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ORIGINAL CONTRIBUTION

Clelia Dispenza
Giuseppe Battaglia
Gaetano Giammona
Mariano Licciardi
Giuseppe Spadaro

'Radiation synthesis of polyaspartamide functionalised hydrogels for sustained release of fragrances

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C. Dispenza (✉) · G. Battaglia
G. Spadaro
Dipartimento di Ingegneria Chimica dei Processi e dei Materiali,
Università degli Studi di Palermo,
90128 Palermo, Italy
E-mail: dispenza@dicpm.unipa.it
Tel.: +39-091-6567210
Fax: +39-091-6567280

G. Giammona · M. Licciardi
Dipartimento di Chimica e Tecnologie Farmaceutiche, Università di Palermo
Via Archirafi 32, 90125 Palermo, Italy

Abstract The aim of the present investigation is to assess the possibility of obtaining a biocompatible material device which is able to deliver oil-soluble fragrances in air over a length of time. Aqueous solutions of polyaspartamide functionalised with glycidyl methacrylate have been crosslinked through gamma irradiation in the presence of a lipophilic model fragrance, emulsified prior to irradiation. Two emulsification conditions have been considered at two different concentrations of both fragrance and surfactant in water. Chemical hydrogels have been obtained in correspondence to two irradiation absorbed doses and have been characterised for their solubility properties and swelling ability in water. Both static and dynamic release experiments of the fragrance in air have been performed and the release behaviour related to the hydrogel network structure and its water retention properties.

Keywords Delivery systems · Emulsions · Hydrogels · Irradiation · Swelling

Introduction

Fragrances, that is, molecules with an odour, are compounds with a sufficiently high vapour pressure and this is normally the case up to a molecular weight of around 300, a relatively low polarity granted. In a history several centuries long, these molecules have been known to be derived from plants and animals and from the second half of the nineteenth century more and more from synthetic chemistry. In consideration of the fact that fragrances are, in general, complex mixtures of different molecules that, in their own and at high concentration, may have a rather unpleasant odour, the formulation work requires the rigour and logic skills of the chemist, the physicist and the analyst, together with a creative fantasy for odours and molecular structures [1]. Fragrances are essential ingredients of cosmetics, together with other components with specific activity that need to be delivered to the skin or cause adhesion to the skin or penetration through the skin, in order to achieve their best performance. These 'active ingredients' can be either solid, such as titanium dioxide, water-soluble or oil-soluble liquids and their delivery, at the right place in the right time, may represent a complicated task. In fact, either a burst effect or a sustained release over several days can be sought or both effects combined. In addition to that, cosmetic products should be stable for about 2–3 years, both the initial aspect, initial odour and the performance effect granted, therefore their formulation and industrial production may be further complicated from these stability issues [2].

As the appearance of a cosmetic product is actually a reckoned part of its performance, the choice of the material vehicle of the cosmetic effect must take into consideration the psychological impact on the consumer. The recent preference for ''oil-free'' gels in cosmetics, as well as in pharmaceutics, is stimulating the research for novel material systems, that can couple the expected bioactivity, that is, the cosmetic effect, with a benign toxicological profile and a pleasant look.

Hydrogels are tridimensional polymeric networks, classified in to two main types: physical hydrogels, where polymer chains are connected by electrostatic forces, hydrogen bonds and/or chain entanglements, and chemical hydrogels, with covalent bonds linking the chains. Hydrogels can be obtained by either chemical processes, generally involving different reactive species, initiators and catalysts, or by radiation processing, where irradiation is used to create reactive sites onto the polymer chains and promote their reactivity [3–7].

Hydrogels crosslinked by radiation processing, because of the low temperature required, are particularly suitable for incorporation of volatile, heat sensitive actives. They can be produced by either irradiating the starting monomers or crosslinking an already formed polymer, either in bulk or in water solution: in the former case the polymer is cross-linked and then let to swell in water; in the latter case the hydrogel is formed 'in situ' and water is incorporated during the formation of the network. It has been shown that irradiation of polymer solutions allows a sensible decrease of the gelification dose due to the enhanced mobility of the reactive groups [8, 9].

