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The role of additives towards increasing the SIMPLE SDD lifetime

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Abstract

The lifetime of a Superheated Droplet Detector (SDD) is limited by the fracture of the gel matrix, due to the growth of the bubble in time caused by Oswald ripening. There are several approaches to increasing the lifetime of a SDD by limiting the fracture phenomenon. We report, here, one of these approaches, which focuses on the gel itself. The lifetime of a SDD is increased if the fracture energy of the gel matrix is raised, leading to a better resistance to the fracture phenomenon. Several additives for the SDD gel were tested, with the results indicating the use of an agarose additive to extend the lifetime by as much as a factor 2.

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Keywords: Agarose; Additives; Fracture energy; Triple helix concentration; Gel matrix; SDD

1. Introduction

The SIMPLE project is a dark matter experiment [1] for detecting Weakly Interactive Massive Particle (WIMPs). It is one of only two such experiments [1,2] based on superheated droplet detectors (SDDs), which consist of a homogeneous dispersion of superheated liquid refrigerant droplets suspended in a polymer or gel matrix of matched density to prevent sedimentation during the fabrication process when the gel is sol. The response of the device is based on the Seitz "thermal spike" model [3]: if the energy deposition is sufficiently large within a sufficiently short distance within the metastable droplet, the droplet vaporizes. The basic insensitivity of the SDD to the majority of low-energy backgrounds which plague more traditional devices (since bubble nucleation typically requires $dE/dx > 200\,keV/\mu m$ at ambient temperatures), together with their high fluorine content, defines the advantage of SDDs for such searches, and enables the SIMPLE experiment to obtain, with low exposure, restrictive limits on the spin-dependent coupling strengths complementary to other larger exposure searches [4].

First introduced by Apfel over 25 years ago [5–9], SDDs have more notably been developed for applications in dosimetry and neutron spectrometry [10–13]. These are generally of small volume ($25\,cm^3$) and active mass (0.03 g). Dark matter searches generally require larger active detector masses. Details regarding fabrication of the SIMPLE SDD, with a factor 10 larger freon concentration, are described in Ref. [1], and yield a radioactively clean (<0.5 events/kg d), stable (40 days) device.

Because the expected rate of events is of order 1 event/kg d or less, the SIMPLE SDD exposure times must be long (which is not the case in the more standard dosimetry and detection applications). The lifetime of a SDD is, however, limited by the fracture of the gel, due to Oswald ripening: after a droplet vaporises, the bubble grows slightly but indefinitely by diffusion of the dissolved freon from the droplets nearest the bubble. These growing bubbles deform the gel until a fracture develops because the gel is too flexible to contain the least overpressure.

When a fracture appears, the detector usefulness ceases because of the high number of events generated (a fracture

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propagation over a few cm causes the vaporisation of more than 100 droplets). The same phenomenon is observed in commercial detectors, so is not a particular limitation of SIMPLE detectors but rather of SDDs in general.

There are three possible approaches to increasing the SDD lifetime by limiting the bubble growth [14]:

- Matrix: increase the matrix resistance to fracture by modifying the gel ingredients or composition, or by adding additives (the matrix is said to be resistant to fracture when its fracture energy is high);
- Interface matrix/droplet: control the mass transfer from the droplet to the bubble at the droplet–matrix interface by adding surfactants to stabilize the bubble size. Some surfactants, at the interface, can limit the mass transfer by creating an interfacial barrier, leading to a limited diffusion of the dissolved gas from the droplet to the bubble;
- Droplet: recompress the SDD to "re-liquefy" the bubbles.

This report focuses on only the first approach: the matrix.

The SIMPLE gel matrix, consisting of water, gelatin (biopolymer), PolyVinylPyrrolidone (PVP) (a neutral polymer) and glycerine, is generally a complex entanglement of these various polymers. The fracturing depends on the physical state of the matrix at the macromolecular scale, which can be grouped in two parts:

- concentration of triple helices made by three polymeric gelatin chains (see Fig. 1),
- polymer chains in loops, dangling ends and free chains (see Fig. 2), due to the PVP polymer and also to the gelatin chains remaining in a coil shape (in a small proportion because the helices create the network [15] of the gel).

