Poly(methyl Methacrylate) as Incorporation Medium for Spent Ion-Exchange Resin. II. Simulated Resin

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Synopsis

The incorporation and final containment of spent ion-exchange resins into poly(methyl methacrylate) (PMMA) was investigated in the present study. Test blocks of PMMA with 50% incorporated inactive resin were subjected to radiation doses of 10^5–10^7 rad at a dose rate of 50 rad/s. The high radiation doses impaired the mechanical properties of the final products. Both compressive strength and hardness decreased with increasing the particle size of the ion-exchange resin. DTA diagrams showed the thermal instability of the final solidification product at about 400°C. Leaching experiments on incorporated blocks of active resins labelled with Cs-137 and Ce-144 showed that cesium activity was more easily released in leachant solutions than was cerium activity. Cumulative leaching rates for both Cs and Ce were lower in deionized water than in underground water. The mechanical, thermal, and leaching data obtained illustrate the suitability of PMMA for immobilization of spent ion-exchange resins with low specific activity.

INTRODUCTION

Ion-exchange purification processes are commonly applied in controlling the chemistry and radioactivity of water streams in nuclear power plants. Spent organic resins are characterized by relatively high specific activity and unstable chemical nature and is, therefore, considered to be a problematic fraction of low- and intermediate-level radioactive wastes.[1]

Treatment involves the incorporation of spent ion-exchange resins in its original forms[2] or after pretreatment[3] into an inert suitable matrix to give a homogeneous solid product having high mechanical and chemical stability favorable for final disposal. The generally proposed incorporation materials are cement, bitumen, organic polymers, or a combination of more than one.[1] The most widely used processes are cementation[4] and bituminization.[5] Different types of polymers,[6–8] as incorporation media, have been used as alternatives for bitumen and cement to achieve an improvement in the solidification process and better specifications of the final products.

The aim of the present study was to evaluate polymethyl methacrylate (PMMA) as incorporation medium for the solidification and final containment of spent ion-exchange resins.

EXPERIMENTAL

The ion-exchange resins used in the present investigation were cationic and anionic Russian types used at the Inshas Reactor (Egypt) with the following specifications: the cationite in H form, grain diameter 0.8 + 1.2 mm, swelling

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TABLE I
Irradiation Effect on Mechanical Properties of PMMA with 50 wt % Ion-Exchange Resin

Radiation dose (rad)	Compressive strength (kg/cm^2)	Hardness (k_p/mm^2)
0	640.82	4.59
7.20×10^5	762.88	6.27
4.32×10^6	777.13	6.50
1.73×10^7	351.18	5.46
3.02×10^7	331.64	5.38
4.32×10^7	135.83	5.34
6.04×10^7	113.085	4.97
7.77×10^7	65.997	4.81

capacity 50%, and filling weight 0.89 g/cm^3, and the anionite in OH form, grain diameter 0.8 + 2 mm, swelling capacity 106%, and filling weight 0.64 g/cm^3. Fresh inactive resins were incorporated into the polymer to study its mechanical and thermal properties. Simulated labeled resins were prepared by treating inactive cation-exchange resin with the desired amount of Cs-137 and Ce-144. The labeled resin was dried at 85°C and used for the preparation of incorporated samples for leaching experiments. In addition, samples of the simulated labeled resin were saturated with water before incorporating into the polymer to study the effect of its water content on leachability. Chemically treated resins were prepared by soaking in 4*M* nitric acid. Methyl methacrylate monomer (E. Merck, A.R.) was freed from inhibitor by distillation under reduced pressure.

Solid homogeneous cylindrical blocks, 3 cm high and 1.5 cm in diameter, were obtained by incorporating 50 wt % ion-exchange resin into PMMA. The dry resin particles were added to an equal amount of matrix solution. After settlement, the mixture was polymerized in the presence of benzoyl peroxide as initiator at room temperature, by heat or by irradiation in a γ-cell (50 rad/s).