Hydrogels have been already proposed for the controlled delivery of different types of active ingredients, especially drugs, in aqueous media, in alternative to capsules, microemulsions, liposomes and other release devices [10–12]. In comparison to other synthetic biomaterials, hydrogels closely resemble living tissues in their physical properties because of their high water content and their soft and rubbery consistency. The release can be either governed by the diffusion kinetics of the active through the swelling medium or by a change in the properties of the surrounding medium (pH, presence of ions, etc.) or an external stimulus (electric field) triggering reversible volume changes of the polymeric network [13–15]. However, much less documented is the development of controlled release systems for flavouring and consumer applications. The incorporation of flavours (aromas) and fragrances in polymers for the purpose of controlled release over a period of 12 or more hours is still an open challenge [16] . The control of the temporal volatile release profile, that is, the shape of the flavour delivery curve, has received little attention. But it is an increasingly important market requirement that a new fragrance or flavour for a particular product should make a specific perceptual impression, for example, a powerful initial impact or a prolonged sensation. Since the rate and the duration at which the volatile flavour component is released influences the perception, there is a rationale that by controlling the temporal release profile the perception can be manipulated. The principal objective of this research is to design novel controlled release systems for consumer application, using non-toxic, non-carcinogenic polymer systems, relatively stable to storage conditions over a long period of time and able to release essential oils or aroma chemicals over a period of 12 or more hours.

Previous investigation proved that it is possible to obtain 'clean' hydrogels through irradiation of aqueous solutions of α,β-poly(N-2-hydroxyethyl)- D,L -aspartamide (PHEA) [17–19]. This polymer is characterised by high water solubility and excellent biocompatibility and, due to this property, it has found application as plasma expander [20]. It has been established that the gel dose is dependent on the molecular weight and concentration of the starting polymer. However, the high irradiation dose (about 550 kGy) required to obtain these matrices prevented their wider exploitation in the area of agricultural, pharmaceutical and personal care industries, as the actives to be incorporated can be sensitive to these high doses of ionising irradiation [17].

The reactivity of PHEA towards γ-irradiation has been improved by introducing groups bearing unsaturations in order to lower the gelification dose. In fact, PHEA structures partially modified by reaction with glycidyl methacrylate (GMA), named PHGs, formed transparent and spreadable gels in correspondence to irradiation doses as low as 2 kGy [21–23]. Spreadability, in particular, refers to the ability of the material to evenly spread onto a substrate, such as skin, forming a thin continuous film, by applying constant, ramped or oscillating forces or flow rates, for example, by rubbing. This property is related to the hydrogel firmness and resilience, in turn related to the network elasticity, and its flow properties, that is, its shear viscosity. It is also worth noting that the doses required to produce compact and stable gels from PHG-water solutions were lower than the doses required for sterilisation treatments (25 kGy) [24].

The incorporation of highly water insoluble actives, as it is generally the case of a fragrance, in highly hydrophilic polymeric networks can be possibly achieved via emulsification techniques. The fragrance is dispersed in the water solution of the crosslinkable polymer. The use of a proper emulsifier should provide sufficient stabilisation to the system until the polymer dissolved in the water-phase is crosslinked.

The size and distribution of the oily essence in the gelled matrix is one critical factor affecting the fragrance release. The crosslinking degree and density of the polymer network can add a further release feature to the one imprinted by the emulsification conditions. In particular, in the present investigation, a fragrance model molecule, tetrahydrogeraniol (THG), has been incorporated, at two different concentrations of both fragrance and surfactant in water, in PHG-based hydrogels obtained through gamma irradiation in correspondence of two integrated doses. The release of the fragrance in air, in 'static' headspace and 'dynamic' headspace conditions, has been monitored and the main factors influencing the temporal release profiles identified.

Experimental Part

Materials

PHEA was synthesised and derivatised with GMA following an experimental procedure already reported in literature [22]. The degree of derivatistion, measured via ^{1}H NMR analysis by comparing the integral of the peaks related to acrylic protons of the GMA residue linked to polymer with the integral of the peaks related to protons of PHEA, and expressed as the mean value of acrylics groups per polymer repeating unit was 0.29.

The weight-average molecular weight of PHG polymer, determined by light scattering measurements, using a Dawn DSP-F Laser Spectra Physics Spectrometer, was 54000 (M_w/ M_n = 1.70).

Tetrahydrogeraniol (3-7-dimethyl-octanol or THG), chosen as a model fragrance and Brij 58P (polyoxyethylene (20) cetyl ether), the surfactant used for preparing THG/ PHG-water emulsions were both purchased from Aldrich Chemical Co.

γ-Irradiation of Surfactant, THG and PHG-Water Micelle Solutions

Brij 58P (polyoxyethylene (20) cetyl ether), with HLB = 15.3, average M_n = 1152, mp 44–46°C, CMC at 25°C 0.007 mM was identified as a candidate surfactant for THG emulsification at room temperature both in water and PHG-water solutions.

Irradiation of pure Brij 58P, pure THG and micelle solutions of Brij 58P in PHG aqueous solutions was carried out using a panoramic 3000 Ci ^{60} Co IGS-3 irradiator in order to assess their chemical stability upon irradiation. The dose rate, measured by a PTW Universal Dosimeter, was 0.5 kGy/ h with an accepted variance of 5% in the absorbed dose. The total absorbed doses of 2.5 kGy and 3.5 kGy were considered.