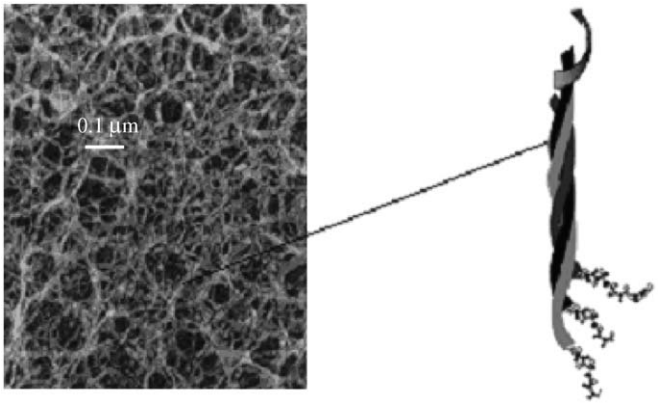

Fig. 1. Representation of the gelatin network (water + gelatine). The "chains" are formed by triple helices of variable length: 10–100 nm. A triple helix is the association of three polymeric chains of gelatine as seen in the right. The concentration of the gelatine is 2% (from Ref. [17]).

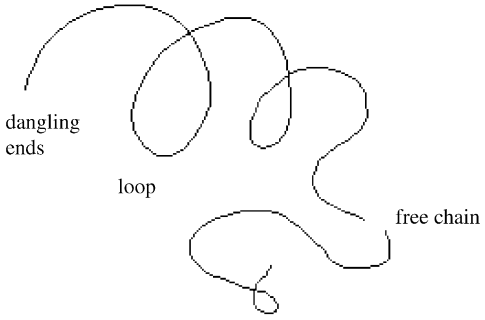

Fig. 2. Naive representation of a single polymer chain (like PVP).

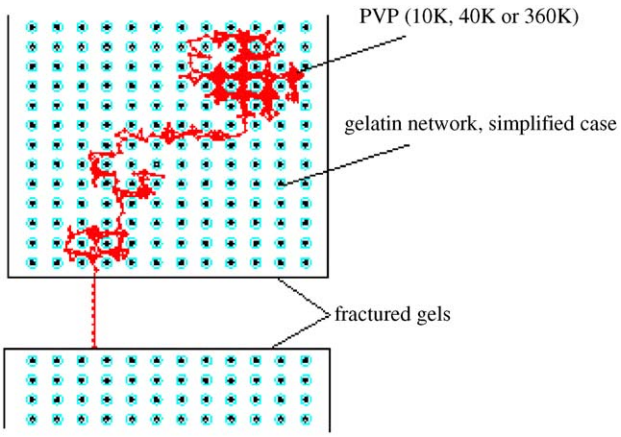

Fig. 3. Schematic representation of the friction of the PVP polymer, embedded inside a gelatin network, during the crack front process.

Following Ref. [15], the network of the gel is composed of semi-flexible triple helices interconnected by flexible strands, as shown schematically in Fig. 1. The PVP polymeric chains make entanglements inside the gelatin network without interaction with the gelatin, whereas the glycerine lacks the helix structure [14].

According to the Tanaka model [16], the fracture energy per unit fracture surface (G_c) can be written as:

$$G_c = G_{cut} + G_{pull}, \quad (1)$$

where G_{cut} is the contribution due to cutting chains in the network, and G_{pull} is the contribution due to friction within the network when a polymeric chain is pulled out during the crack process as shown in Fig. 3. If the chain, in the crack front plane, is a dangling end or loop or free chain (Figs. 2 and 3) of the matrix gel, then it will be pulled-out during the fracture and will only contribute to G_{pull}. If the chain is, however, a network chain (Fig. 1), it will be cut before being pulled out: the essential contribution will be G_{cut}.

