Interaction of La^{3+} and Ce^{4+} with Polyethylene and Polypropylene Polymeric Matrices

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ABSTRACT: The different modes of interaction of La^{3+} and Ce^{4+} as simulated radioactive lanthanides found in the backend of the nuclear fuel cycle with polyethylene and polypropylene macromolecules were considered. The various compositions were characterized before and after irradiation at different gamma ray doses. The mechanical properties including stress–strain parameters were also tested. The morphological and mechanical behaviors of the various composites were different from those of the corresponding pure polymers and affected by the chemistry of the interacting elements. Besides, the leaching characteristics were carried out using the short- and long-term procedure; the leaching rates were evaluated as an index for immobilization of these lanthanides. Two semiempirical models were applied to find out the dominant leaching mechanism of La^{3+} and Ce^{4+}. Dissolution associated with diffusion was the dominant leaching path and the elemental leaching characteristics depended upon its solubility in water. Diffusion coefficients and dissolution rate constants, the main parameters in the long-term prediction model, were obtained using short- and long-term experimental data. The model was found to be useful in predicting the long-term behavior of such elements to assess the stability of the used waste forms. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2141–2151, 2007

Key words: La^{3+} and Ce^{4+}; nitrate waste solutions; polyethylene and polypropylene; encapsulation; mechanical properties and leaching behavior

INTRODUCTION

The production of newly promising industrial materials of advanced applications requires the blending of different kinds of homopolymers of specific chemical characteristics.[1] This fact can be assigned to the improved optical and mechanical properties obtained in case of blended batches over the individual properties of the constituting homopolymers.[2] However, composites were recently developed to be used in different applications. Carbon black was used in many industrial facilities, especially as a filler in rubber matrix so that highly reinforced construction blocks are obtained.[3,4] Also, the mechanism of interaction of the filler with the used rubber was studied.[5–8]

Other researchers used silica powders to enhance the physical and chemical properties of polydimethylsiloxane. They were able get tailored chemical and physical properties.[1,9–12] These composites were stable for decades against numerous stresses inducing aging mechanisms: thermal and mechanical loads, environmental deterioration, irradiative and chemical attack.

However, in nuclear facilities, especially in radioactive waste management, the use of composites is less studied; most of the studies were concentrated on the use of ion exchange and solvent extraction techniques in liquid radioactive waste treatment.[13] Nowadays, the situation has been changed to encourage the concept of composite formation in the conditioning and treatment of low level and intermediate active wastes as they are chemically stable and have good resistant against ionizing radiation.[14] Most of the research was directed to use different types of cements as ordinary Portland Cement and Pozzolanic Cement as matrices for immobilization of radioactive wastes. However, the use of polymeric materials to immobilize the various radioactive nuclides was less emphasized.[15]

In addition to mechanical properties, chemical durability, which is considered as a measure for the leaching resistance, was studied. Leaching behavior is known to be the most important factor in the assessment of waste forms, which can be examined through the different leaching tests.[16] Experimental leaching data can be analyzed with a variety of parameters, including the diffusion coefficient and dissolution rate constant, to predict the long-term leaching behaviors.[17,18] According to some authors,[19,20] the leaching could be classified into two different stages during the leaching period. In the initial stage less than 1–2 months (about 50 days), some components leach out very fast, usually being controlled by diffusion, then after a few months the leached quan-

tity of specified metal becomes very small, uniform, and steady. Therefore, one can specify an initial stage less than 50 days as a short-term period, while that over 100 days and even more up to several hundreds of years can be specified as a long-term period. In this concern, if a model can predict the long-term leaching behavior of some hazardous components in a certain waste form using short-term experimental data, it will be very useful to determine its long-term stability or chemical durability for ensuring the safety during the final disposal period.

Therefore, this work has developed to use polyethylene and polypropylene as matrices and depicting the possible mechanisms of interaction of these polymeric substances with some simulated radioactive waste materials, especially lanthanides which may exist in the nuclear waste streams during the different stages of the nuclear fuel cycle. The prepared matrices were subjected to different leaching procedures. The first was the short-term Soxhelet one for 28 days. To assess their chemical durability, a long-term leaching test has been conducted by an ISO leaching method for 500 days. Leaching characteristics such as cumulative fraction leached and leach rate for waste constituents are examined. Leaching behaviors are also analyzed by two simple semiempirical models to determine the controlling leaching mechanisms of such components. For the assessment of the long-term stability, a theoretical leaching prediction model is applied to the long-term behavior of lanthanum and cerium simulated nuclides in the polymeric waste forms. It predicts the long-term leaching behavior using two parameters obtained from the short- and long-term leach test results.

EXPERIMENTAL

Materials

High density polyethylene was supplied by Union Carbide, USA, with a melting temperature of 130–140°C, while polypropylene was supplied by Merck Co, Germany, having a melting point between 165 and 170°C. Cerium was used as ceric ammonium nitrate, while lanthanum was obtained as lanthanum nitrate hexhaydrate, supplied by Sigma–Aldrich, USA, as analytical reagents and used without further purification.

Preparation of the matrices

Ceric ammonium nitrate and lanthanum nitrate hexahydrate were used to prepare cerium(IV) iodate and lanthanum(III) iodate, respectively. The two nitrate salts are highly soluble and were converted to the corresponding insoluble iodates by treatment of the salts with the corresponding metal iodates. The conversion process was optimized so that high surface areas of iodate powders are obtained. The specific surface areas of lanthanum and cerium iodates were measured using N_2 gas adsorption by means of the BET method, using NOVA 3200 surface analyzer (Quantachrom Corp., FL.)

The composites used in the present investigation have varied in composition so that different amounts of both cerium iodate and lanthanum iodate as representative examples of the lanthanides were used to be incorporated in polyethylene and polyethylene matrices. They ranged in compositions between 10 and 50 wt % of the corresponding iodates, namely, 10, 20, 40, and 50 wt % of the iodates are used.

Accurately weighed ingredients were mixed carefully together by means of a mixer of the electronic plasticorder type (CW Brabender Instruments, Hackensach, NJ). The mixing temperature was kept at 140°C in case of using polyethylene and at 170°C when using polypropylene as a matrix. The thermoplastic was first added to the mixer, then the simulated waste filler was added, and mixing was continued at a constant rotor speed of 50 rpm for about 5 min to obtain the required composition. This was then passed through an open two-roll mixing rubber mill size (300 × 470 mm^2) with a gear ratio of 1.14 : 1 at 80°C. The last step allowed the formation of sheets of the composite.

