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Preparation and evaluation of crosslinked plastic scintillation microspheres (CPSm)

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ABSTRACT

Plastic scintillators in the form of microspheres (PSm) have emerged as a sustainable solution for the determination of alpha and beta radioactivity, reducing hazardous wastes and improved selectivity when combined with selective extractants (PSresin). To overcome challenges like solubility in organic solvents, researchers have developed crosslinked scintillating microspheres (CPSm) using divinylbenzene (DVB) as a crosslinking agent. This study focuses on optimizing CPSm synthesis and assessing their morphological characteristics, resistance and scintillation capabilities. The findings indicate that increasing the DVB proportion in the monomeric mixture leads to a reduction in microsphere size while maintaining high detection efficiency. CPSm demonstrate enhanced resilience to temperature and organic solvents compared to PSm. Despite some solute extraction by specific solvents, CPSm maintain their essential properties. In summary, CPSm provide similar scintillation performance to linear polystyrene PSm while offering increased durability, broadening their applicability and facilitating further advancements in plastic scintillator technology.

1. Introduction

The liquid scintillation technique is the most widely employed for the determination and quantification of alpha and beta radioactivity [1]. However, this technique has certain drawbacks, such as low selectivity, challenges in automatization or continuous analysis, and the generation of mixed wastes that are both radioactive and hazardous. In recent years, an alternative to liquid scintillation has emerged, replacing scintillation cocktails with plastic scintillating materials (PS) [2]. Plastic scintillators, when combined with selective extractants (PSresin) [3,4], offers increased selectivity and the potential for being used in online continuous detectors [5–8]. Additionally, plastic scintillators can be washed and reused, minimizing the generation of mixed wastes.

Research has shown that plastic scintillators with optimal performance are those shaped as microspheres (PSm) with a diameter ranging from 20 to 100 μm [9]. Within this diameter range, the attenuation of beta and alpha particles emitted from a source located in the interstices between the microspheres is minimal, and optical transmission of the produced photons is adequate. These PSm can be obtained through an evaporation-extraction process, where linear polystyrene and the fluorescent solutes such as 2,5-diphenyloxazole (PPO) and 1,4-bis-2-(5-phenyloxazolil)-benzene (POPOP) are dissolved in dichloromethane. The solution is then dispersed in an aqueous solution containing a surfactant, such as polyvinyl alcohol, to stabilize the mixture. After removing the organic solvent, spherical polystyrene particles with controlled median size and trapped fluors are obtained [10].

Nevertheless, linear polymer PSm have certain limitations, including solubility in organic mediums and low resistance to strong alkaline and acid mediums. Moreover, in PSresin made of linear PSm the extractant is adhered to the surface of the PSm and lixiviation of the extractant may occur, as it is weakly adsorbed to the surface. One potential solution to this limitation is the chemical modification of the PSm surface and the linkage of the extractant through covalent bonding. However, this modification can only be done under very soft conditions regarding the solvent used, as most of the organic solvents will dissolve the PSm or extract the fluorescent solutes.

The use of polymerizable fluorescent solutes can solve their leaching when in contact with organic solvents [11,12], however, the polymer will be still soluble, and producing polymerizable fluorescent solutes on a larger scale is challenging. Another possible solution would be the preparation of microspheres by polymerization, incorporating a crosslinking agent into the polymeric structure to generate crosslinked polymers as described in the literature for block PS [13,14]. Dispersion polymerization with mixtures of styrene and divinylbenzene (DVB) monomers produces spherical crosslinked polymer particles with a three-dimensional structure, enhancing their resistance to organic and

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strong inorganic media due to the crosslink between polystyrene chains (CPSm) [15–18]. Obtaining these materials could potentially improve the capacities of the plastic scintillators. For example, it could allow the use of organic solvents during syntheses to introduce porosity [19,20], increasing surface area, or enable the use of organic or aggressive media during surface functionalization reactions [21,22], broadening their applications. In contrast, the inclusion of a cross-linking agent may affect the scintillation process, particularly the non-radiative transfer of energy between the polymer and the fluorescence solutes.

While the synthesis of cross-linked plastic scintillators has been described in previous works, producing blocks, nanoparticles, or microspheres of hundreds of micrometres, the effect of divinylbenzene on scintillation efficiency or the trapping of fluorescent solutes has not been thoroughly evaluated. This work proposes a synthesis method for obtaining crosslinked plastic scintillation microspheres (CPSm) with a diameter of 30–100 μm. Furthermore, a detailed study on the scintillation capacities and their behaviour after prolonged contact with organic solvents, comparable to that use in surface modification reactions, has been conducted.

2. Experimental

2.1. Reagents

Styrene 99 % stabilized purchased from Acros Organics (Geel, Belgium), and DVB 80 % stabilized purchased from Alfa Aesar (Kandel, Germany). Both were purified with α-phase aluminium oxide from Alfa Aesar (Kandel, Germany). 2,5-diphenyloxazole (PPO) 99 % purchased from Acros Organics and 1,4-bis-2-(5-phenyloxazolil)-benzene (POPOP) provided by Sigma Aldrich (St. Louis, USA), were used as fluorescent solutes. AIBN (Fluka Analytical) was used as initiator. PVA partially hydrolysed (degree of hydrolysis ≥85 %) with an average molecular weight of 30 000 obtained from Sigma Aldrich (St. Louis, USA) was used as a suspending agent. NaCl 99.8 % provided by Acros Organics (Geel, Belgium) was used as a stabilizer. Methanol for HPLC–Isocratic Grade and Dichloromethane for HPLC were provided by VWR Chemicals (Briare, France).