Preliminary studies [14] of the contributions of various concentrations of the gel constituents to the fracture energy are shown in Fig. 4 and gave the following results:

- PVP and glycerine provoke more dangling ends and loops inside the matrix: the G_{pull} term, which is a cubic

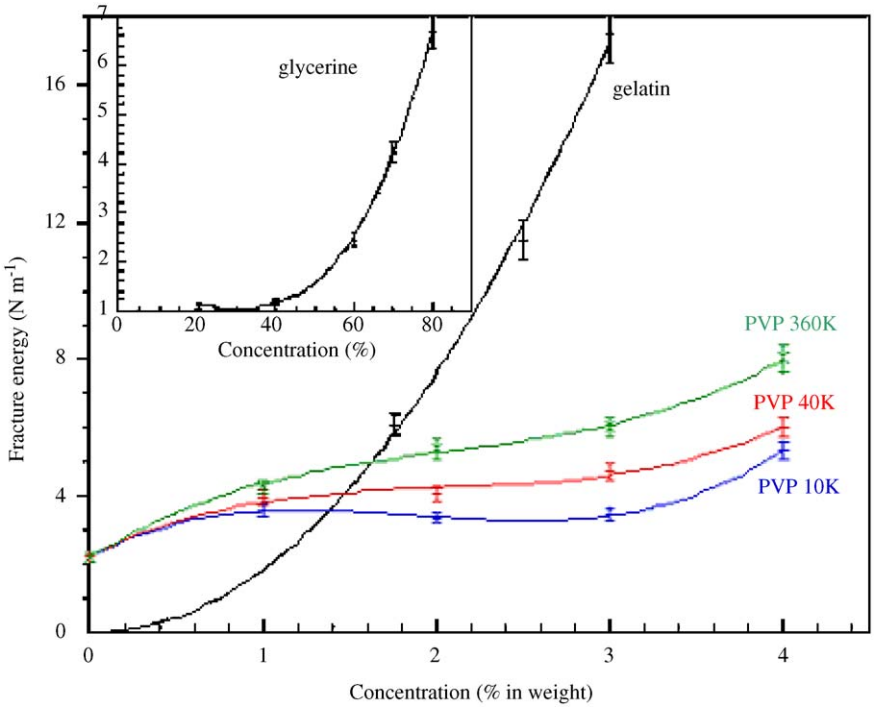

Fig. 4. Fracture energy of the various gel components with variation in their respective concentrations. Insert: the results for glycerine. The PVP is available commercially with different polymerisation index N: 10, 40 and 360 K (Sigma Aldrich supplier).

function of the concentration (c), dominates the G_{cut} term.

- Gelatin: $G_{cut} \propto c^2$, and dominates G_{pull}.

A priori, it seems preferable to raise the fracture energy via the "viscosity" term, i.e. by increasing dangling ends, loops or free chains instead of raising the helix concentration, since the cubic function varies more quickly than the parabolic function. The modification of the glycerine percentage and/or substitution with another component is, however, generally excluded, since this ingredient is necessary for matching the density with the liquid freon during the fabrication process. Increasing the polymerisation index of the PVP chain (at 360 K) would also increase G_c via G_{pull}; however, a long entangled polymer chain, in the vicinity of a droplet, may cause expansion by reptative motion [18] (a chain is topologically constrained by its neighbours from undergoing transverse displacements inside a virtual tube), which can transmit energy to the droplets. This energy, if sufficient, can produce spontaneous bubble nucleations. Moreover, contact with a droplet can cause bubble nucleation and increase the number of events. Although in dosimetry or spectrometry this has no importance since the number of background events due to the matrix is drowned by the flux of calibration neutrons, in a dark matter search, this choice cannot be permitted due to the low rate of hypothetical WIMPs.