Sheets of 1 mm thickness were then obtained by compression molding between Holland cloth in clear and polished molds of an electrically heated hydraulic press. The molds were heated before handling to the melting temperature of high density polyethylene for about 10 min. A pressure of 18 MPa was applied by the press (Weber Pressen, Paul-Otto Weber GmbH, Rem Shalden, Germany) on the mold surfaces for 3 min. Molds were then cooled under compression by passing cold water through them.

Prior to pressing, the prepared samples were gamma preirradiated at 30 kGy to facilitate free radical formation, then irradiated after forming to the required dose using an irradiator of the Indian gamma chamber 4000 A type (Shirgaon, Ratnagiri, Maharashtra, India) with a dose rate of about 7.6 kGy h^{-1}. The irradiation doses ranged between 10 and 60 kGy; the absorbed dose was 4 kGy h^{-1} measured by Fricke dosimetry (G (Fe^{3+}) = 1.62 µmol J^{-1}); the error in dose estimation is ±3%. Irradiation was carried out under atmospheric conditions at a temperature of about 40°C.

Mechanical properties of the matrices

The stress–strain properties were measured on dumbbell shaped specimens of 4 mm width and 50 mm length. The thickness of the test specimens was determined to the nearest 0.001 mm. Yield strain and yield stress were measured using a universal testing machine of the Instron type, model 1195 (Bucking-

hamshire, UK) with a crosshead speed of 50 mm min^{-1}. The obtained results are the mean of three separate specimens values. The error in these measurements was ±5%.

Morphology of the matrices

The morphology of the prepared composites at different irradiation doses was studied using scanning electron microscopy. Samples were washed with acetone, dried at 50°C, and mounted on an SEM support and then made conductive with sputtered gold. The surface observations were made using JEOL JSM-5400 Scanning Electron Microscope (JEOL Inc., Peabody, MA).

Durability of the prepared matrices

Short-term leaching tests were carried out using Soxhelet-leaching method. Acetone was used to clean the specimen surface to be free of fine particles or dust, and the dimensions of these specimens were measured. The specimen was suspended in a perforated porous suspending device made of glass, and both were suspended in the sample cup. The leachant, deionized water 300 mL was used and the boiling rate of the leachant was adjusted so that the sample cup being empty every 12 ± 2 min, according to the international standards, and finally the produced solution was collected for analysis; the test was stopped after continuous action for 72 h and the leachates were then analyzed. Samples are analyzed using a Flame Atomic Absorption Spectrophotometer (Model 2380, Perkin–Elmer), they were fitted with a deuterium lamp background correction, and the appropriate hollow cathode lamps were used for the determination of the studied lanthanides. The source of the flame gases was cleaned and dried by filtration to remove oil, water, and other foreign substances. Working standard solutions were prepared by appropriate dilution of the corresponding stock solution. All measurements were made in triplicate.

In long-term leaching, the ISO leaching test (changing leachant) was applied to assess the long-term chemical durability of the prepared waste forms. The experimental conditions used are set to be as follows: leachant was deionized distilled water, surface area/volume was about (992–1215 mm^2)/(99.2–121.5 mL), test temperature was kept at 70°C, and test time was extended to 500 days. The concentration of specified elements in the leachate was also analyzed by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Mechanical properties of the encapsulated forms

The stress–strain behavior was determined for the different waste-loaded composites to get information about their break characteristics, namely, ε_b and σ_b.
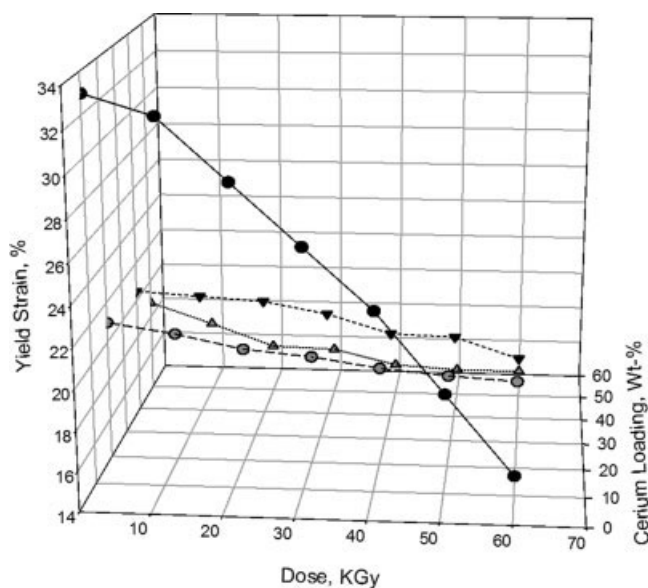

Figure 1 Variation of the percentage yield strain with irradiation dose of polyethylene with different cerium loading.

Variation of the strain at break, ε_b, as a function of irradiation dose is depicted in Figure 1 for the waste-loaded composites composed of polyethylene and different wt % of cerium iodate. The values of ε_b for the raw composites before irradiation are higher than the corresponding values of the irradiated ones. The values of the strain at break for composites containing waste greater than 10 wt % are close to each other. Moreover, the rate of decrease of strain for composites containing 10 wt % or less with increasing irradiation dose is considerably higher than the others, which their strain values either remained constant or decreased very slowly with increasing irradiation dose.

The values obtained for ε_b, given in Figure 1, represent homogenous extension deformations experienced by different composites at the point of break. Hence, the values of ε_b would be expected to be a function of the extent of interaction whether primary or secondary of certain compositions as a result of irradiation and/or the percentage of additives. The higher the level of interaction, the lower the value of ε_b. In case of absence of any waste material, or even in the law waste contents, radiation-induced crosslinking takes place and its magnitude increase with increase in the radiation dose. The considerable decrease in the strain may then be attributed to the crosslinking that took place in amorphous phase of high-density polyethylene. It was reported earlier that the number of crosslinks formed for 100 eV of energy absorbed, i.e., the G(X) value[21,22] was reported to be about 0.8–1.25.