Pure Brij 58P chemical stability to γ-rays was confirmed by FT-IR analysis and thin layer chromatography using a $CHCl_3$/ CH_3OH mixture as eluent on samples irradiated at 3,5 kGy. Micelle solutions of the Brij 58P surfactant in PHG aqueous solutions at a concentration of 2 wt./ vol.-% of Brij 58P to water and 5 wt./ vol.-% of PHG to water were also irradiated at 3.5 kGy. FT-IR spectra were determined and compared to those of PHG hydrogels. In both cases samples were repeatedly washed with distilled water, then centrifuged at 10000 rpm, lyophilised and characterised.

Tetrahydrogeraniol stability upon irradiation was assessed by a comparison of the GC traces of the not irradiated and irradiated samples at 3.5 kGy. Gas chromatography was carried out with HP 6890 plus GC system equipped with a HP 5 MS crosslinked (5 wt.-% PHME Siloxane) general purpose capillary column (30 m×0.25 mm×0.25 μm of film thickness) and a FID analyser. The chromatography conditions were 20°C/ min temperature ramp from 80°C to 120°C and helium gas carrier at a flow rate of 1 ml/ min.

THG/water and THG/PHG-Water Emulsification

Tetrahydrogeraniol/water emulsions were prepared using different emulsifiers, at different surfactant concentration and oil to water volume ratios. Brij 58P was selected as the best performing emulsifier among those investigated by a comparison of performance in terms of speed of emulsification and shelf stability of the THG/ water systems. Emulsion stability was assessed by visual inspection at regular time intervals over a minimum of two weeks, of the emulsions kept within 10 ml measuring cylinders, in 'dark' conditions, at room temperature. The emulsion obtained at 20 vol.-% THG/ water and 2 wt./ vol. -% Brij 58P/ water was subjected to gamma irradiation to assess if irradiation affects the stabilisation of the oily essence in water. Then, two different types of tetrahydrogeraniol/PHG - water emulsions, using Brij 58P as emulsifier, were prepared, one at a high THG content (20 vol.-% THG/water and 2 wt./vol. -% Brij 58P/ water) and a 'microemulsion' at a much lower oil phase content (1 vol.-% THG/ water and 3 wt./ vol.-% Brij 58P/ water). The polymeric surfactant and the PHG polymer were pre-dissolved in double-distilled water, by stirring at room temperature for at least one hour, and then THG was added, while stirring, by means of a micro-litre syringe. Agitation was provided after addition of THG for further two hours. The PHG dissolved in the water phase were always at 5 wt./ vol.-% of PHG to water content.

Both the emulsions prepared were assessed for shelf stability at room temperature for a period of time of two weeks.

γ-Irradiation of THG/Water and THG/PHG-Water Emulsions

THG/water and THG/PHG - water emulsions were prepared, according to the procedure described above, from water solutions of either Brij 58P or PHG and Brij 58P previously purged with gaseous nitrogen. Further to that, the emulsification was performed in a sealed volume thoroughly washed with nitrogen. Emulsions were irradiated hermetically closed in cylindrical glass vials of 2 cm diameter, that were opened afterward, constituting the reservoir for the THG release experiments.

Solubility Tests and Swelling Ratio Measurements

For gel fraction measurements known volumes of polymer-water solutions were irradiated and, after irra-

diation, repeatedly washed with distilled water, lyophilised and weighed. The gel fraction was calculated as the ratio of the solid residue after lyophilisation and the total amount of polymer present in the solution. Values reported are the average of minimum three measurements.

The swelling ability of the produced hydrogels was determined by experiments carried out on samples previously dried and weighed with a precision balance and, afterwards, kept immersed in double-distilled water at 37°C until the equilibrium sorption conditions were attained, as revealed by the constancy of the hydrated sample weight. Swelling ratios were calculated as the final weight of the equilibrium swollen gel to the initial weight of the dry sample.

Tetrahydrogeraniol Release from Hydrogels

For the quantitative determination of THG released in air from the hydrogels a chromatographic method of analysis was selected.

In order to determine the dependence of the chromatographic peak area on the THG concentration in air, pure THG was placed in the release chamber, set it free to evaporate until its equilibrium value was reached. A calibration curve was determined carrying out experiments at different temperatures and plotting the corresponding peak areas against the concentration values, calculated according to the Othmer and Yu method [25], using two THG boiling point data (3.41 Pa at 20°C and 8.66 Pa at 30°C) known from literature [26].

Tetrahydrogeraniol release from hydrogels was studied in two different experimental conditions: 'static headspace' and 'dynamic headspace'.