As is clear from Fig. 4, the highest G_c are associated with the variation in gelatin concentration, indicating the gel matrix resistance to fracture is increased by an increase in the helix concentration. If the gelatin concentration is higher, the gel will, however, become brittle, which is to be avoided since one bubble nucleation might provoke a quick fracture damaging the detector. For these reasons, the gelatin concentration cannot be modified.

Without the possibility to modify the basic gel ingredients, the alternative is an additive which can reinforce the gelatin network by raising the helix concentration ($G_{cut} > G_{pull}$).

We report measurements of the fracture energy of various additives which increase the fracture resistance by reinforcing the gelatin network (i.e. by increasing G_{cut}) or by creating another network gel (polysaccharides) instead of adding a polymer, which increases the friction (see Fig. 3) of pulling out the polymer chain via G_{pull}. Optical rotation measurements [19,20] were additionally made, in order to obtain information regarding the amount of helix structure.

2. Experiments

The additives examined included dextran (a neutral polysaccharide), Poly Ethylene Glycol (PEG), Carboxy Methyl Cellulose (CMC, a negatively charged polysaccharide), gum arabic (a negatively charged polysaccharide), agarose (a neutral polysaccharide), glyoxal (an aldehyde) and dimethylurea. The additive percentages are limited by the constraint of not drastically changing the SDD properties, and were kept to no more than 0.5%.

Measurements of G_c were performed using the Compact Tension (CT) technique [21], which consists of fracturing

the gel by tearing it longitudinally. Using this technique, Tanaka et al. [16] have investigated the fracture energy in acrylamide (AA) and methylene bisacrylamide (BIS) gel, the effect of the fracture propagation speed V on the fracture energy and also the effect of the cross-linking density on the fracture energy. Our method is similar to Ref. [16], with each gel of different compositions fractured in the same way, as shown schematically in Fig. 5. A reduction motor is located well above the gel (2 m) in order to assure a 90° peeling geometry, and that the rolling speed will be equal to the crack speed. A strain gauge, connected to the nylon wire between a hook in the gel and the reduction motor, is connected to a computer. A LabView program records the tension voltage and time as a thin layer of gel is peeled-off by operation of the reduction motor.

G_c depends on the crack speed [16]: in the SIMPLE SDD, the fracture behaviour is a slow phenomenon, so the crack speed is chosen as the minimum of the reduction motor (0.022 cm/s). The measurement requires 8–9 min to fracture one gel sample, with a reproducibility of ~10%.

The gel used for SIMPLE SDD fabrications contains essentially 4 ingredients, listed in Table 1.

Samples of 100 g were prepared for each test. The gelatin (1.8 g) was mixed with water (7 g), melted by heating at 60 °C for 20 min and homogenized by gentle stirring to avoid incorporating air bubbles by cavitation. All the solutions were covered by a parafilm to avoid the evaporation of water.

The PVP (3.6 g) was mixed with water (~5 g), and the solution heated to 60 °C for 20 min and stirred. The additive was mixed with the remainder of the water, stirred and heated at 60 °C for 20 min. The three solutions were then blended together, and the solution agitated at 300 turns/min at 60 °C for 10 min. The glycerine (78 g instead of 78.6 g, due to the additives proportion) was then added step-by-step to the hot blend, and the gel solution left at 60 °C with agitation (300 turn/min) for 30 min. A reference sample (see Table 1) was prepared identically, without additives.