Four radioactive solutions were used: A ^{3}H active stock solution of 4304 (151) Bq/g in water from Eckert & Ziegler (California, United States); a ^{14}C-glucose stock solution of 136 (3) Bq/g in water from Cerca-Lea (Paris, France); a ^{90}Sr/^{90}Y active stock solution of 38.45 (0.29) Bq/g in a water solution of strontium (100 μg g^{-1}) and yttrium (100 μg g^{-1}) in 0.1 M HCl from Amersham International (Buckinghamshire, England); and a ^{241}Am active stock solution of 47.4 (1.2) Bq/g in 0.5 M HCl from Amersham International, (Buckinghamshire, England).

2.2. Instruments

The radioactive samples were measured in a 1220 QUANTULUS Wallac liquid scintillation spectrometer from PerkinElmer using 6 mL HDPE counting vials provided by PerkinElmer. Cross-linked plastic scintillation microspheres (CPSm) were analysed with a JEOL J-7100 FESEM microscope from Jeol at the Scientific and Technological Centres of the University of Barcelona (CCiTUB).

Particle diameter and particle size distributions were obtained with a Laser Diffraction Particle Size Analyser LS 13 320 from Beckman Coulter at CCiTUB.

Thermal degradation temperatures of the CPSm were obtained by Differential Scanning Calorimetry (DSC) with a DSC analyser DSC-822e/400 from Mettler Toledo at CCiTUB.

Solutions obtained in the degradation experiments of the polymer with organic solvents were analysed by HPLC-PDA using a Waters UPLC Acquity equipment with a XBridge C18 3.5 μm column at the CCiTUB (Barcelona, Spain).

2.3. Synthesis of CPSm

CPSm were synthesised via dispersion polymerization based on a free radical reaction. First, 10 g of PVA were dissolved in 100 mL of double-deionized water previously deoxygenated at 80 °C. For samples synthesised with NaCl in the aqueous phase, 1 g of NaCl was added. The organic phases were prepared according to the styrene and DVB ratios (v/v) shown in Table 1. Fluorescent solutes and the initiator were added to the organic phase and dissolved in the following proportions: 2.5 % (w/w) of PPO, 0.07 % (w/w) of POPOP, and 0.08 % (w/w) of AIBN. These weight proportions were calculated based on the total mass of solids in the polymer, considering purity and density of the monomers (99 % purity and ρ = 0.9060 g/mL for styrene; 80 % purity and ρ = 0.9140 g/mL for divinylbenzene).

The organic phase was added slowly into the aqueous phase using a plastic syringe and a needle. The mixture was stirred at 11 Hz using a magnetic stirrer and maintained at 80 °C for 20h to complete the polymerization. After this period, the resulting suspension was filtered and rinsed three times in cycles of double-deionized water and ethanol. The CPSm were dried in an oven at 40 °C. The syntheses of the 1:2 and 1:1 St:DVB (v/v) ratios, with and without NaCl respectively, were conducted in triplicate.

2.4. Radioactivity measurements

Radioactive samples were prepared by adding 0.5 g of CPSm and 200 μL of the corresponding radioactive solution, or double-deionized water for background samples, into 6 mL HDPE counting vials. The vials were homogenized using a vortex mixer at 50 Hz during 3 min. To determine the detection efficiency, each vial was measured using the Quantulus detector for 15 min. The activity in the measurement samples were approximately 4000 Bq/g for ^{3}H, 33 Bq/g for ^{14}C, 13 Bq for ^{241}Am samples and 19 Bq for ^{90}Sr/^{90}Y. All solutions and samples were prepared by weighting.

To evaluate the capability of the CPSm for discrimination between alpha and beta particles, vials containing ^{241}Am and ^{90}Sr/^{90}Y were measured using the alpha/beta MCA configuration default setting of the Quantulus detector. In this configuration, pulses are classified as alpha (in the alpha part of the multichannel analyser) or beta (in the beta part of the multichannel analyser). The PSA value, which determines the threshold level for classifying a pulse as alpha or beta, can be selected by the user and varied from 1 to 250. Measurements were performed for PSA values that varied from 1 to 250.

2.5. Solvent degradation experiments

Polymers with St:DVB ratios (v/v) of 1:2, 1:1, 2:1.5 and 2:1 were treated with various organic solvents. 5 g of the polymer were added into glass vials with hermetic seals, each containing 10 mL of respective solvent: dichloromethane, acetone, methanol, toluene or hexane. The vials were shaken using an end-over-end agitator for 24 h. A 3 mL aliquot from each vial was filtered and washed with methanol to remove all residual polymer dissolved. Each extract was analysed by HPLC-PDA at 303 and 360 nm to determine the amount of PPO and POPOP extracted [23].

The treated polymers were filtrated and washed several times with double-deionized water. These polymers were then used to measure radioactive standards, following the procedure described in section 2.4.

Table 1
Volumes of monomers added for every proportions used.

Proportion (v/v)	1:2	1:1	2:1.5	2:1	4:1	6:1
Styrene (mL)	5.00	7.50	8.57	10.00	12.00	12.86
Divinylbenzene (mL)	10.00	7.50	6.43	5.00	3.00	2.14

2.6. Data analysis

Detection efficiencies for the radioactive measurements, in percentage, were calculated by comparison between the count rate and the activity added into each vial. All obtained spectra were smoothed using the Savitzky-Golay algorithm (order 1, frame length 21) included in the Matlab® R2021 a software (Mathworks, Natwick, USA).