The results given in Figure 1 indicate that most of the cerium iodate was incorporated into the matrix
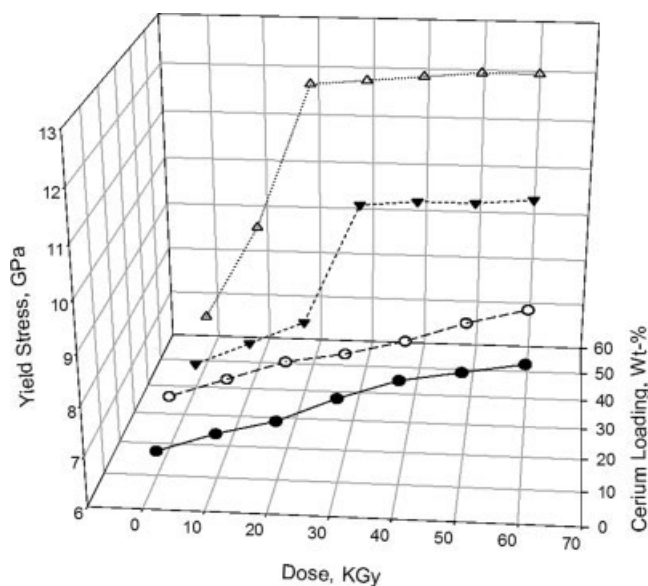
Figure 2 Variation of the percentage yield stress with irradiation dose of polyethylene with different cerium loading.

during the early stages of irradiation. The reinforcement of cerium iodate may also be ascribed to an adhesion type of interaction between amorphous particulates of waste and polymer macromolecules. This type of interaction was reported in other systems that use silica-filled polyisoprene rubber composites[23] using NMR studies in combination with SEM for elucidation of their structure; the so-called bound rubber that corresponds to an adjacent layer of rubber to silica particles is being developed and the principal mechanism of formation of bound rubber was physical adsorption of rubber molecules onto silica particles. As expected, augmentation of both the dose and the waste content as filler has resulted in increasing the level of interaction of the composite which accounts for the lowest value of ε_b obtained in the case of using 50 wt % of waste as filler.

The effect of irradiation dose on the stress at break, σ_b, for either the raw polymer when loaded with waste is shown in Figure 2. The value of σ_b for the lowest waste loading increased very slowly up to 50 kGy and then remained constant. For the enhanced waste loading composite with 20 wt % of cerium iodate, it increased in a linear manner with increasing the irradiation dose, but with a relatively slow rate. In case of reinforcement of the polyethylene composite with 40 wt %, σ_b remained constant up to 20 kGy, and then increased appreciably up to 30 kGy, after which remained constant. On applying the lowest dose of irradiation, i.e., 10 kGy, σ_b for the composite containing 50 wt % increased effectively from about 7.1 to 9.2 GPa. It then exhibited continuous increase up to irradiation dose 20 kGy

and then remained almost constant at doses higher than 30 kGy.

The data obtained indicate that the value of σ_b has increased but only to a limited extent with increasing the extent of crosslinking induced by irradiation.[24] Composites made of polyethylene and cerium iodate gained more strength, mainly because of the formation of physical interaction at the interface between the metal iodate particles and units of the polymer.[23]

Figures 3 and 4 illustrate the variation of ε_b and σ_b as a function of irradiation dose for the polyethylene composites loaded with lanthanum iodate. The data in Figure 3 indicate that almost similar behavior of ε_b is attained when lanthanum iodate is used as a simulated waste instead of cerium iodate; comparable values of strain were obtained in both cases.

In contrast, composites reinforced with lanthanum iodate showed differences from those reinforced with cerium iodate concerning variation of σ_b with irradiation dose. As can be seen from Figure 4 that for the polyethylene composite reinforced with 40 wt % σ_b attains a moderately high value compared with the composites containing lower waste content at the lowest irradiation dose, namely, 10 kGy; this remained almost constant with slight alterations at higher doses. Moreover, the value of σ_b for the samples reinforced with 50 wt % of lanthanum iodate increased gradually with irradiation dose, reaching its maximum value at about 40 kGy and then decreased for higher doses. The differences in σ_b may thus be attributed to different modes of interaction of the two waste materials when ionizing radiation
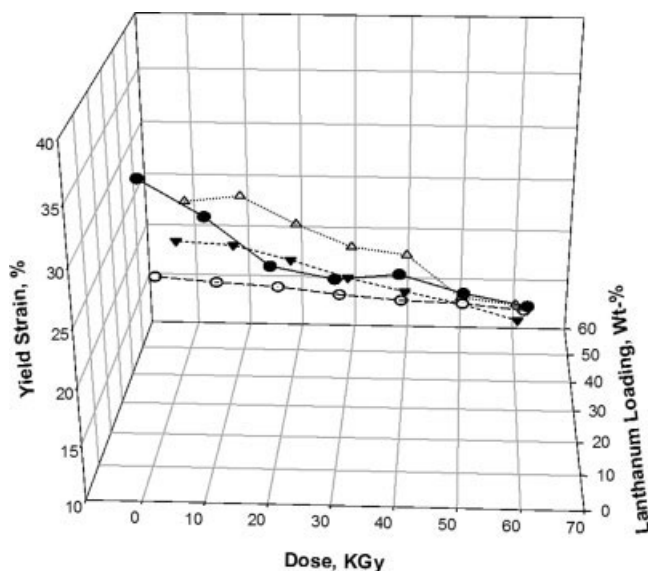