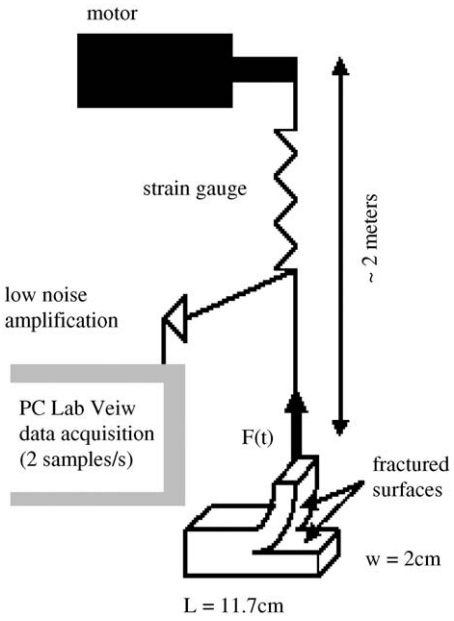

Fig. 5. CT set up, as described in the text.

Table 1
Proportions of each ingredients composing a standard SDD gel, without additives

Ingredients	Bi-distilled water	Gelatine	PVP ($[C_6H_9NO]_n$)	Glycerine ($C_3H_8O_3$)
Composition (% weight)	16	1.8	3.6	78.6

The final solution was placed inside a vacuum-dessicator for 30 min under a reduced pressure of 0.3 bar, to remove air bubbles trapped during the gelation process which might modify the fracture energy measurement. Once degassed, the solution was poured into an aluminium mould of 11.7 cm length (L), 2 cm width (w) and 2 cm height (h). A filter paper of the same dimensions as the mould was positioned on the gel top, and a plastic hook attached at one of the two extremities. The mould was refrigerated for around 14 h at 0–1 °C for the gelification process, then removed and left for 35 min at ambient room temperature for thermalisation (24 °C). Before measurement, a horizontal notch (4 mm of depth) was made at 2 mm from the top surface of the gel.

3. Results

A typical result of the CT test is shown in Fig. 6. The first spike is the necessary force for tearing off the higher part of the gel, which is drawn by the filter hook. The traction (F_{fract}) is constant with time so the linear rise following the spike is due to the progressive increase of the weight (P) of the pulled material (filter paper plus a thin film of gel), seen in Fig. 6 as the horizontal line at the measurement end, plus the fracture force contribution (F_{fract}):

$$F = F_{fract} + P. \tag{2}$$

The fracture energy is given by the work per fracture surface increase in units of $N\,m^{-1}$ [16,22] as

$$G_c = \frac{F_{fract}}{w}, \tag{3}$$

where w is the sample gel width.

The results for the various additives are displayed in Fig. 7. The gel became opaque for dextran, PEG, CMC and gum arabic, i.e. for long molecular chains, since the addition of a small molecule like glyoxal and dimethylurea does not alter the colour and the transparency of the samples. The additives having a long polymeric chain produced an opaque solution, except in the case of the agarose, which was translucent.

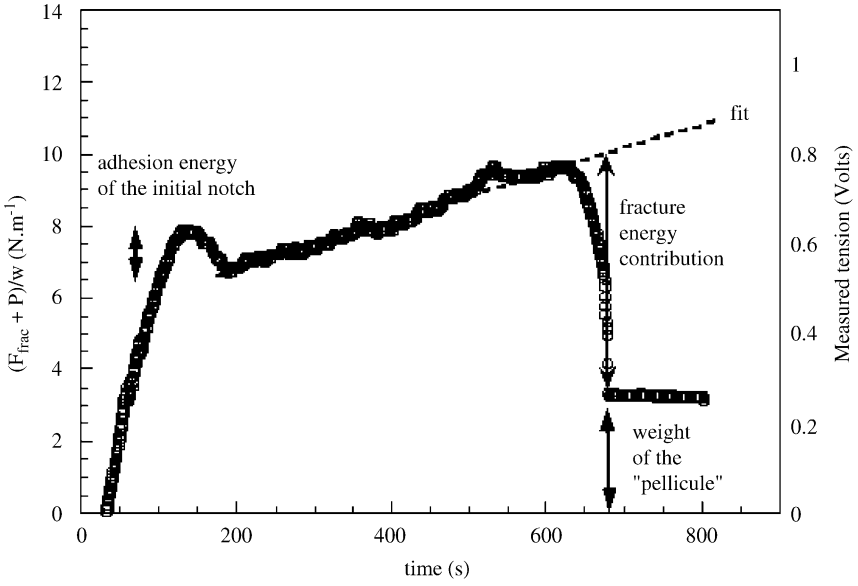

Fig. 6. Variation of the fracture energy with time during the crack front (8–9 min) at 24 °C. The equivalent voltage and fracture energy are represented on the two ordinates, obtained from calibration before and after each fracture measure.