The specification of two to five prepared solid blocks such as thermal and mechanical properties were determined using NETZSCH-Geratbau GmbH, simultaneous thermal analysis apparatus STA 409, Wolpert Hardness Tester HT 2004, and Instron Universal Testing Instrument Model 1178.

Leaching experiments were carried out according to Hespe's[9] method using deionized or underground water as leaching solutions. The method was modified so that the whole surface area was exposed to leaching solutions. The underground water used was obtained from the Abu-Zaable well, the nearest well to the Inshas Reactor site.

Coated samples, were prepared to achieve better protection for the resin particles and to reduce leachability of the different radionuclides. The already prepared solid blocks were coated by immersing them in an equal volume of partially polymerized MMA solution and the polymerization was then completed as mentioned above. The thickness of the outer layer of PMMA was 2 mm.

RESULTS AND DISCUSSION

Mechanical properties are one of the important factors to be taken into consideration in evaluating the final solidified products. The effect of irradiation on both hardness and compressive strength was studied by subjecting the so-

TABLE II
Effect of Mesh Size on the Mechanical Properties of PMMA

Mesh size (mm)	Compressive strength (kg/cm^2)	Hardness (k_p/mm^2)
0.841	956	6.59
1.000	980.27	6.17
1.410	741.27	6.11
2.000	679.14	5.77

lidified blocks of inactive incorporated resin to radiation doses ranging from 7.2 $\times 10^5$ to 7.77×10^7 rad using cobalt-60 source (50 rad/s).

From the data represented in Table I, it is clear that the compressive strength increases at first and then decreases with increasing irradiation doses. This may be due to the fact that low radiation doses complete the polymerization process, whereas high doses result in degradation of the polymer matrix.

Hardness measurement values (Table I) follow the same trend of compressive strength. The results obtained indicate the limited use of PMMA as an incorporation medium specially for spent resins with high specific activity.

It was found that the moisture content of the incorporated ion-exchange resin has a great effect on its compressive strength.[10] Thus, samples prepared by incorporating dry resins and water-saturated resins show a drop of compressive strength from 597.50 to 95.54 kg/cm^2. Methyl methacrylate could not be polymerized when loaded with ion-exchange resin having water content more than 50%.

Mesh size of the incorporated resins affects the mechanical properties of the final products. The results represented in Table II indicate that the compressive strength and hardness decrease with increasing particle size.

Tensile strength was measured for rod samples (diameter 6 mm) to study the effect of different factors such as polymer/resin ratio, type of resin, and irradiation doses as shown in Table III. It was found that a low percentage of ion-exchange resins incorporation in polymer results in sedimentation of resin particles leaving the polymer at the top. The decrease in tensile strength by in-

TABLE III
Effect of Polymer/Resin Ratios, Type of Resin, and Irradiation on the Tensile Strength of PMMA

	Tensile strength (kg/cm^2)
Polymer/resin ratios	
0.9:1.0	158.53
0.9:0.5	108.71
Type of resin	
Cation	120.03
Anion	76.99
Cation + anion (1+1)	95.65
Radiation dose (rad)	
7.20×10^5	183.44
4.32×10^6	118.90
1.30×10^7	56.62