Figure 3 Variation of the percentage yield strain with irradiation dose of polyethylene with different lanthanum loading.
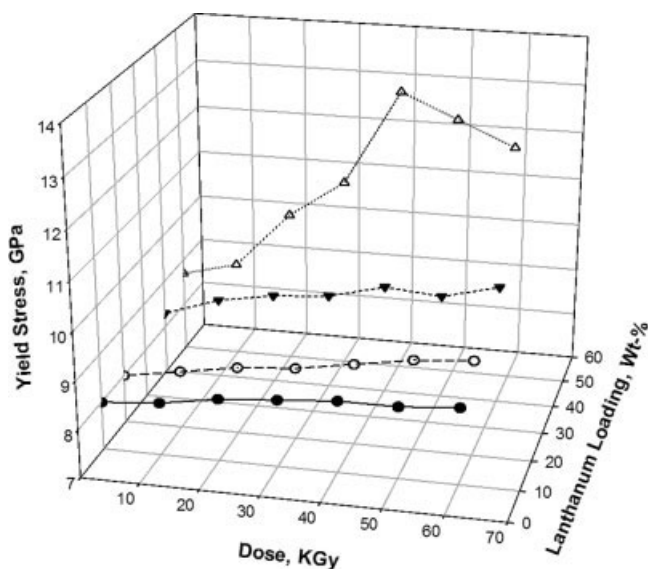
Figure 4 Variation of the percentage yield stress with irradiation dose of polyethylene with different lanthanum loading.
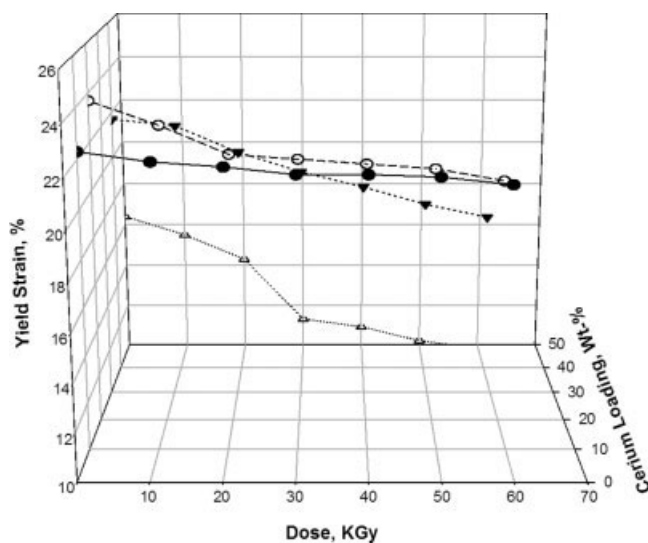

Figure 5 Variation of the percentage yield strain with irradiation dose of polypropylene with different cerium loading.

is used to induce linking with polyethylene; the surface area of lanthanum is 124.66 m^2 g^{-1}, which allows its particles to be wetted by the matrix polymer. Hence, the physical bonding would be expected to take place. The surface chemistry of different types of grouping[25] would allow for covalent bonding during gamma irradiation. Therefore, the attainment of relatively high values of σ_b may be attributed to the occurrence of bonding, whether physical or chemical, at the interface between polymer matrix and the waste filler particles. The magnitude of linking would then increase with irradiation dose; the decrease in σ_b at the higher irradiation doses may be possibly being attributed to the degradation of the polymer components.

Figure 5 illustrates the variation of ε_b with irradiation dose for polypropylene matrix reinforced with varying concentrations of cerium iodate. The value of ε_b decreases with increasing irradiation dose for the same extent of loading, and the same time decrease with increase in the extent of waste loading at the same irradiation dose. This expected behavior may be attributed to increase crosslinking together with increased interfacial linking, as discussed above.

The variation of σ_b with irradiation dose for composites loaded with different waste contents of cerium iodate is given in Figure 6. With the exception of the sample containing 50 wt % of cerium iodate, the σ_b increased only slightly when irradiation dose is increased. With the same exception, the σ_b increased with the amount of waste in the composite at the same irradiation dose. In case of polypropylene composites loaded with 50 wt %, σ_b increased with irradiation dose up to 60 kGy, then

remained constant for higher doses. Moreover, it may be observed that the values of σ_b for this composite are higher than those obtained with higher waste loading during the optimization process. The increase in σ_b with increased content of cerium iodate at the same irradiation dose may ascribed to the occurrence of some interface adhesion between the high surface area cerium iodate (170.77 m^2 g^{-1}) particulates and polypropylene. However, on loading the polymer with waste contents higher than
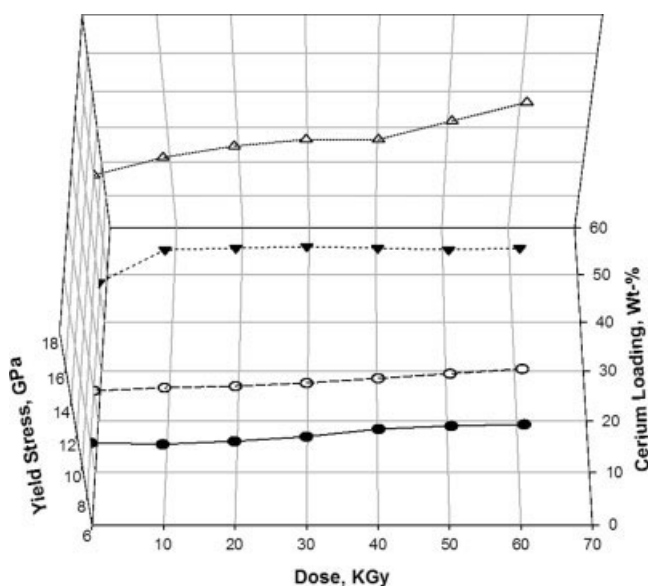

Figure 6 Variation of the percentage yield stress with irradiation dose of polypropylene with different cerium loading.
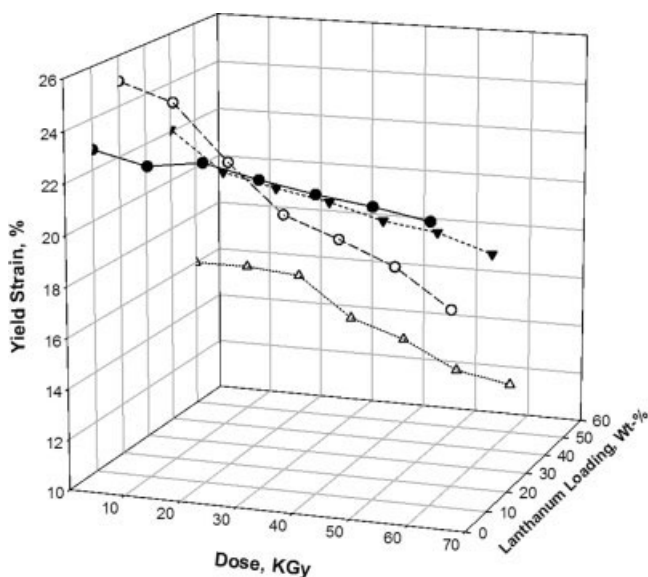
Figure 7 Variation of the percentage yield strain with irradiation dose of polypropylene with different lanthanum loading.