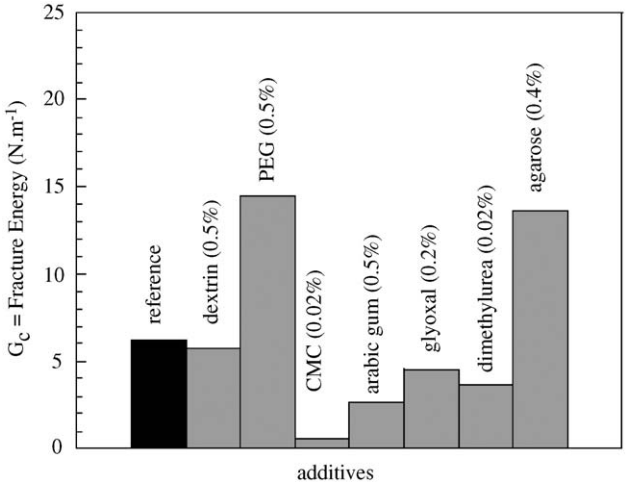

Fig. 7. Fracture energy for different additives. The reference sample is displayed on the left.

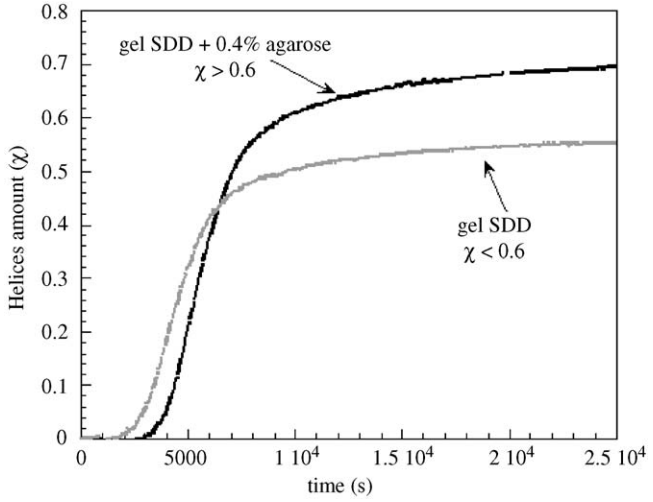

Fig. 8. Comparison of the helix amount for a SDD gel and a SDD gel + agarose, with increasing time; only the cooling and quenching steps are shown.

4. Discussion

From Fig. 7, two candidates are seen to have a G_c higher than the reference: PEG and agarose. PEG is excluded due to the opacity caused by the crystallisation of the glycerine [23] (the glycerine crystals inside the gel, surrounding all the superheated droplets, might break their metastability leading to spurious events) leaving agarose as the sole additive permitting an increase of the fracture energy.

The gelification agarose process is physical, i.e. there is no chemical bond for the cross-linking. The agarose is formed by a double helix (as DNA) during the gelification process, and has a specific rotation. These macromolecules are joined in small junctions, which are the association of a double helix formed after cooling (transition temperature sol–gel ~36 °C) and also stabilized by weak hydrogen bonding such as the gelatin.

Separate optical rotation measurements [19,20,23] made for a sample containing agarose are shown in Fig. 8 for only the cooling and quenching step. These confirm a high helix amount (χ), reaching 70% against 50% for the classic SDD gel, leading to a higher helix concentration $c_{hél}$ since $c_{hél} = \chi\ c_{gel}$ where c_{gel} is the gelatin concentration. These results, combined with the fracture energy, test indicate that the agarose is a potential additive for increasing the SDD lifetime by increasing the resistance to fracturing (= high fracture energy).