In the first type of experimental conditions the THG-loaded hydrogel, contained in the cylindrical glass vial where it was previously irradiated, was placed in a sealed release chamber, where the alcohol is free to evaporate until the saturation pressure in the headspace is reached. In order to avoid concentration gradients, a magnetic stirrer agitates the THG vapours within the headspace air. The release chamber was immersed in a water bath, equipped with a temperature controller in order to maintain a constant temperature of 37°C (± 0.5°C). The gases from the chamber headspace, captured by a 50 µl gas-tight syringe, whose volume can be considered negligible with respect to the headspace volume, were analysed by the gas chromatographic apparatus, already described. Chromatography conditions were the same as those set for THG stability upon irradiation evaluation.

'Dynamic headspace' release experiments were carried out by setting up an inlet to the same release chamber, connected to a chromatographic air cylinder through a flux meter, and an outlet from the release chamber, connected to the GC apparatus. A constant air flow was ensured, so that the headspace air volume could be completely displaced every 7 min and regular sampling at fixed time intervals of 4 min was performed by means of the sampling valve of the chromatographic apparatus. The release was always carried out at a constant temperature of 37°C. Pure THG evaporation in these experimental conditions was measured at three different temperatures for calibration purposes.

After any dynamic headspace release experiment the residual THG present in the hydrogel was leached out using refluxing ethanol, and the amount of THG extracted quantitatively determined by gas-chromatography. This procedure was set in place to cross check the data obtained from the release measurements. In all cases, the mass balance between THG loaded, THG released and residual THG closed fairly well.

Considering that in the experimental conditions of the dynamic headspace release significant amount of water can also evaporate from the hydrogel, as the vapour pressure saturation conditions cannot establish, the loss of weight of hydrogel samples as function of time were also measured through dedicated experiments. The hydrogel was kept in the same release chamber used for the THG release experiments, at the same temperature and air flow conditions, withdrawn from the chamber at time intervals, sealed and weighed by means of a precision balance. The weight loss is caused by the release of both THG and water, but being the water in the gelled microemulsions in large excess with respect to oily essence, the weight loss can be regarded as a measure of water release.

Results and discussion

The homogeneous distribution of a water insoluble active in a hydrogel requires that an uniform dispersion of the former in the water solution is maintained until the polymeric network is formed, assuming that the polymeric mesh could impair oil-phase coalescence. In the present investigation this has been achieved by using a non-ionic polymeric surfactant, aiming at a sufficient stabilisation of the o/w emulsion until the PHG based hydrogel forms upon irradiation. On having accomplished this role, the surfactant should remain entrapped within the polymer network, either physically or chemically bonded, and should not migrate to the surface, as this would worsen the toxicological profile of the hydrogel.

Brij 58P (polyoxyethylene (20) cetyl ether) was identified as a surfactant for the purpose of the present study. All the THG/water emulsions showed high speed of emulsification and good shelf stability at room temperature; one of the best performing system being that obtained for 2 wt./vol.% Brij 58P/water and 20 vol.%

THG/water. These emulsions proved to be stable for longer than two weeks, when stability tests were interrupted and considered passed. The emulsion stability was not influenced by the irradiation at both 2.5 kGy and 3.5 kGy.

In order to investigate the influence of the surfactant in the PHG ability of producing hydrogels under irradiation, micelle aqueous solutions of surfactant and PHG were irradiated at 2.5 kGy and 3.5 kGy. In both cases a homogeneous, compact hydrogel was obtained. FT-IR spectra, here not reported, of the lyophilised gel fractions of the irradiated PHG-Brij 58P micelle solutions have been compared to those corresponding to the lyophilised gel fractions obtained from irradiated PHG-water solutions. The presence of the surfactant in the lyophilised residues, as obtained after repeated washings with distilled water, is revealed from the appearance of a new band at 1112 cm^{-1}, attributable to the C–O bond stretching of the polyoxyethylene chains of Brij 58P also present in the spectrum of the pure surfactant. Therefore part of the surfactant is irreversibly linked to the PHG network. On the contrary, THG proved to be insensitive to irradiation in the chosen experimental conditions, as revealed by gas chromatographic analysis carried out prior and after irradiation of pure THG. It also appears that THG is not grafted to either Brij 58P or PHG by irradiation. In fact, FTIR analysis carried on the solid residue obtained by removal of water and THG, after irradiation of the system THG/water/ Brij 58P at 3.5 kGy showed that the spectrum coincides with that of the irradiated micelle aqueous solution of the surfactant. Furthermore, the extraction of residual THG from the hydrogel, after the dynamic release experiments, shows that the amount of THG released and the residual THG equal the amount of THG initially loaded in the gel, therefore no THG seems to be irreversibly linked to the polymer network.