50 wt %, it was found that the matrix of the composite prepared would no longer be composed of continuous phase because cerium iodate particulates would adhere to each other in the form of weakly bonded agglomerates.[26] In such a situation, the composite would lose some of its inherent strength. Accordingly, the elements of such a composite would be expected to undergo necking at relatively lower stresses than in the case of composites loaded with 50 wt % of waste.

Figure 7 illustrates the variation of ε_b as a function of irradiation dose for polypropylene polymer reinforced with different lanthanum iodate waste amounts. It was observed that their behavior is comparable with that of cerium iodate containing composites, which again may be attributed to the increased crosslinking by irradiation together with an increase in the different types of linking between the matrix of the polymer and the filler particulates.

The variation of σ_b as a function of the irradiation dose for the above-mentioned composites is shown in Figure 8. The data given show that σ_b increased either with irradiation dose for the same composite or with the waste concentration at the same irradiation dose. This behavior may be ascribed to increased strength of the composite sample with increasing magnitude of these two parameters and hence composite may sustain high stresses before necking. It was observed that the values of σ_b in case of lanthanum containing composites are less than those for composites containing cerium iodate in the same polypropylene matrix. This may be assigned to the difference in charge and hence the availability of

the two iodates to form covalent linking with the polypropylene matrix.

Topography of the specimens

Figures 9 and 10 show the morphology of representative samples of polypropylene reinforced with different amounts of cerium iodate and lanthanum iodate, respectively. All the selected composites are irradiated at 60 kGy to reflect the ability of the polypropylene matrix to be loaded with waste iodates. The micrographs show that cerium iodate is composed of spherical particles in the micrometer range and uniformly dispersed in the polypropylene matrix while the lanthanum iodate particles are less in size and nonuniform in their shape. However, the difference in the chemistry of the two simulated waste iodates allows the cerium(IV) iodate to form multiple covalent links and enhance its distribution in the matrix, which can raise the values of σ_b in case of cerium iodate loading compared with that lanthanum(III) iodate.

Durability of the prepared matrices

The efficiency of polyethylene and polypropylene to immobilize cerium(IV) iodate and lanthanum(III) iodate was tested by applying the short- and long-term leaching behaviors after irradiation of the samples at 60 kGy.

Short-term Soxhelet leaching behavior

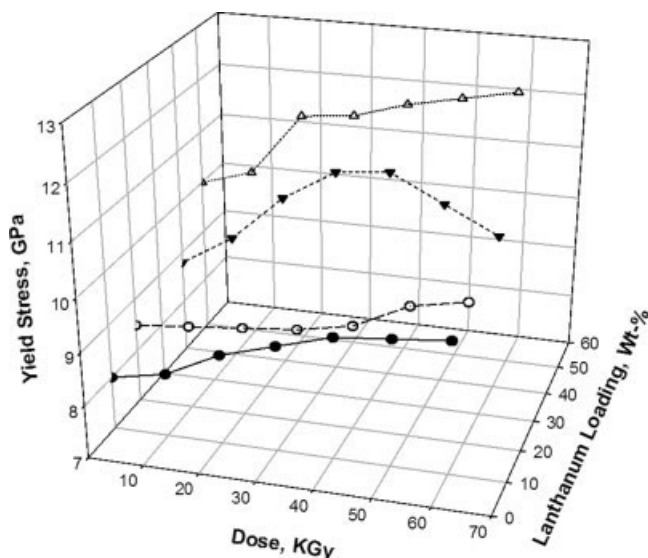The leachability of the polyethylene and polypropylene matrices containing different waste loadings was

Figure 8 Variation of the percentage yield stress with irradiation dose of polypropylene with different lanthanum loading.
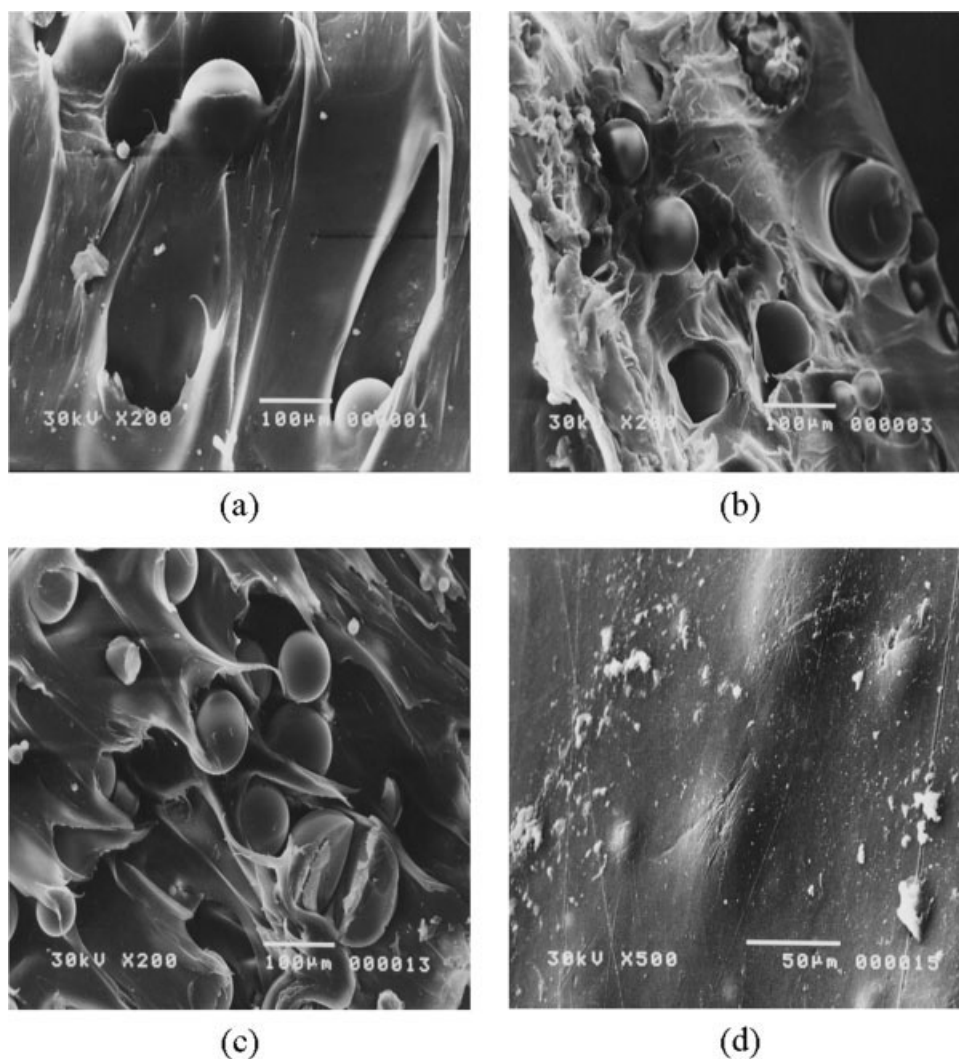
Figure 9 Scanning electron micrographs of polypropylene with different cerium loading and gamma irradiated at 60 kGy. (a) 10 wt % cerium iodate, (b) 20 wt % cerium iodate, (c) 40 wt % cerium iodate, (d) 50 wt % cerium iodate.