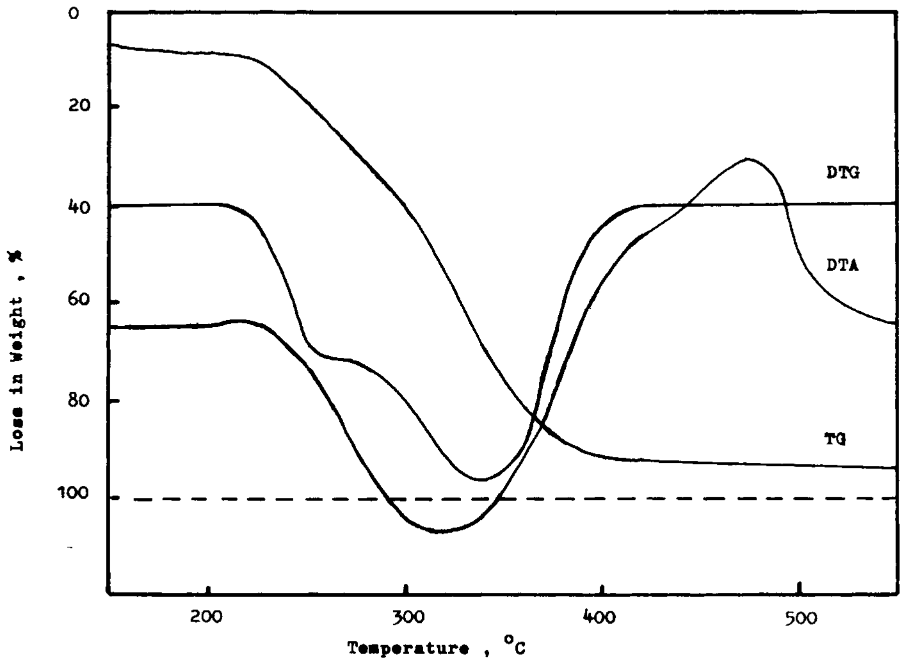

Fig. 1. Thermal analysis of PMMA. Heating rate = 5°C/min; sample weight = 0.666 g; reference material = Al_2O_3 (in closed atmosphere).

creasing the polymer/resin ratio may be due to the formation of a weak point between the excess free polymer and the loaded one. From Table III it is clear that irradiation doses cause a decrease in the tensile strength, which may be due to the degradation of the incorporation matrix. These findings are in agreements

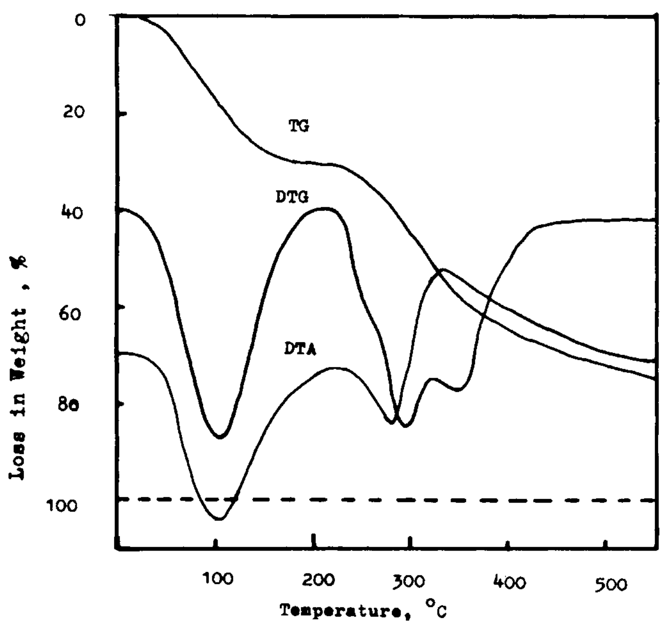

Fig. 2. Thermal analysis of loaded PMMA. Heating rate = 5°C/min; sample weight = 0.666 g; reference material = Al_2O_3 (in closed atmosphere).