Misclassification in alpha/beta discrimination, in percentage, was determined by the count rate of the corresponding isotope in the inappropriate section of the multichannel analyser (alpha part of the MCA for ^{90}Sr/^{90}Y samples and the beta part of the MCA for ^{241}Am samples) with respect to the total count rate (alpha plus beta part of the MCAs).

HPLC-PDA results were processed using the Empower software from Waters Corporation (Milford, USA).

3. Results and discussion

3.1. Synthesis method

The geometry and size of particles obtained through suspension polymerization are influenced by the polymerization yield and the form and size of the droplets formed when the organic and aqueous phases are mixed. The size and shape of these droplets depend on factors such as the composition and proportion of the two phases, the polarity of both, the speed and type of agitation, and the reaction temperature [24]. Consequently, the effects of incorporating a crosslinking agent into the procedure were evaluated based on synthesis yield, particle geometry, and size.

As illustrated in Fig. 1, there is a significant increase in synthesis yield with the increasing proportion of DVB. In all cases, a suspension of particles was obtained, indicating that the reaction occurred. However, at lower DVB concentrations, minimal polymer was retained on the filter paper, suggesting the formation of excessively small polymer particles, likely short polymer chains. This is partially attributed to changes in the polarity of the organic phase. The higher proportion of DVB decreases the polarity of the organic phase, improving the separation between the organic and the aqueous phases. DVB is less polar than styrene, as indicated by their predicted $\log K_{ow}$ (3.5 and 2.9 respectively, computed by XLogP3 3. o, PubChem release 2021.10.14). Therefore, increasing the amount if DVB reduces the polarity of the mixture. Additionally, the crosslinking effect of DVB should be considered, as it renders the polymer less soluble in the monomers, facilitating its growth.

It is also observed that the addition of NaCl in the aqueous phase results in a slight increase on synthesis yield. Similar to the explanation provided earlier, the addition of NaCl enhances the interface forces between the organic and aqueous phases, leading to improved phase separation and increased synthesis yield due to the stabilization of droplets.

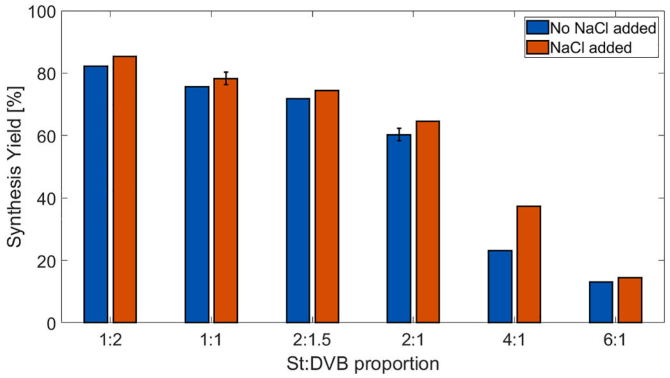

Fig. 1. Synthesis yield obtained at for different St:DVB (v/v) ratios and with or without NaCl addition to the aqueous phase.

Samples synthesised in St:DVB (v/v) ratios 4:1 and 6:1 were discarded because complete polymerization could not be ensured, and the synthesis yield was excessively low.

To evaluate the reproducibility of the synthesis method, polymers with St:DVB (v/v) ratios 2:1 (without NaCl) and 1:1 (with the addition of 1 % of NaCl) were conducted by triplicate. The synthesis yield were 60 (2)% and 76(2)%, with a relative standard deviation of 3.3 % and 2.6 % respectively. These values indicate that the method's yield is reproducible under the studied conditions.

All synthesised polymers were analysed by SEM. As depicted in Fig. 2, particles obtained in all cases were spherical, with some agglomerates present. Nanoscale irregularities were observed on the particle's surfaces, possibly due to a non-homogeneous polymerization inside the droplets.

The diameter size distribution of the particles can be observed in Fig. 3. Firstly, it is evidenced that the median size oscillates in the range of 45 μm and 75 μm, being in general around 60 μm which is adequate for radioactivity measurements using the microspheres or with PSresin prepared by immobilization of extractants on the surface. Scintillating microspheres with diameters below 10 μm suffer significant optical quenching. Additionally, column separations with PSresin of such diameter require excessive pressure, making them impractical. Conversely, PSm with a diameter exceeding 100 μm exhibit particle quenching due to the considerable distance between radionuclides and scintillators, and PSresin has lower surface area, resulting in reduced capacity. The results obtained indicate the possibility of obtaining crosslinked plastic scintillation microspheres of an appropriate diameter using this method. The proportion of DVB and the presence NaCl in aqueous phase do not produce any appreciable effect in particle sizes.

The dispersion in diameter is higher than the obtained using the evaporation-extraction method (PSm in Fig. 3), likely due to the more complex composition and evolution of droplets during the particle formation process. No discernible trend is observed regarding DVB or NaCl content. The high dispersion in certain samples, such as 2:1 proportion with NaCl, can be attributed to procedural variability and the presence of agglomerates in the final product. Therefore, the use of NaCl is recommended as it allows for slightly higher synthesis yields.