expressed by the leaching rate R (cm per day) as seen in the following equation:

$$R_n^i = \frac{(a_n^i/a_0^i)}{(F/V)t_n} \qquad (1)$$

where n denotes the Ce^{4+} or La^{3+} ion, a_n is the mass of leached Ce^{4+} or La^{3+} ion at certain period (g), a_0 is the mass of the initial addition for Ce^{4+} and La^{3+} ion the specimen (g), F is the surface area of the specimens (cm^2), V the volume of the specimen (cm^3), and t$_n$ the leaching time.

The leaching rate has the dimension of speed and the data are represented in Table I. The results shows that, in polyethylene matrix, the diffusion rates of both cerium and lanthanum are less than those of the same elements when polypropylene matrix is used. However, the diffusion of lanthanum is slightly greater than the diffusion of cerium from its matrix; the values of the diffusion rates of both elements are almost comparable. This may be ascribed by the extra links showed by the physical and chemical forces in case of using cerium iodate as a simulated waste of higher surface area than the lanthanum iodate. With increasing the waste content from 10 to 50 wt %, the aforementioned elements are undetectable in concentrations less than 10 wt %; the diffusion rates are in general greater than some reported values in using some ceramic matrices to immobilize some heavy metals as simulated radioactive waste elements.[27] This fact is augmented by the higher strength values obtained at break and the shift of the parent matrix to higher values with increasing the iodate content.

Long-term ISO leaching behavior

In this test, the mechanism of leaching as well as the long-term prediction of the leached ions from the polymeric matrices was conducted using the
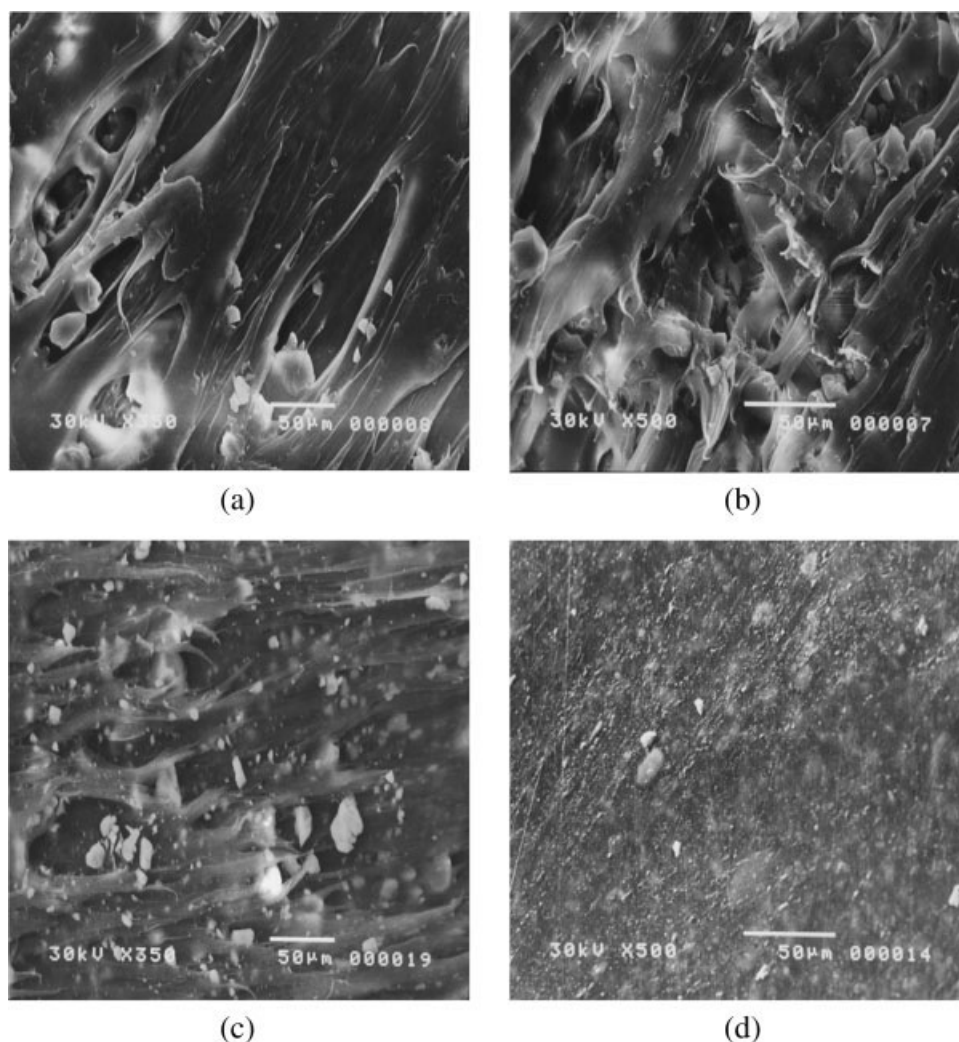
Figure 10 Scanning electron micrographs of polypropylene with different cerium loading and gamma irradiated at 60 kGy. (a) 10 wt % lanthanum iodate, (b) 20 wt % lanthanum iodate, (c) 40 wt % lanthanum iodate, (d) 50 wt % lanthanum iodate.

maximum waste loading (50 wt %) and irradiation of the samples at 60 kGy.