In Table 1 gel fractions and swelling ratios for PHG/ water solution and PHG/ Brij 58P/ water micelle solutions are reported. It can be observed that increasing the irradiation dose gel fraction increases and swelling ratio decreases for both systems, thus indicating an increase of both crosslinking degree and density. A comparison between the two systems shows that hydrogels obtained from the micelle solution presents lower gel fractions and higher swelling ratios.

This last result can be expected considering that the Brij 58P is approximately 28 wt.-% of the polymeric species present in water and is relatively insensitive to γ-irradiation compared to PHG, thus lowering the overall crosslinking yield.

Tetrahydrogeraniol/ PHG - water systems obtained using Brij 58P as emulsifier, showed a stability drastically reduced to few hours. Homogeneous hydrogels were then produced by providing stirring during irradiation. Hydrogels, obtained in correspondence to both the irradiation doses here considered, were compact and spreadable, although slightly hazy in colour and presenting small amounts of a supernatant liquid phase. These hydrogels were tested for 'static headspace' THG release after wiping out the liquid from the surface. The THG equilibrium concentration at 37°C was calculated using the Raoult's law and is equal to 826 ppm. It is worth noting that, for the release chamber of the dimensions described in the experimental section, 1.4 µl of fragrance are sufficient to saturate the headspace air and, therefore, the 'loaded' hydrogel always presented a significant amount of residual THG in the gel after the headspace saturation conditions were approached. In Figure 1 the amount of THG released in the headspace as function of the elapsed time for the two hydrogels is reported. The release from the unirradiated emulsion was also monitored for comparison. It can be observed that the presence of a polymeric network sensibly delays the THG release: the not irradiated emulsion reaches the equilibrium value in about 20 min, the system irradiated at 2.5 kGy approaches this concentration after approximately 20 hr and the system irradiated at 3.5 kGy presents a sensible reduction of the release rate after an initial burst effect and reaches a plateau after 50 hr, but not quite the vapour pressure value. The burst effect, presented by all systems, is possibly due to the fast desorption of THG from the surface.

An indefinitely 'stable' system has been obtained in correspondence to a drastically lower concentration of THG in water (1 vol.-% THG/water) and an increased concentration of surfactant (3 wt./ vol.-% Brij 58P/water). The obtained system presented the characteristic translucent optical properties of a 'micro-emulsion'. When irradiated at 2.5 and 3.5 kGy compact, spreadable and transparent hydrogels were obtained with no evidence of a supernatant liquid phase. The amount of THG in these systems is close to the typical concentration of fragrances in cosmetics and is still one order of magnitude higher than the amount required to saturate the headspace air in the release chamber as set up for this work [27] In Figure 2 the release of THG from the not irradiated emulsion and micro-emulsion are compared: the saturation of the headspace air occurs in 20 min for the former and in approximately 12 hr for the latter. The remarkable difference between the two

Table 1 Insoluble fractions and swelling ratios for irradiated solutions of PHG and water and micelle solutions of Brij58P, PHG and water

System	Dose, [kGy]	Insoluble fraction [%]	Swelling ratio [Ws/ Wd]
PHG-water	2,5	86	10
PHG-water	3.5	91	9
Brij 58P - PHG-water	2,5	65	27
Brij 58P - PHG-water	3.5	75	19

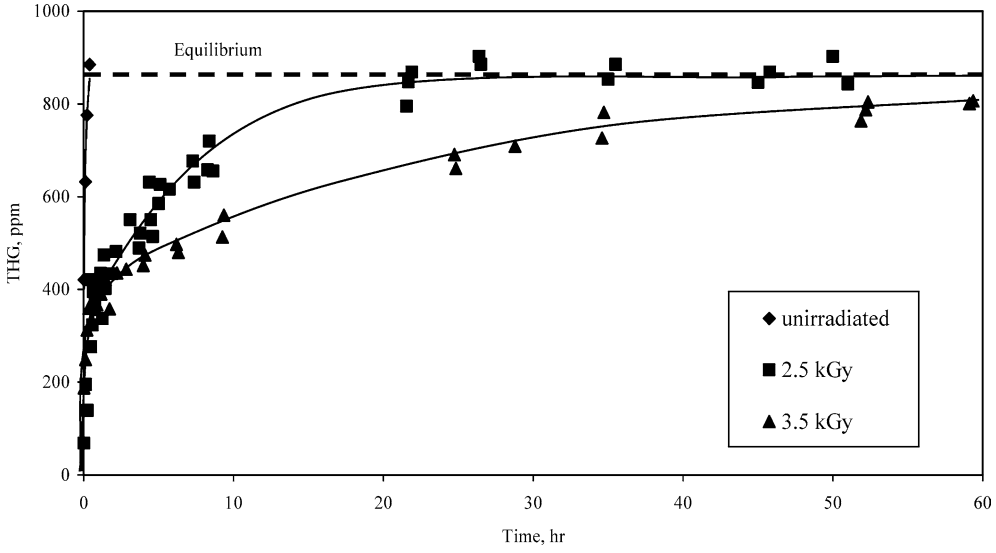

Fig. 1 'Static headspace' release: THG released as function of the elapsed time from the not irradiated emulsion and the two hydrogels obtained in correspondence to different irradiation doses