3.2. Radiometric capabilities

All the obtained polymers were used to analyse radioactive solutions with known activity. The radioactive solutions correspond to a low energy beta emitter (^{3}H, $E_{max:}$ 18.6 keV), a medium energy beta emitter

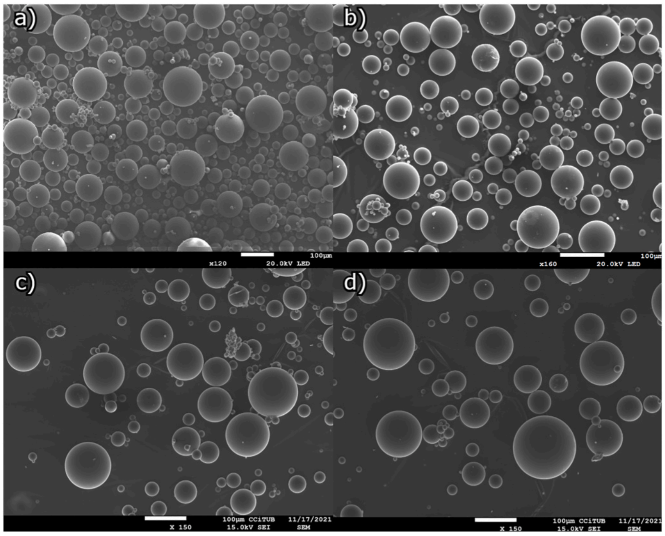

Fig. 2. SEM images of samples in St:DVB (v/v) ratios: a) 1:1 b) 2:1 c) 1:2 with NaCl and d) 2:1.5 with NaCl.

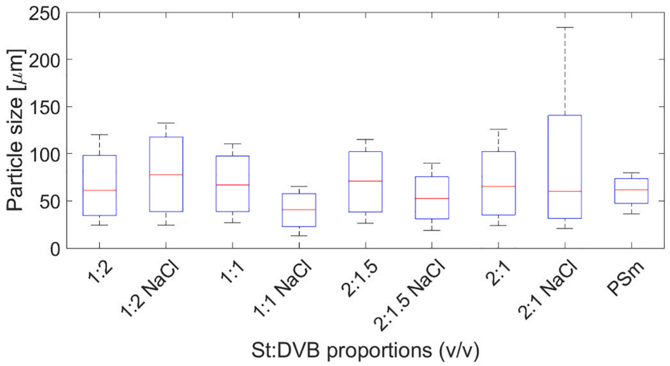

Fig. 3. Dispersion in the particle size obtained for each sample synthesised by granulometric analysis compared with a linear polymer PSm.

(^{14}C, E_{max}: 156.5 keV), a high energy beta emitter (^{90}Sr/^{90}Y, E_{max}: 545.9 keV and, E_{max}: 2279.8 keV respectively) and an alpha emitter (^{241}Am, E: 5552 keV).

3.2.1. Detection efficiency

Fig. 4 illustrates the detection efficiency values for different polymers, compared to those of linear polystyrene microspheres (PSm) prepared by the evaporation-extraction method, represented by a dashed line. Generally, the detection efficiency values for each CPSm are comparable to those of PSm. This confirms that fluorescent solutes are effectively encapsulated in the CPSm, and the presence of DVB in the polymer structure does not significantly cause chemical quenching by interfering with the energy transmission process from the polymer to the encapsulated fluorescent solutes.

For tritium, the radionuclide that emits the lowest energy beta particles, there is a decreasing trend as the proportion of DVB increases. This behaviour can be attributed to two factors: chemical quenching effect of DVB or inefficient mixing. On one hand, DVB introduces rigidity on the polymer structure and can consume part of the energy in non-scintillating processes, leading to a quenching effect that could be clearly seen in the spectra from ^{3}H and ^{241}Am (Fig. 5). On the other hand, although styrene and divinylbenzene have similar chemical structures, their polarities differs, with DVB being less polar.

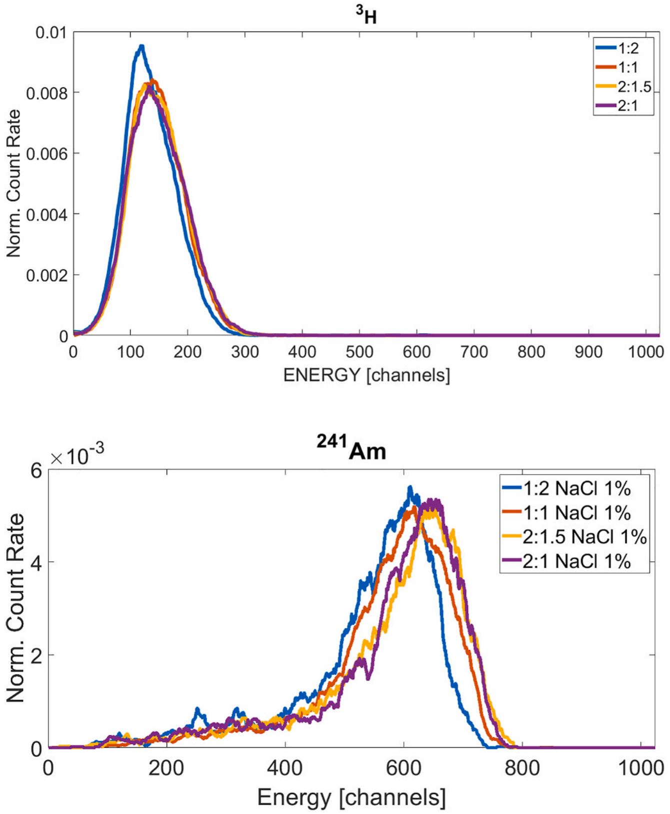

Fig. 5. Spectra obtained for the analysis of ^{3}H and ^{241}Am standard for samples synthesised adding NaCl in the aqueous phase.