Determination of leaching mechanism

The leaching mechanism of the components in waste forms can be classified into wash-off, diffusion, and dissolution at the interface. The following time-dependent terms for the cumulative fraction leached, which describe several important rate-limiting leaching mechanisms, were used to investigate the leaching behavior of simulated La^{3+} and Ce^{4+} radionuclides with time and to determine the leaching mechanisms:[28]

$K_1(1 - \exp(-K_2t))$: wash-off (chemical reaction between the matrix surface and the aqueous solution),

$K_3 t^{1/2}$: transport by diffusion in a porous matrix, and

$K_4 t$: leaching as a result of matrix dissolution.

These terms were combined into a general expression to describe the overall leaching behavior:

$$F(t) = K_1(1 - \exp(-K_2t)) + K_3t^{1/2} + K_4t \qquad (2)$$

By comparing the K_i values, one can estimate which mechanism controls the leaching behavior.

Another semiempirical method to determine the leaching mechanism was obtained from the cumulative release, B_t, in g/m^2 with leaching time in the diffusion model as:

$$\log(B_t) = \frac{1}{2}\log t + \log\left[2C_s\frac{D}{\pi}\right]^{1/2} \qquad (3)$$

The leaching mechanism can be determined by analyzing the slope of the logarithmic plot of the cumu-

TABLE I
Leaching Rates of Ce^{4+} and La^{3+} Ions (cm day^{-1}), Diffused from Polyethylene and Polypropylene Matrices after Irradiation at 60 kGy

Waste content, %	Polyethylene		Polypropylene	
	Ce^{4+}	La^{3+}	Ce^{4+}	La^{3+}
0	–	–	–	–
10	–	–	–	–
20	3.59×10^{-9}	3.78×10^{-8}	1.61×10^{-7}	6.33×10^{-6}
40	2.32×10^{-9}	5.56×10^{-8}	7.22×10^{-7}	7.41×10^{-6}
50	9.01×10^{-9}	7.28×10^{-8}	7.91×10^{-7}	9.52×10^{-6}

lative elemental release versus leaching time. From the slope of the graph, the mechanism of leaching can be derived: a slope below 0.4 means the leaching is controlled by wash-off, 0.4–0.6 by diffusion, and above 0.6 by dissolution.[29]

The two semiemperical models can be used in a synchronism for analyzing the dominant leaching mechanism of the prepared matrices. The constant K_i in eq. (2) that determines leaching mechanisms could be obtained from regressional analysis of the leach data for nuclides in polymeric waste forms. The results of experimental and regressional analysis for PE and PP loaded with 50 wt % Ce^{4+} and La^{3+} are shown in Figure 11, and the resulting K_i values are shown in Table II.

For La^{3+}/PE, the leaching mechanism could be considered to be both diffusion and dissolution because the degree of contribution of $K_3 t^{1/2}$ and $K_4 t$ to eq. (2) was much larger than that of other terms but was similar mutually. The same conclusion was reached when applying eq. (3), and dissolution associated with diffusion was found to be the controlling mechanism because the slope was between 0.54 and 0.66. For Ce^{4+}/PE, dissolution associated with diffusion was also found to be the dominant leaching mechanism from K_i shown in Table II. The assessment of leaching mechanism according to eq. (3) shows that it is controlled by dissolution associated with diffusion because the slope lies in the range between 0.51 and 0.67. For La^{3+}/PP and Ce^{4+}/PP, the leaching was controlled by the mechanism of dissolution associated with diffusion. The slope of the graph for La^{3+}/PP and Ce^{4+}/PP was 0.49–0.61 and 0.53–0.62, respectively.

The cumulative fraction leached of La^{3+} and Ce^{4+} in polymeric waste forms containing 50 wt % lanthanum- and cerium-iodate are shown in Figure 11. The CFL decreases in the order of La^{3+}/PP, Ce^{4+}/PP, La^{3+}/PE, and Ce^{4+}/PE. The leach rate and the leached amount of La^{3+}/PP and Ce^{4+}/PP from the waste matrix were much more than those of La^{3+}/PE and Ce^{4+}/PE. Because the free energy of the hydration reaction of lanthanum is more negative (-683.7 kJ mol^{-1}) than that of cerium (-503.8 kJ mol^{-1}), lanthanum is easily leached out from matrix. Solubility of the leached species also is an important factor controlling the chemical durability of the polymeric matrices in aqueous solution and thus affects the cumulative fraction leached. The solubility of lanthanum iodate is about 1.7 g/100 g H$_2$O, while cerium iodate is insoluble in H$_2$O and found to be partially soluble in 6MHNO$_3$.[30,31]

Long-term prediction model

For the case where a species is present in both an immobile and a mobile form initially in a state of chemical equilibrium, leaching of the mobile form will establish a difference in chemical potential to drive the reaction from immobile to mobile phase. The reaction rate at which less mobile forms can be converted to more mobile forms can be considered to be proportional to the difference in concentration between the initial concentration representing a saturation level and the concentration of the mobile species at any time. If the reaction is slow, the kinetics of production of the mobile form has to be taken into account. Therefore, the mass transport equation

TABLE II
Constant K_i Values, Diffusion Coefficients, and Dissolution Rate Constants of Ce^{4+} and La^{3+} in PE and PP Matrices as 50 wt % Waste Loading at 70 ± 1°C and Irradiation at 60 kGy

Waste form	K_1	K_2	K_3	K_4	D	k
La^{3+}/PE	1.62×10^{-3}	7.95×10^{-2}	2.35×10^{-4}	1.82×10^{-5}	8.17×10^{-7}	1.18×10^{-3}
Ce^{4+}/PE	8.24×10^{-4}	9.36×10^{-2}	1.81×10^{-4}	9.34×10^{-6}	9.55×10^{-7}	9.11×10^{-4}
La^{3+}/PP	9.61×10^{-3}	3.11×10^{-2}	2.64×10^{-4}	3.11×10^{-5}	5.03×10^{-6}	4.24×10^{-4}
Ce^{4+}/PP	4.33×10^{-3}	7.27×10^{-2}	5.14×10^{-4}	2.72×10^{-5}	1.53×10^{-6}	4.12×10^{-4}

with a uniform initial concentration of the mobile species equals to C_s and with the mobile species being produced at a rate $k(C_s - C)$ obtained from a mass balance across a differential section leads to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + k(C_s - C) \qquad (4)$$

The solution of this differential equation was first presented by Goodbee and Joy[19] for a semi-infinite medium of the uniform initial concentration and zero surface concentration. At short and long times, the solution of this differential equation leads to the following equations, respectively:

$$R_n = d\left[\left(\frac{\sum a_n}{A_0}\right)\left(\frac{V}{S}\right)\right]\Big/ dt \quad \left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \qquad (5)$$

$$R_n = d\left[\left(\frac{\sum a_n}{A_0}\right)\left(\frac{V}{S}\right)\right]\Big/ dt \quad (Dk)^{1/2} \qquad (6)$$

These two equations can be used to predict the leach rates at different intervals and to evaluate the diffusion coefficient, D (cm^2 day^{-1}) and dissolution rate constant, k (day^{-1}).