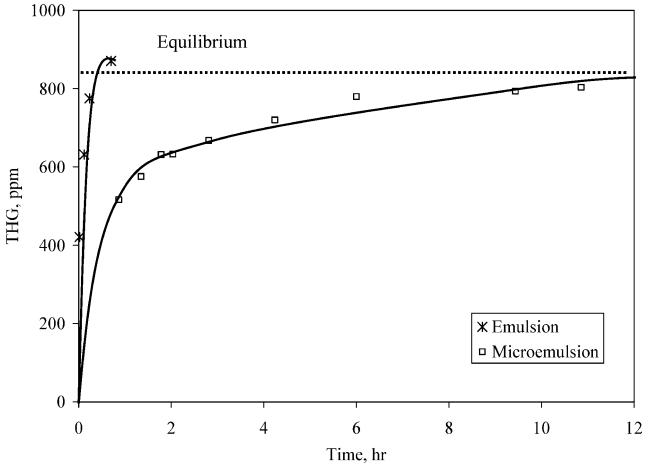

Fig. 2 'Static headspace' release: THG released from the not irradiated emulsion and the not irradiated micro-emulsion

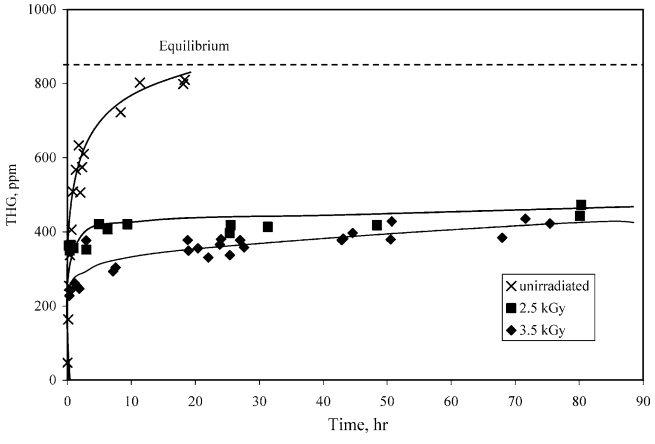

Fig. 3 'Static headspace' release: THG released as function of the elapsed time from the irradiated micro-emulsions. Curve relative to the not-irradiated micro-emulsion also reported for comparison

temporal release profiles is mainly attributable to the lower amount of THG loaded in the gel and, to a lesser extent, to the fact that a thermodynamically stable system, such as a micro-emulsion, presents a lower driving force for THG redistribution compared with a macro-emulsion. The finer dispersion of the oil-phase, on the contrary, should play in the direction of a decrease of saturation time. The irradiation of micro-emulsions causes a further reduction in the release rate: release data reported in Figure 3 show that the amount of THG released in air increases with time, but for none of the systems the calculated THG equilibrium concentration value is reached within the experimental time scale. The different behaviour of hydrogels obtained in correspondence to the two irradiation doses can be related to the above-discussed effect of irradiation dose on both crosslinking degree and density.

The release behaviour of THG from irradiated micro-emulsions has also been investigated in a different experimental condition. A constant chromatographic air flow was fed to the release chamber and the THG concentration in the flow was measured at regular time intervals. W(t), the cumulative THG released in the time t, is calculated by numerical integration and plotted as function of the time in Figure 4. The behaviour of the three systems, the not-irradiated and the irradiated at 2.5 kGy and 3.5 kGy micro-emulsions, is highly differentiated: while all the THG incorporated is released from the not irradiated micro-emulsion, the irradiated systems always present a 'plateau' value, corresponding to a zero value of the release rate Δ W(t)/ Δ t, calculated as the measured amount of THG in the volume of air sampled at the time t, Δ W(t), divided by the sampling time interval, Δ t. For both systems the 'plateau' value of W(t)