This is applicable to the creation of new SDDs based on other refrigerants (e.g. R-12, C_3F_8), for either dark matter searches (high fluorine content of these refrigerants) or dosimetry/spectrometry by using safe compounds like food products for the matrix gel. Indeed, to make a SDD, two materials are necessary: a matrix gel and a liquid refrigerant having a matching density. Fig. 9 shows that for all refrigerants having a liquid density between 1.2 and 1.3 g/cm^3 (R-115, R-12 and C_3F_8), a single gel will be necessary. For liquid refrigerants having a density between 1.4 and 1.5 g/cm^3 (C_4F_8, C_4F_{10},), a different gel will be necessary to match the density. For the case of all refrigerants having a liquid density between 1.2 and 1.3 g/cm^3, the SIMPLE SDD gel + agarose can be chosen to make the droplet suspension. This SIMPLE gel is a food gel and its manipulation is easy and safe. In fact, the manipulation of chemical gels, like acrylamide, needs specific precautions and its purification remains a major problem [2] for dark matter use; food products can in contrast be manipulated very easily.

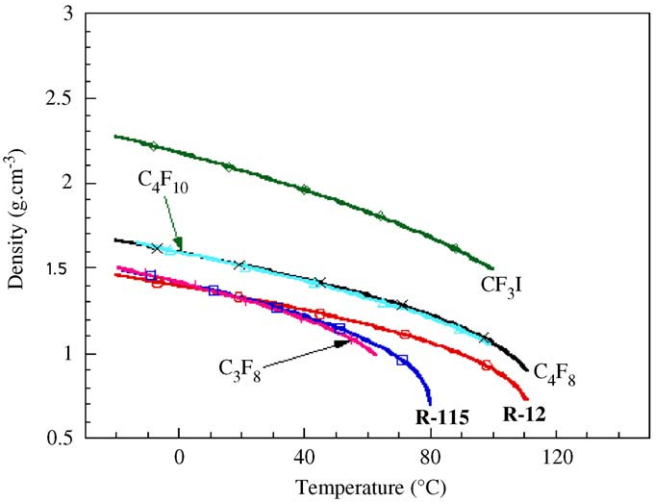

Fig. 9. Density variation of several refrigerants with temperature. The C_3F_8, R-15 and R-12 possess almost identical densities, which allows the same gel to be used in SDD fabrication.

Moreover, the optical rotation studies show that the sol–gel temperature transition of the SDD gel, with the addition of the agarose, is shifted toward higher temperatures. Calibrations are necessary to determine the response of the detector either for dark matter searches or dosimetry/spectrometry. Fig. 10 shows a simulation of the recoil energy of each nucleus by increasing the temperature for both R-12 and R-115, at 2 and 1 bar (insert in Fig. 10). For the case of the R-12, a problem appears at 2 bar: the inherent problem of the physical gel is that it becomes a solution after crossing the gel–sol temperature (~35 °C) leading to the sedimentation, with time, of all the superheated droplets because at this temperature the density of the droplet is slightly higher than the gel under the sol state. At 2 bar, for R-115 and detection of the recoil nucleus lower than 200 keV, the calibration can be made at lower temperature. For the R-12, the calibrations by increasing the temperature must be done at higher temperature. For a recoil energy of the nucleus (F, C and Cl) lower than 250 keV, by increasing the temperature, a gel without agarose will not allow detection of events up to 35 °C at 2 bars (see arrow in Fig. 10, showing the T_{sol} for a SDD gel), because the temperature