Experimental data at various initial leaching periods were applied to the prediction model to determine the period producing acceptable diffusion coefficient without a wash-off effect to the model. Because the phenomenon of wash-off was the main leaching behavior during the first few days, major parameters in the prediction model were used with the experimental data after 7 days. So, the diffusion coefficient D was calculated by applying leaching data between 7 and 14 days to the prediction model, and dissolution rate constant k in eq. (6) was calcu-
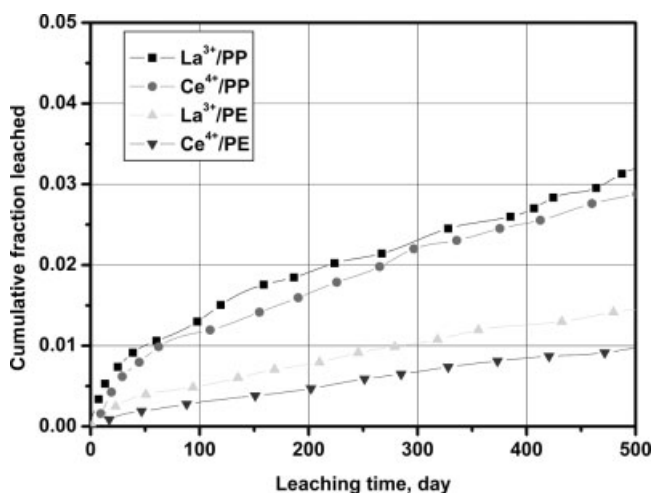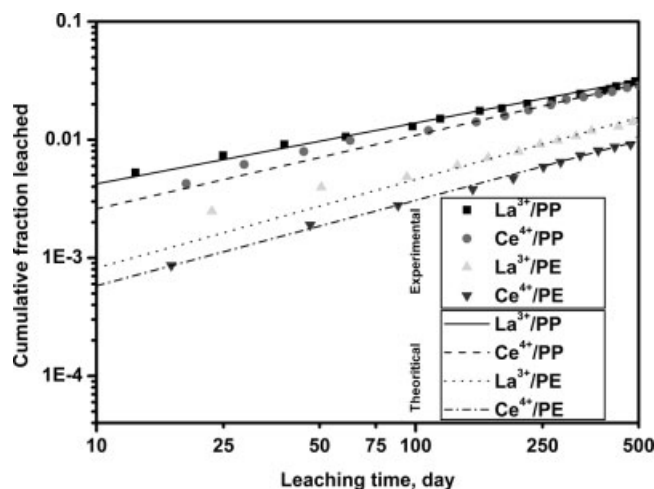

Figure 12 Comparison of calculated and experimental results of La^{3+} and Ce^{4+} in PE and PP forms containing 50 wt % of simulated wastes by a long-term prediction model.

lated from long-term leaching data for 500 days. Table II shows parameter values that were used for the prediction of the leaching of lanthanum iodate and cerium iodate in PE and PP matrices.

The long-term prediction of cumulative fraction leached with increasing leaching period was made by successive iteration using two parameters, the diffusion coefficient and dissolution rate constant, which were obtained from eq. (5) for short-term and eq. (6) for long-term. Diffusion coefficients of La^{3+}/PE were 3.22×10^{-7}, 8.17×10^{-7}, and 8.46×10^{-7} cm^2/day at a short period of time (14 days) as the content of simulated radioactive waste form increased from 20 to 50 wt %. Dissolution rate constants (k) ranged from 4.89×10^{-3} to 8.43×10^{-3} day^{-1} at a long period of time (500 days) with various contents of simulated incineration ash. A comparison of the experimental and predicted values for lanthanum and cerium using eq. (6) is shown in Figure 12. The correlation coefficient (R^2) of the cumulative fraction leached between experimental and predicted values for lanthanum and cerium was above 0.99. Therefore, the prediction model offers the advantage of assessing very long-term leaching behavior using short and long-term leach data.

CONCLUSIONS

Simulated radioactive La^{3+} and Ce^{4+} wastes were encapsulated in polyethylene and polypropylene forms by thermomechanical mixing of the corresponding metal iodates with the preirradiated polyethylene and polypropylene at 30 kGy in the required composition. After preparation of the matrices, the mechanical properties were measured at break including both stress and strain behaviors that are so

Figure 11 Cumulative fraction leached of La^{3+} and Ce^{4+} in PE and PP forms containing 50 wt % of simulated wastes.

critical in the final disposal of the waste matrices; the matrices are really subjected to either tension and or compression during their handling and transport. Following to that, leaching tests have been carried out using both the Soxhelet and the ISO methods to determine the main leaching mechanism and to find an appropriate long-term prediction model. Two semiempirical models were applied to find out the dominant leaching mechanism of waste elements. The estimation of leaching mechanism using both models showed similar results. Dissolution associated with diffusion was found to be the dominant leaching mechanism for simulated nuclides. The cumulative fraction leached of La^{3+} and Ce^{4+} in polyethylene is larger than that of the same elements in polypropylene, which could be explained by the difference in the mechanical properties of the main matrices. The leaching characteristics of waste components were also dependent on their solubilities. A theoretical prediction model was applied to the long-term leaching behavior of simulated waste nuclides in polymeric waste forms. Diffusion coefficients and dissolution rate constants, which are the main parameters in the long-term prediction model, for La^{3+} and Ce^{4+} simulated nuclides, were obtained using experimental short and long-term leaching data. The predicted value from the model agreed well with the experimental data and the model could offer the advantage of assessing very long-term leaching behavior using short- and long-term leach data in waste disposal facilities.

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