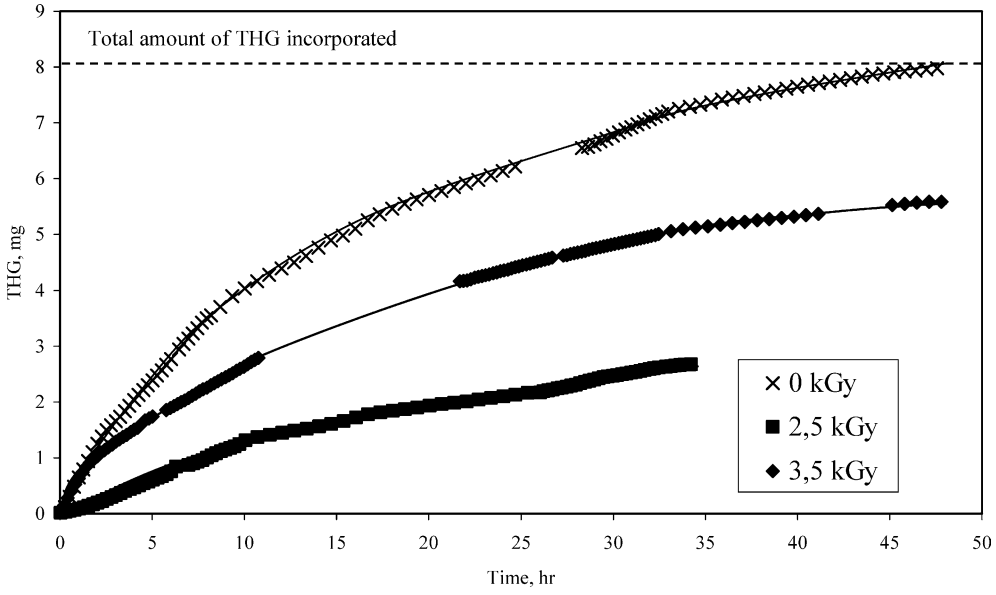

Fig. 4 'Dynamic headspace' release: cumulative amount of THG released in the time t as function of the elapsed time from hydrogels obtained from micro-emulsions in correspondence to different irradiation doses

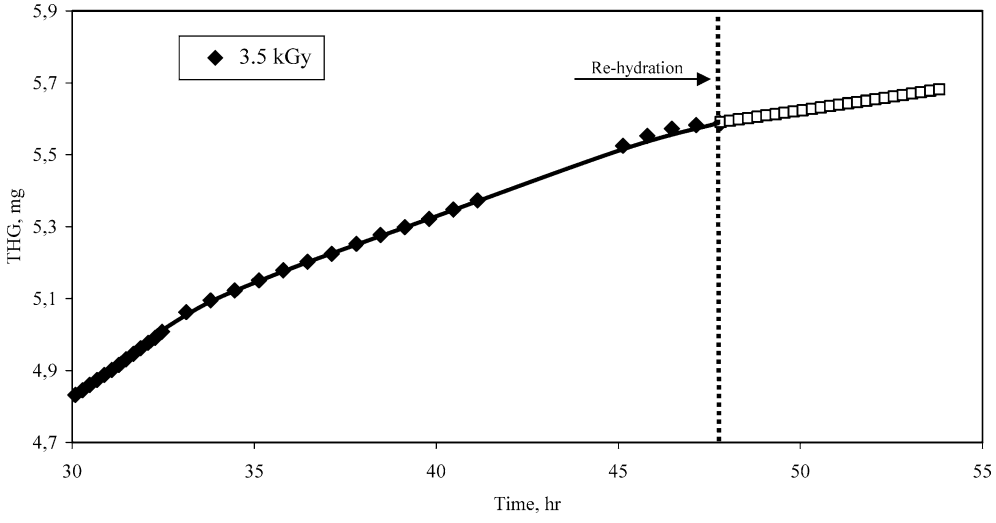

Fig. 5 'Dynamic headspace' release: influence of re-hydration of the hydrogel surface on the THG released as function of elapsed time

is lower than the amount 'loaded', so implying that, also in these experimental conditions, part of the alcohol remains entrapped into the gel. Differently from the 'static headspace' release, in dynamic conditions the hydrogel obtained in correspondence to the higher irradiation dose releases more THG and at higher rate than the one obtained at the lower dose. It was also observed that only the not-irradiated micro-emulsion is able to release all the volatile species and transforms in a powdery solid after 50 hr. On the contrary, the two hydrogels form a dry, impermeable film on the surface that prevent the complete loss of both the water and the fragrance. As it is shown in Figure 5 for the system irradiated at 3.5 kGy, rehydration of the surface of the hydrogel eliminates the skin effect, thus allowing the release process to continue, without restoring, though, the initial release rate as both the THG diffusion coefficient and the driving force for diffusion are now different.