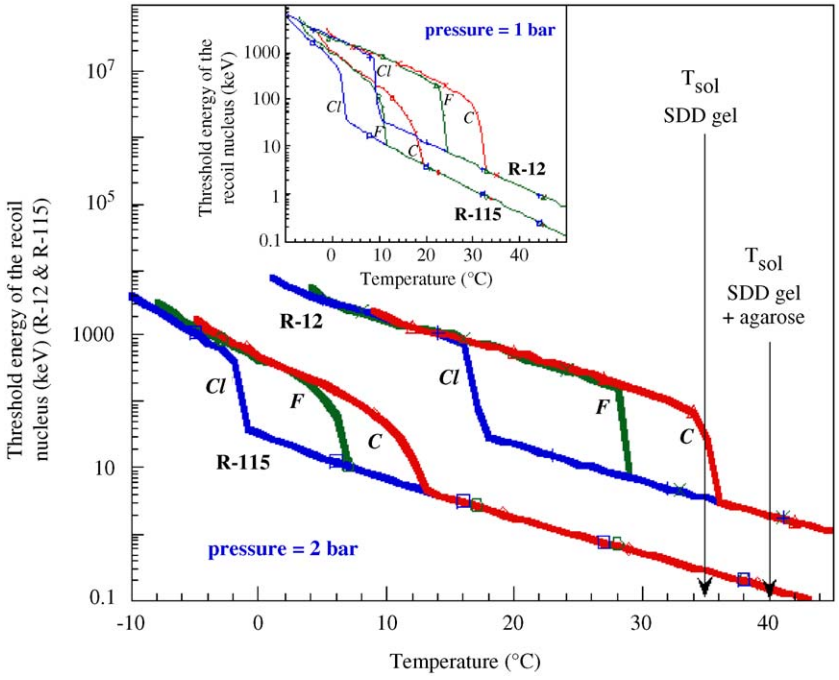

Fig. 10. Variation in threshold energy of the recoil nucleus with temperature for the R-12 & R-115 at 2 bar. At this pressure, the threshold energy of the fluorine and carbon reach the sol–gel (T_{sol}) transition of the matrix. Insert: the same curves at 1 bar.

equivalent to the threshold energy of each recoil nucleus (F and C) is shifted to near the sol–gel transition temperature at which the gel is liquid, as seen in Fig. 10; with agarose (the second arrow, showing the T_{sol} for a SDD gel + agarose), the phase transition of the gel–sol is shifted towards 40 °C.

5. Conclusions

We have investigated the influence of additives on the matrix itself in order to increase the lifetime by increasing the fracture energy via G_{cut} (by choosing polysaccharide additives). For a dark matter search, the choice leads us to the polysaccharide agarose. Moreover, the sample matrix gel + agarose gives an increase of the helix amount ($\chi > 0.6$), measured by optical rotation, leading to an increasing helix concentration. The fracture experiment shows that the fracture energy of the SIMPLE gel + agarose is twice higher than the SIMPLE gel without agarose, indicating a matrix twice resistant to fracture and hence a similar increase in the SIMPLE SDD lifetime.

With this new reinforced gel, it should be possible to fabricate easily and safely SDDs based on refrigerant liquids which possess the same density, such as R-12 and R-218 (C_3F_8). These refrigerants can be used as dark matter detectors due to the high fluorine content (in the spin-dependant channel).

The SDD gel is of interest because the purification protocol of food products like glycerine, gelatin or PVP (and agarose) is well-known in the food industry, whereas use of acrylamide gel necessitates the addition of heavy salts to give a heavier gel for matching the density with the refrigerant liquid, leading to a higher background event rate which becomes inherent to the chemical gel. While in dosimetry this has no consequences, it is critical in dark matter search applications.

The shift toward the higher temperature for the sol–gel temperature transition by adding the agarose is important for the application of R-12 devices, which have a higher recoil threshold energy for the fluorine and carbon at 2 bar than the R-115. This new resistant matrix, which gels at a higher temperature, would allow study of the response of the R-12 SDD at 2 bar.

Acknowledgements

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