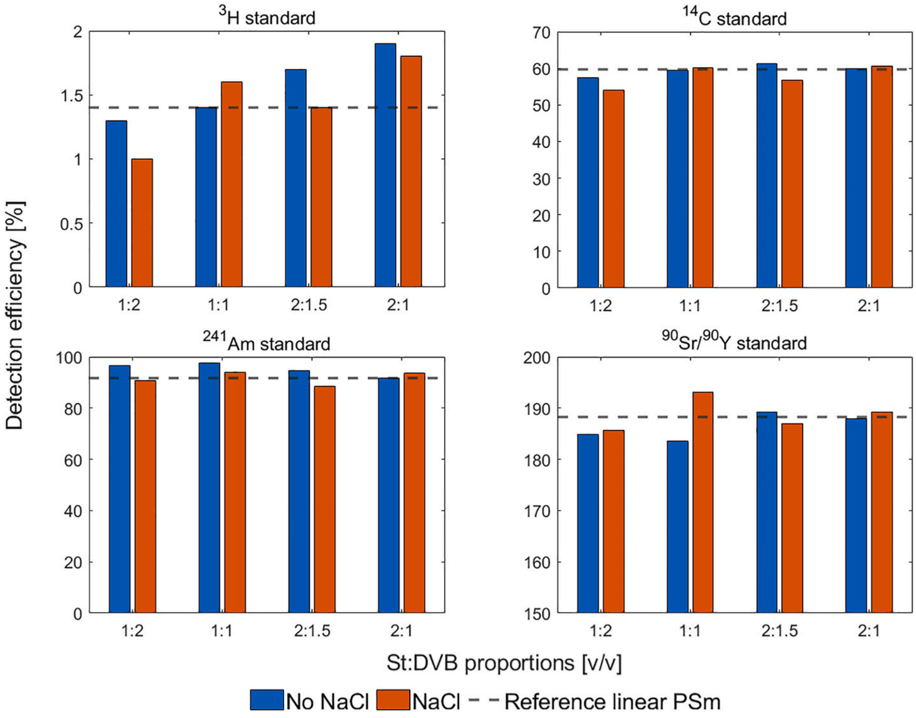

Fig. 4. Detection efficiencies obtained for the analyses of ^{3}H, ^{14}C, ^{241}Am and ^{90}Sr/^{90}Y standards and comparison with a reference linear polymer PSm.

Incorporating DVB into the polymeric structure reduces the polarity of the microspheres and increases their hydrophobicity. Since radioactive standards used for the analysis were aqueous, the reduced polarity hinders the interaction between the solution and the CPSm. This prevents the solution from adequately wetting the CPSm surface, causing segregation between the solution and CPSm and increasing the distance between the scintillator and the radionuclide. For ^{3}H, due to low energy of its emission, both effects leads a decrease in detection efficiency.

This effect is less significant for ^{14}C and ^{90}Sr (in equilibrium with ^{90}Y). Only the low energy beta particles from these emissions, which are very low in proportion, are affected, making the overall impact negligible. For ^{241}Am, the detection efficiencies are close to 100 % (i.e., nearly all particles are detected), and no variation is detected, probably because the increase in the distance due to the poor wetting effect caused by DVB is lower than the minimum path that the alpha particles need to travel to reach the scintillators (around 50 μm).

The addition of NaCl during the polymerization has a negligible effect on the scintillating properties of the CPSm produced. Generally, the detection efficiency values obtained for syntheses performed with or without NaCl are equivalent. The observed differences, particularly in tritium analysis, are associated to the intrinsic variability of the measurements and minor variation in the mean diameters of the microspheres.

3.2.2. Spectra analysis

In Fig. 5, the spectra obtained for ^{3}H and ^{241}Am are presented as an example.

It is evidenced that spectra shift to lower energies with an increase in crosslinker content in the polymeric structure, indicating a quenching effect caused by the presence of DVB. This quenching may arise from the increased stiffness of the polystyrene chains with the inclusion of more DVB, resulting in inefficient energy transmission in solvent-solvent and solvent-PPO interactions. In scintillators, non-radiative energy transfer between molecules (solvent-solvent and solvent-primary fluorescent solute) can occur through geometric coupling of molecules. This coupling is favoured in liquid scintillators by molecular movement or in plastic scintillators by rapid energy transmission through the polymer chain (plastic scintillators). Incorporation of DVB into the polystyrene chain may reduce chain mobility and thus transmission probabilities though coupling. Nonetheless, the effect is not very strong, and the presence of DVB, even at very high proportions, does not significantly diminish the scintillation properties of the CPSm, except for ^{3}H. These results prompt a review of other instances where DVB was used in plastic scintillators in the form of microparticles [25]. In this work, an exceptional reduction in detection efficiency was observed with an increase in DVB content. According to the present results, this behaviour could be attributed more to the poor wetting capabilities of the PS-DVB microparticles, especially when the particles are a few micrometres in size, rather than to the chemical quenching of DVB, as suggested in a recent work [13].