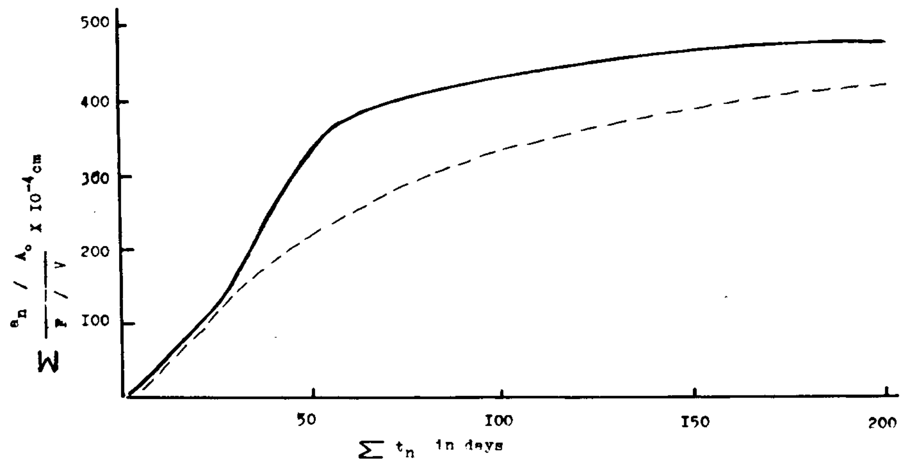

Fig. 3. Cumulative leach rate of Cs–137 using underground water as leachant: (- - -) dry resin; (—–) wet resin.

with the results illustrated in Table I for compressive strength and hardness. Also, Table III shows that incorporated anion-exchange resin exhibits lower tensile strength than the cation-incorporated one, which may be due to the fact that the anionite is characterized by a relatively large particle size.

Thermal conductivity, thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA) were performed for PMMA and PMMA loaded with ion-exchange resin. The results show only slight variation in thermal conductivity values for the different samples investigated and were found to be 1.465×10^{-2} W/m·°K.

TG, DTG, and DTA measurements of powdered samples were performed using

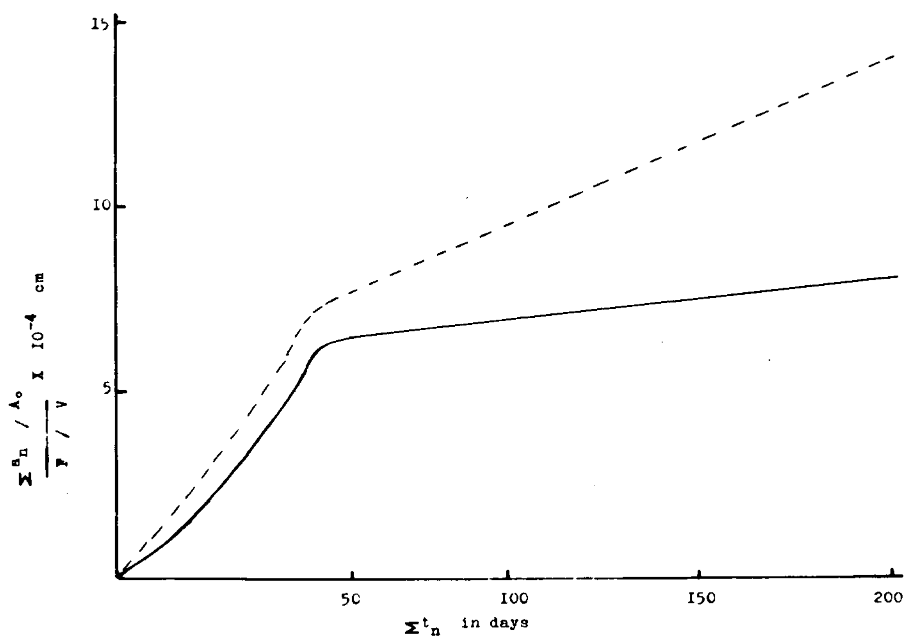

Fig. 4. Cumulative leach rate of Ce–144 using underground water as leachant: (- - -) dry resin; (—–) wet resin.

TABLE IV
Chemical Composition of Underground Water Leachant (Abu Zaable Well No. 202)

TDS		Soluble cations in PPM				Soluble anions in PPM		
(g/L)	pH	K	Na	Mg	Ca	Cl	SO_4	HCO_3
1.05	7.2	23	149	13	74	137	317	272

aluminium oxide as reference material and programming rate 5°C/min. Figures 1 and 2 show the thermograms of PMMA and the loaded one. DTG diagram of PMMA shows two main peaks, the first at 255°C and the second at 335°C, which indicate the thermal degradation of the polymer.

At the same temperature range, the DTA curve shows two endotherms completely overlapped. The first peak seems to display at about 265°C and the second one at about 320°C. The exothermic peak with maximum around 475°C may illustrate thermal changes.

