequency of 2,450MHz), at IPEN-CNEN/SP in two different types of double boiled. That equipment consists of a magnetron valve, a wave guide and a cavity (where the samples were disposed). The following process parameters, irradiation time and microwave power were determined in several assays previously developed. The samples temperature was controlled by using a "K type" thermocouple, Panasonic.
Sets of samples of 400g (total weight), whose the percentages are shown in Table 1, were irradiated according to the following procedures.

TABLE 1: Percentage of bitumen, resin and rubber in the samples, to make blends.

MATRIX	BITUMEN (%wt)	RESIN (%wt)	RUBBER (%wt)
Sample 1	50.0	50.0	0.0
Sample 2	47.5	52.5	0.0
Sample 3	45.0	55.0	0.0
Sample 4	47.5	47.5	5.0
Sample 5	47.5	42.5	10.0
Sample 6	47.5	37.5	15.0
Sample 7	45.0	40.0	15.0
Sample 8	42.5	42.5	15.0
Sample 9	40.0	45.0	15.0

- Procedure 1: bitumen was irradiated for 15min in a glass recipient, double boiled in magnetite powder Fe_3O_4 (density of 5,3g/cm^3 at 25°C) of same mass, equally distributed. This material was used because it is one of the minerals that contain good microwave absorbing. [7]
The bitumen and the magnetite levels were the same. After irradiations, those materials still remained for 5min, in order to have the temperature equally distributed in the recipient. The bitumen temperature was controlled during irradiations and cooling stage so as not to be over 250°C (flash point temperature) and to be under 85°C (softening point), respectively.

- Procedure 2: blend of resin/rubber was irradiated according procedure 1, during 5min. The bitumen temperature was controlled between 100°C and 160°C to make possible mix rubber and resin without the bitumen become hard or solid.
After those procedures were followed, the blends of resin/ rubber were put in paraffin paper cups and next the bitumen was added. The mixture was manually shaken to get more homogeneity. After some cooling, the molds were easily separated in samples.

Samples Characterization

The matrices obtained in procedures 1 e 2 (*samples preparation*) were submitted to the following physical tests: penetration, softening, flash and fire points. These characterizations were made to identify the matrix that showed the best immobilization efficiency and the highest mechanical resistance.
Tests description:
- Penetration test: the Brazilian standard NBR 6576 (1998) covers determination of penetration of semi-solid and solid bituminous materials. Penetration is the distance (in millimeters) a standard needle penetrates the sample vertically, under predetermined load condition, with 100g of sample in 5s at 25°C.
- Softening point test: the Brazilian standard NBR 6560 (2000) covers the determination of the softening point of bitumen. The ring and ball apparatus is used to determine the transition point between solid and liquid state and indicates the trend of the material flow under that temperature.
- Flash and fire points test: the Brazilian standard NBR 11341 (2004) describes the determination of flash and fire points of petroleum products by a manual or an automated Cleveland open cup apparatus. This is a dynamic method and depends on definite rates of temperature increase. It is used to determine the fire point, which is the temperature above the flash point, at which the test specimen will support combustion for a minimum of 5s.

Results and Discussion

Based on the results obtained in the flash point test, often used in the adjustment of transportation and safety, it was possible to determine the safe operation temperature of those materials employed in the matrices production. From these results, the temperature monitoring was done along with the process to prevent the bitumen and resin temperature from reaching 250°C (flash point) and 160°C (releasing explosive aminoacids), respectively.
A series of assays to determine the irradiation time and the microwave power applied in the samples was performed for pure bitumen sample. The results showed that by keeping the microwave power applied in 100% it was possible to irradiate that sample for 15min to get the necessary fluidity to prepare the matrices, having the material temperature kept within the safety limit, without degrading the sample. Also a similar series of assays was performed for polymer and it was observed that under 100% of microwave power applied, 5min of irradiation were necessary to reach the ideal temperature by addition and homogenization of the blend without exceeding 160°C.
From these results it was observed that the addition of rubber (EVA) in the immobilization matrix reduced the penetration value from 7 to 2 tenth part of millimeter (Figure 1). These data indicated a previous measure of material deformation. The smaller was the penetration measure, the higher was the matrix hardness, and the compression resistance increased when it was compared to a matrix consisted of pure bitumen.
The matrix behaviour, varying the percentage of EVA, is shown in Figure 2. It can be seen that the addition of EVA led the softening point to reach 120°C. Concerning these results, it was possible to get a previous idea of the supported maximun temperature to keep the matrix for future embedding of radioactive waste, in solid state.
According to the blends analysed by penetration tests, two matrices showed the smallest penetration values: 47.5%wt bitumen/10%wt EVA/42.5%wt resin (sample 5) and 42.5%wt bitumen/15%wt EVA/42.5%wt resin (sample 8).

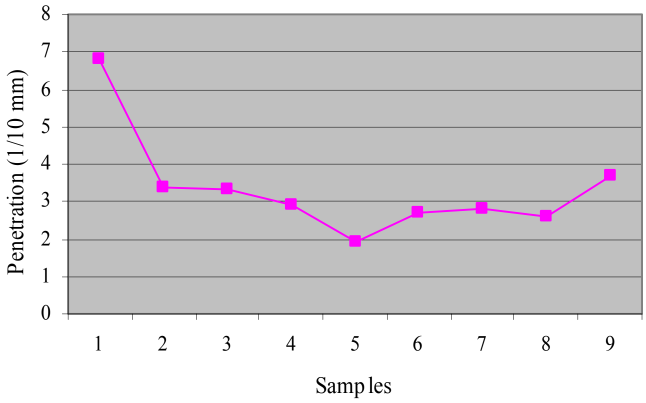

Figure 1 – Results of penetration test of blends (bitumen/resin/rubber).

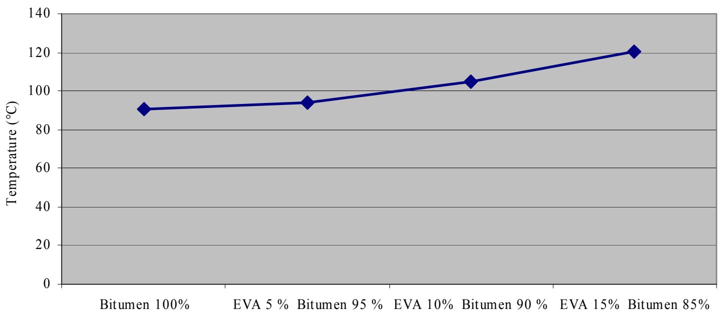

Figure 2 – Softening point of bitumen/EVA matrix.

Conclusion

Based upon the characterization results it was possible to verify that the addition of rubber in the bituminous matrix improved the performance regarding the mechanical property. Herewith, it could be assumed an increase in the resistance to weariness, in the permanent deformation and a reduction of thermal crack for the developed blend, when it was compared with the matrix of pure bitumen.

Concerning all materials analysed, the EVA rubber showed the most suitable results of mechanical resistance when they were compared to the results obtained to pure bitumen.

The choice of both matrices with incorporated resin can be refined through additional chemical tests. These tests will give evidence of leaching resistance of the matrices.

The efficiency of microwave technology for immobilization of radioactive waste has been evaluated and its application on this area is still in the first steps of development. In the present study, the microwave irradiation time and the microwave power applied to optimize the process were controlled to keep the safety limits established for those materials, providing fast, uniform and selective bulk heating of the material.

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