3.2.3. Alpha/beta discrimination

To complete the analysis of the impact of crosslinking with DVB on the scintillation properties of CPSm, an alpha/beta discrimination analysis was conducted based on the pulse shape analysis capability of the detector. The shape of scintillation pulses depends on the type of radioactive particle and the properties of the scintillator. Alpha particles produce more triplet states upon interaction with the scintillating material compared to beta particles, which predominantly produce singlet excitation states. Triplet state relaxation is slower than singlet state relaxation because two triplet states must coincide to lead to the relaxed state. Additionally, certain compounds can either enhance or delay the relaxation of energy states, thereby accentuating the differences between alpha and beta scintillation pulses. This analysis involved measuring the samples of CPSm with an ^{241}Am (pure alpha emitter) and a ^{90}Sr/^{90}Y (pure high energy beta emitter) standards at different values of the pulse shape analysis parameter of the Quantulus detector (PSA). The results on misclassification (i.e. particles wrongly classified) are depicted on Fig. 6.

It is observed that higher classification errors for beta particles occur at low PSA values, whereas for alpha particles, errors are higher at high PSA values. Furthermore, in polymers with a higher proportion of DVB, beta particle classification improves while alpha particle classification deteriorates. This fact can be attributed to a shortening of pulses when DVB is added, favouring the classification into beta pulses. As observed in the spectral analysis, the addition of DVB induces chemical quenching, resulting in a lower generation of photons during the scintillation mechanism and consequently shorter pulses. Moreover, the crossing points appear at lower PSA values, leading to increased misclassification in polymers containing higher proportions of DVB. It can be concluded that DVB primary affects alpha/beta discrimination due to the quenching effect rather than by modifying the rate of triplet or singlet state formation during polymer excitation.

3.3. Physical properties

The physical resistance of the synthesised materials was evaluated through thermal resistance and structural alterations, as well as the ease of extracting encapsulated fluorescent solutes when exposed to various organic solvents.

Fig. 7 presents the decomposition temperature determined for each material synthesised. It can be observed that the decomposition temperature increases as the proportion of crosslinker in the polymer increases. This finding confirms that the presence of a crosslinking agent enhances the thermal resistance of the material compared to linear polymer structures.

Finally, a test was conducted to assess the resistance of all CPSm to organic solvents. This test involved exposing the CPSm to solvents with varying polarity (methanol, hexane, heptane, toluene, acetone and dichloromethane) for 24 h. The CPSm were then observed using SEM microscopy to determine the effects of these organic solvents on the surface of the microspheres. As shown in Fig. 8 and in the supplementary material, no degradation effects were detected, the surface remained smooth, free of pores or deformities, and the microspheres retained their completely spherical shape. This demonstrates that the crosslinking agent confers resistance to the polymers compared to linear chain ones, which dissolve in almost all tested organic solvents.

The solutions of the organic solvents collected after contact with the

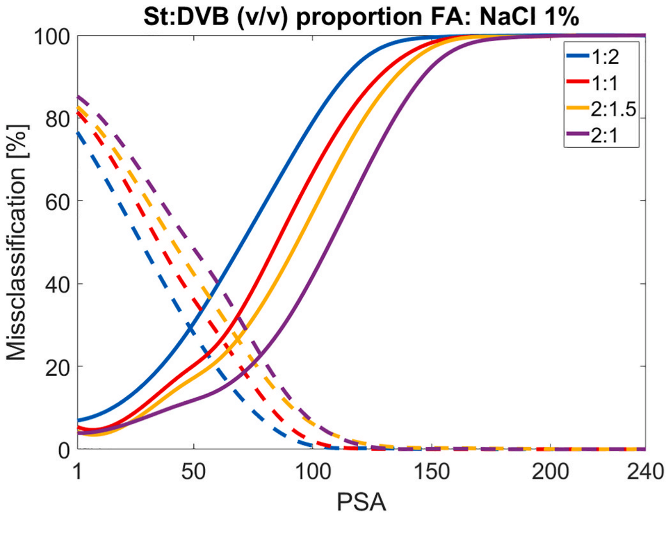

Fig. 6. misclassification of alpha (continuous line) and beta (dashed line) signals in front of the PSA parameter obtained for samples in St:DVB proportions 1:2, 1:1, 2:1.5 and 2:1 synthesised by adding NaCl in aqueous phase.

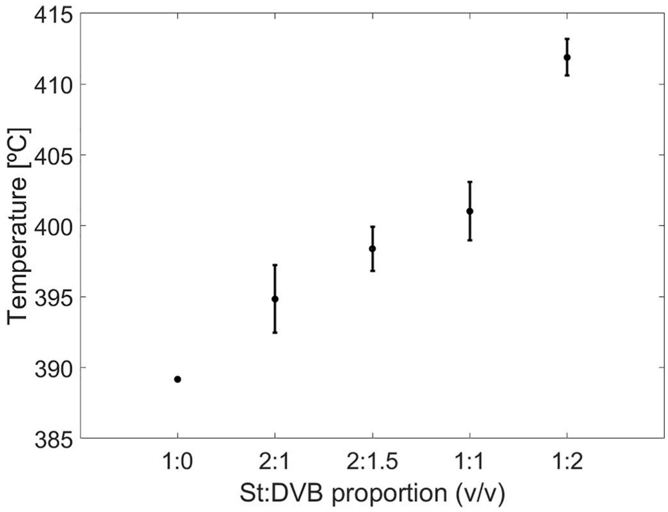

Fig. 7. Decomposition temperature determined for each material obtained.