DTG and DTA curves of the loaded PMMA show another peak at 100–120°C, which may be due to the loss of interinsic water in the incorporated ion-exchange resin.

Incorporation of spent resin into an inert matrix protects the particles and lowers the release of the different radionuclides to the biosphere. Hence leachability is of vital importance in choosing the suitable medium for immobilizing radioactive wastes in the present investigation the chemical behavior of the individual radionuclides (Cs and Ce) on the surface of spent resins was studied, when the final solid products come in contact with leachant solutions. The labeled simulated resins either in dry or wet form was incorporated in PMMA to study its leachability in deionized or underground water as leachants. The chemical composition of the underground water used is represented in Table IV. The results shown in Figures 3–7 are expressed by plotting the cumulative leach fraction $(a_n/A_0)/(F/V)$ vs. t_n, where A_0 = radioactivity initially present in specimen, F = exposed surface area of the specimen (cm^2), V = volume of the

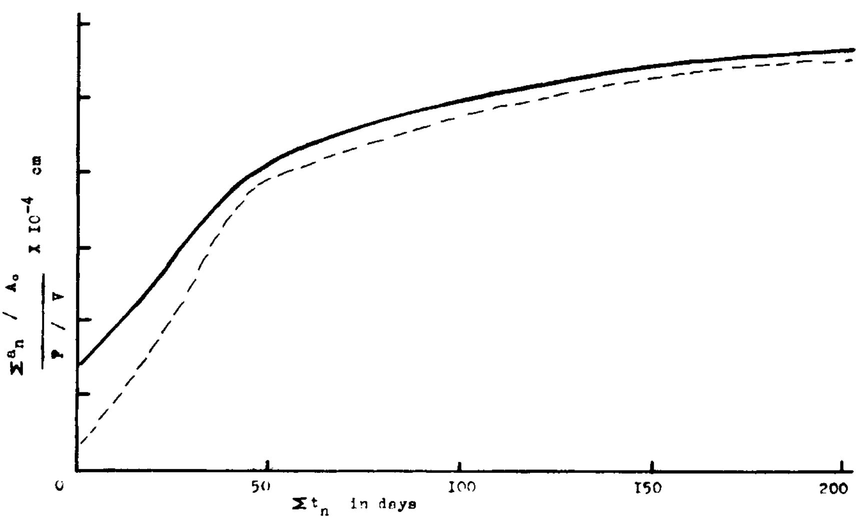

Fig. 5. Cumulative leach rate of Cs–137 acid-treated resin using underground water as leachant: (- - -) dry resin; (——) wet resin.

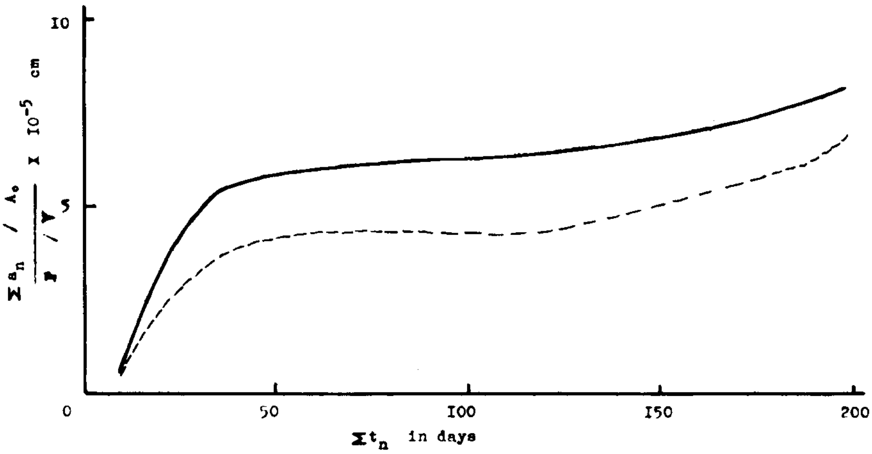

Fig. 6. Cumulative leach rate of labeled dry incorporated resin using deionized water as leachant: (- - -) Cs-labeled resin; (—) Ce-labeled resin.

specimen (cm^3), t_n = duration in days of leachant renewal period, a_n = radioactivity leached during the leachant renewal period n.