Therefore, it appears that the kinetics of de-hydration of the hydrogel during the THG release, affected in turn by the structure of the polymeric network, add another feature to the fragrance release behaviour. In order to confirm this hypothesis, weight variations as a function of the time for hydrogel samples of the same geometry and placed in the same release chamber, at the same temperature and in the same air flow conditions as for the 'dynamic headspace' release experiments, have been measured. In Figure 6 the two ratios, the amount of water and THG lost at the time t over the total amount of water and THG initially present in the gel and the THG released in the same conditions over the THG 'loaded' in the gel, are reported as function of the time.

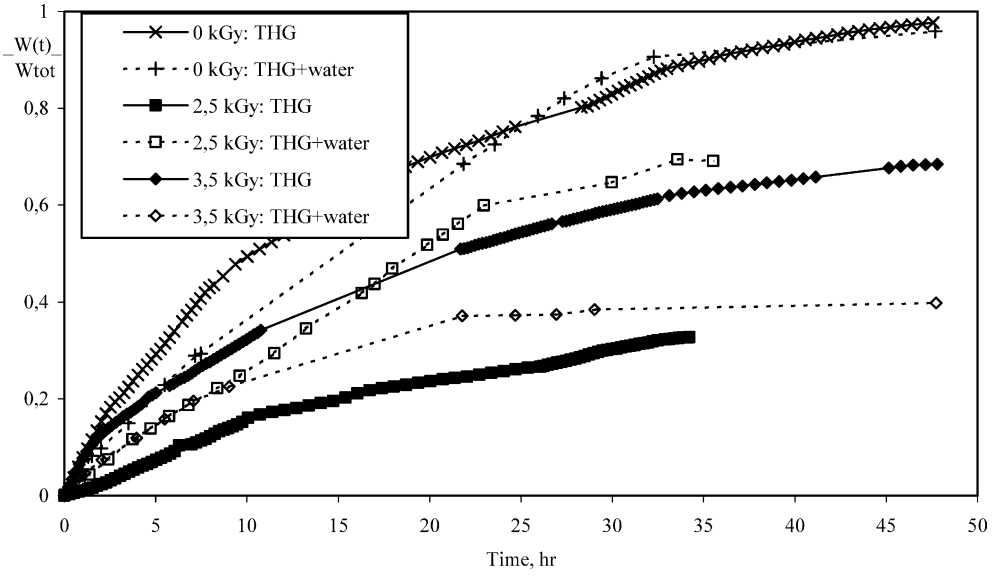

Fig. 6 'Dynamic headspace' release: THG released at the time t over the THG 'loaded' in the gel and water and THG lost at the time t over the total amount of water and THG initially present in the gel as function of the time

Not surprisingly, the looser is the network, as in the case of the hydrogel obtained in correspondence to the lower irradiation dose (2,5 kGy), the faster is the loss of weight. Considering that, essentially, the larger amount of the volatile species released in dynamic headspace conditions are represented by water, the looser is the polymer network the faster is the release of water, therefore the consequent shrinkage and collapse of the gel propagates more rapidly from the surface to the bulk and may take into account for both the faster decrease of the THG diffusion coefficient with time, causing a decrease of THG release rate and its early interruption when the impermeable skin is formed. Conversely, when the polymer network density is higher, a higher level of hydration of the gel is maintained, thus favouring a more prolonged release of the fragrance diffusing through and out the hydrogel. When the micro-emulsion is not irradiated and no polymer network is present as a restraint for both water and THG release, the kinetics of both water and THG evaporation are very similar.

Conclusions

The present investigation has shown that ionising irradiation can be a stimulating tool to obtain crosslinked hydrogels from water-soluble functionalised hydrophilic polymers. The crosslinking degree and the network mesh size can be controlled through the irradiation conditions, in turn affecting the water retention properties of the gels.

In particular, it has been observed that irradiation doses required to obtain hydrogels from PHG polymers are lower than those normally used for sterilisation of drugs, cosmetics and medical tools. The PHG-based gels are transparent, spreadable and able to undergo to several hydration—dehaydration cycles.

Oil insoluble fragrances can be incorporated by coupling irradiation and emulsification techniques. At the low doses of irradiation required to produce hydrogels from PHG also unstable, highly oil content emulsions can be 'stabilised' by the formation of a polymer network in the water phase that prevent coalescence phenomena, without affecting the chemical stability of the fragrance. The mesh of the polymer network affects the fragrance release behaviour, by either directly offering a diffusion barrier to the fragrance, as observed in the 'static headspace' release measurements, or by controlling the kinetics of gel dehydration in 'dynamic headspace' release experiments. The formation of an impermeable layer on the surface of the hydrogel in the initial stage of shrinking can be one of the most important factors affecting performance of these devices./Para >

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