CPSm were analysed using HPLC-PDA to quantify the amount of extracted fluorescent solutes. Fig. 9 illustrates the amount of PPO extracted from each sample for each solvent used. It is evidenced that the extraction follows a decreasing trend with an increase in crosslinker content in the polymer. Specifically, the amount of PPO extracted was less than 40 % for samples with a styrene:divinylbenzene ratio of 1:2, up to 60 % for those with a 1:1 ratio, reaching 90 % in samples with a lower proportiont of divinylbenzene. This phenomenon can be attributed to the fact that the polymer chains are linked one to another by the crosslinker, providing a more rigid structure. Consequently, sovents have less penetrating power to reach and extract the solutes that are deeply encapsulated within the microsphere or located in a highly rigid area of the microspheres.

Also, it is observed that the amount of PPO extracted is significantly higher in dichloromethane, acetone and toluene compared to methanol, hexane and heptane. This variation may be due to the penetrability of each solvent into the CPSm structure, as well as the solubility of solutes in these solvents. Dichloromethane and acetone, known to be more aggressive solvents towards polymers, and particularly toluene, which has a similar structure to polystyrene, exhibit higher extraction rates due to enhanced interaction with the polymer. Conversely, hexane and heptane, being relatively larger molecules, have significantly lower ability to penetrate into the polymeric structure. The lower extraction exhibited by methanol could be attributed to the limited solubility of fluorescent solutes in this solvent.

The results obtained for the extraction of POPOP indicate that a 100 % extraction is generally achieved in all cases. This may be attributed to the larger size of POPOP compared to PPO, allowing it to occupy more external cavities in the polymeric structure or accessing larger and more accessible cavities, thus facilitating the contact with solvents and enhancing dissolution and extraction.

Finally, the radiometric capabilities of the CPSm after solvent treatment have been studied (Fig. 10). It is evidenced that the decrease in the ^{14}C detection efficiency is either not relevant (methanol) or minor (hexane and heptane) for solvents with lower extraction power. However, a noticeable reduction in detection efficiency is observed for all CPSm materials when treated with solvents that have higher extraction power. The spectra obtained for CPSm exposed to each solvent indicate that dichloromethane, acetone and toluene produce higher

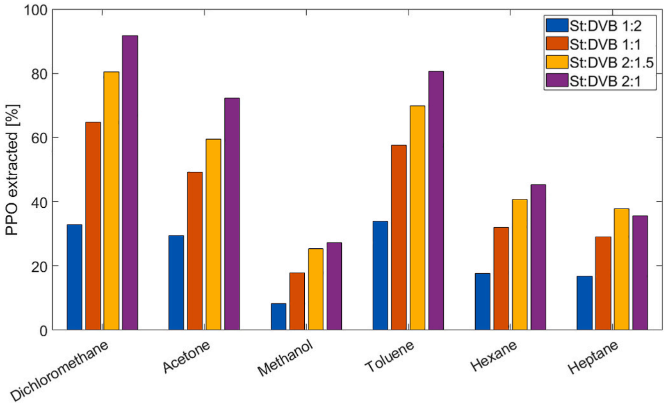

Fig. 9. Proportion of PPO extracted (in %) for each sample and solvent studied.

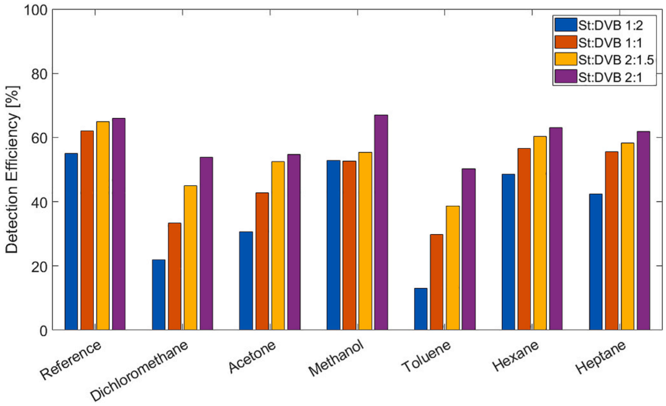

Fig. 10. Detection efficiency determined for ^{14}C in each sample attacked with different organic solvents, compared with reference values obtained before the attack.

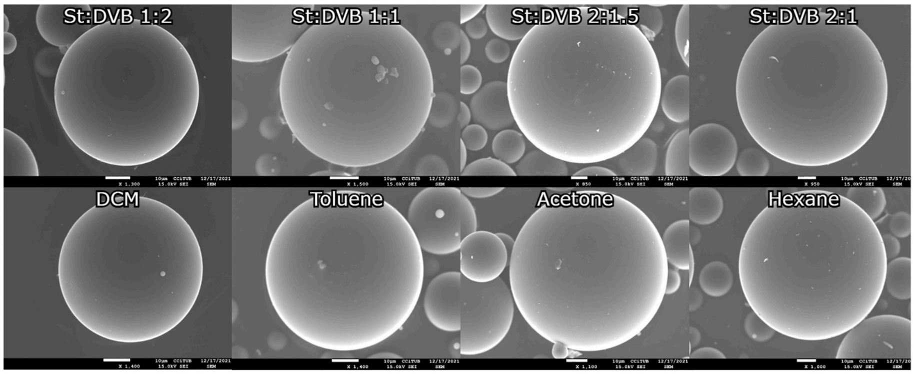

Fig. 8. SEM images obtained before (top) and after (bottom) treatment with organic solvents for some CPSm (the others are shown in the supplementary material).

displacements compared to heptane and hexane. The spectral shift resulting from methanol extraction is not significant (an example of the spectra can be observed in Fig. 11). It is plausible that this is due to solvent trapped in the polymer structure causing chemical quenching. However, toluene, a solvent historically used in liquid scintillation because of its aromatic rings, significantly impacts the scintillation of the CPSm. Therefore, it can be concluded that the decrease in radiometric performance is primarily due to the removal of fluorescent solutes by these solvents.