Cesium activity, being easily exchangeable and loosely bounded to IX resins,

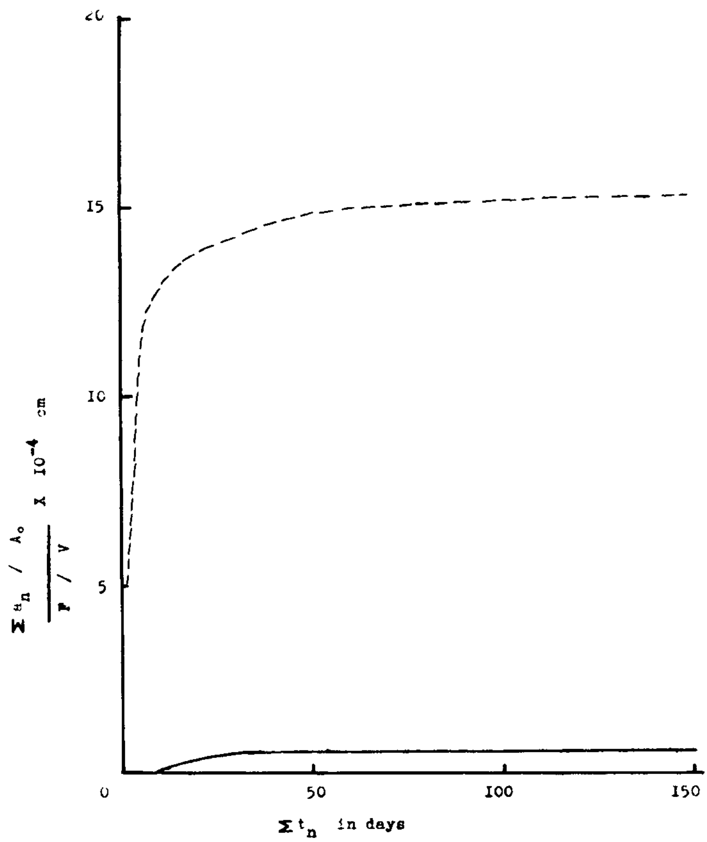

Fig. 7. Cumulative leach rate of Cs–137 using dry resin and deionized water as leachant: (- - -) noncoated samples; (—) coated samples.

was more easily released in leachant solutions than cerium activity for both wet and dry incorporated resins, (Figs. 3–5). Using cerium-labeled resin and underground water as leachant (Fig. 4), dry incorporated resin shows a higher leachability than wet incorporated one. This may be due to swelling of the incorporated dry resin, which results in an increase of the exposed surface area of the product to leaching solution. On the other hand, the reversed results obtained in case of cesium-labeled resin shown in Figure 3 may be due to surface contamination. Comparing the results shown in Figures 6, 3, and 4, it is clear that the cumulative leaching rate for both Cs and Ce are lower in deionized water than in the underground water. Exchange reaction is supposed to take place between the relatively high salt content of underground water used and the radionuclides fixed on the surface of the resin particles. The exchange phenomenon is considered to be responsible for the high leachability observed in case of underground water. Figure 7 indicates that coating the prepared blocks with a thin outer layer of the polymer matrix results in a decrease in cerium leachability, as expected. Hence, improvement in swelling and leaching properties was effectively achieved by using coated samples.

In conclusion, the results obtained concerning chemical, thermal, and mechanical properties of the final solidification products are promising and allow the consideration of PMMA as a possible incorporation medium for spent ion-exchange resin with low specific radioactivity. PMMA as incorporation matrix still show acceptable properties when compared with the most commonly used matrices namely cement and bitumen and thermosetting material.[2,3,6]

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