Regarding the proportion of crosslinker in the polymer, it is also noticed that the decrease in radiometric capabilities occurs inversely to the extraction of solutes. This suggest that materials more resistant to the extraction exhibit poorer scintillation capabilities. After solvent treatment and removal of fluorescent solutes, the same trend observed before treatment becomes more pronounced. It seems that the effect of the crosslinker on scintillation capabilities becomes more noticeable when solutes are extracted from the materials. These results highlight the importance of the polymer's ability to transfer the energy through the chain until reaching the fluorescence solutes. This ability may be influenced by crosslinking agents (Fig. 12), where a higher proportion of fluorescence solutes is necessary to facilitate an effective conversion of energy into photons. In linear or poorly crosslinked polymers, energy transfer is more efficient, and even at low fluorescence solute concentrations, photon production is adequate.

4. Conclusions

The dispersion polymerization method used in this work allows obtaining crosslinked plastic scintillation microspheres with size (20–100 μm) and shape (spherical and plane) comparable to that of linear polymer scintillation microspheres obtained by the evaporation-extraction method. The polymerization process provides larger size dispersion.

Regarding on the effect of the crosslinker, it has been shown that its impact on detection efficiency is negligible, even at high proportions, for medium and high energy beta emitters, as well as for alpha emitters. However, the presence of the crosslinker does have an effect on the spectra position and on alpha/beta discrimination capabilities, indicating a chemical quenching effect. For low-energy beta emitters, it is observed that addition of DVB significantly affects the performance of scintillators, resulting in a spectral shift towards lower energies leading to a loss of detection efficiency.

In terms of particle resistance, it has been shown that the addition of a crosslinker into the polymeric structure provides an increase in the decomposition point, improving thermal resistance. Moreover, the plastic scintillators are not dissolved when mixed with organic solvents. Contrarily, it has been observed that the addition of crosslinker does not prevent the partial extraction of the encapsulated fluorescent solutes by organic solvents, although it difficult the process and prevents the dissolution of the particles as well as morphological modifications. Extraction depends on the solvent and on the amount of crosslinker, although results suggest that effect on the scintillation properties is more correlated with the amount of crosslinked than on the amount of fluorescent solute.

As a final conclusion, it can be said that CPSm can be a good scintillator in radiochemical determinations. Additionally, they allow the use of organic solvents like dichloromethane, toluene, heptane or methanol for morphological modification by adding pores and increasing the specific surface, as well as functionalization of its surface by chemical reactions in organic medium. Among the various St:DVB ratios tested, the 1:1 ration in a 1 % NaCl dispersive media appears as the optimal, as it exhibits a balanced combination of synthesis yield, scintillation capabilities and resistance.

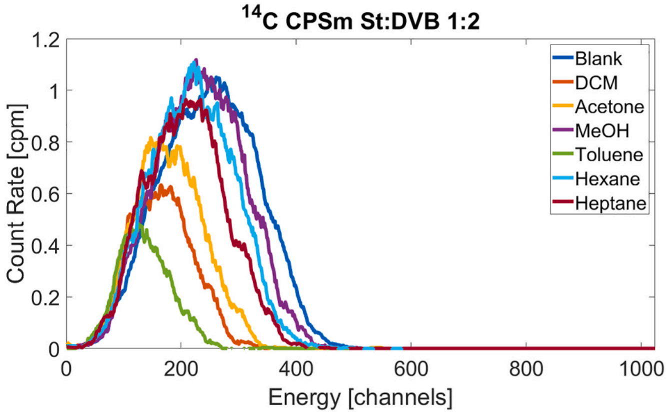

Fig. 11. Spectra obtained in the analysis of a ^{14}C standard with CPSm in St:DVB 1:2 proportion.

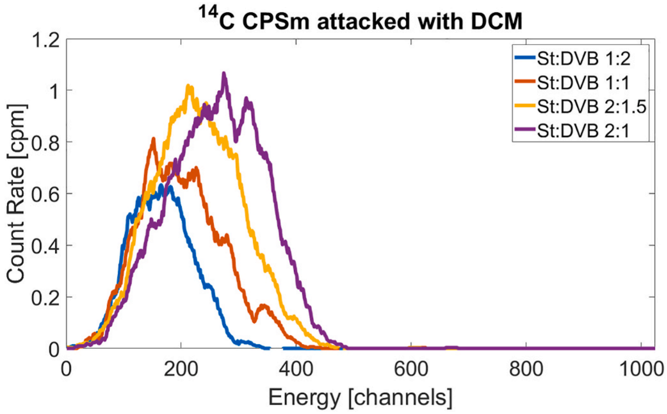

Fig. 12. Spectra obtained in the analysis of a ^{14}C standard with CPSm in St:DVB 1:2 proportion after the extraction with dichloromethane.

CRediT authorship contribution statement

A. Coma: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **H. Bagán:** Validation, Supervision, Conceptualization. **A. Tarancón:** Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2024.108514.

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