1000 at 1000: the lightest bakelite and beyond

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Organic aerogels represent a unique category of carbon materials. They are the lightest solids in existence, not much denser than the air on a foggy morning. They may sound like next to nothing, but they certainly are stronger than they look. A piece of this material can withstand over 4000 times its own weight. Unlike any other porous materials, their composition, chemical properties and porosity can be built from scratch (like polymers can be made from smaller building blocks) to match practically any specific application through carefully controlling the synthesis conditions [1–3].

Highly efficient supercapacitors and catalysts are now obtained starting from these organic aerogels, and it was all possible thanks to a very humble material, not much different in chemical composition than the commonplace phenolic resin.

These aerogels did not stay in their box for long. As quick as a flash photograph or starting a car takes (on a materials development timeframe), they managed

to “glue themselves” (since phenolic resins are also adhesives) to their inorganic counterparts, creating new (sticky) bridges between the organic and the inorganic realms. Through combining the excellent toughness, flexibility and high surface area of organic aerogels with the thermal stability of inorganic aerogels, unique materials can be tailored.

The first aerogels (both inorganic and organic) were prepared since the early 1900s by T. Graham and S. Kistler (the latter coining the term “aerogel”). Organic aerogel-like materials were obtained through solvent exchange and supercritical drying of various polymeric gels (pectin, albumin, cellulose, agar, nitrocellulose, polystyrene and so forth) [2]. To be fair, however, since the starting polymer gels underwent significant collapsing and pore shrinkage in the solvent exchange step, they should be included in the category of xerogels by the current terminology.

This editorial is part of our series “1000 at 1000”, highlighting the Journal of Materials Science’s most highly cited publications as part of the journal’s celebration of 1000 issues. In this issue: “Organic aerogels from the polycondensation of resorcinol with formaldehyde” by Richard W. Pekala (then) of Lawrence Livermore National Laboratory from California, the U.S. [1].

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These wonderful materials never actually found their place in the world until the late 1980s. For nearly four decades since their first successful synthesis attempt, Kistler's statement that "apart from the scientific significance, the new physical properties developed in the materials are of unusual interest" held [2]. Even if various applications were envisaged over the years for aerogels, such as thermal and sound insulating panels, radiation detectors or sensors, the broad interest in these materials remained dormant. They were too difficult and expensive to obtain in large quantities. Until the early 1970s, the synthesis of aerogels in small batches (1–2 g) typically took more than two weeks to complete [3].

It was in this general context that the scientists at the Lawrence Livermore National Laboratory started to synthesize organic aerogels from phenolic resins in the mid-1980s. Pekala reported in 1989 the obtaining of a completely synthetic organic aerogel, through a sol–gel polycondensation process between resorcinol (R) and formaldehyde (F) in an aqueous environment, similar in principle to that of silica alcosols. The choice of the two primers was very inspired because the resulting resin was sufficiently rigid to avoid its pores collapsing under the force of surface tension.

The chemistry involved in the organic aerogels obtaining was the same as in obtaining well-known resins such as novolac or bakelite, except that the pH conditions are more rigorously controlled to allow the process to unfold through a sol–gel mechanism. Without pH control, the polycondensation is a non-sol–gel process that leads to uncontrolled porosity [4].

The monomers involved in the polycondensation reaction, resorcinol (R) and formaldehyde (F) were allowed to react for 30 h at 90 °C when a low molecular weight resole (polyhydroxymethylated resorcinol) is formed. This resole was subsequently allowed to cure for a week, a period during which cross-linked sol particles (RF clusters with diameters of 7 to 10 nm) were allowed to grow and aggregate into a gel-like structure (Fig. 1). The way sol clusters form and aggregate (like some tangled bead garlands) is essential because it dictates the pore structure of the final aerogel material.

A final three-day inter-cluster cross-linking step in acidic medium was further employed to increase the mechanical resistance of the resulting thermosetting gel. Finally, the solvent was eliminated in three steps: exchanging the water in the swollen gel for acetone

(for four days), acetone replacing by supercritical carbon dioxide (for three days) followed by drying at ambient pressure.

The resorcinol–formaldehyde (RF) aerogels were transparent, dark red-coloured, with densities and specific surface areas ranging from 0.03 to 0.079 g/cm³, respectively, 717 to 513 m²/g, as a function of the reaction media pH and R:F molar ratios [1]. Compared to their inorganic silica counterparts, the RF aerogels were more lightweight, flexible (like a synthetic elastomer) and more accessible to machine.

Due to their red hue, which deepened over time (some phenolic rings get oxidized into yellowish-red chromophoric quinoids), the RF aerogels were less appealing at that time as thermal insulators for windows or passive solar collectors [5]. Pekala stated that other phenols such as catechol and phloroglucinol could be used instead of resorcinol to obtain non-coloured organic aerogels with similar properties [1, 5].

The impact of the newly reported RF aerogels on materials science was so profound that starting with the publishing of Pekala's work, these *RF aerogels* have become synonymous in many instances with *organic aerogels*, even if nowadays, almost any pre-swollen polymer gel can be used to obtain organic aerogels ("if it swells, it (aero)gels") provided that the drying conditions are appropriate.

How did this particular finding reported in *J Mater Sci* have an impact on the knowledge in its domain? Did it lead to the development of new ideas and materials? One evident approach in answering these questions is to look at the variation in the number of citations that Pekala's paper received from 1990 up to date (Fig. 2a), data obtained from Clarivate Analytics Web of Science.

It can be seen that the organic aerogels synthesis route that Pekala proposed did not have an immediate impact, but had a slow onset of citations for a decade since its publishing (from two citations in 1990 to 15 in 1998). This behaviour is not uncommon: many published papers from the age of print have this slow onset in the beginning. What is particularly interesting in the case of this paper is the relatively long time it took from its publishing until it could see a steady exponential increase in its number of citations (starting from 2000), compared to more recent high-impact papers from *J Mater Sci*.

An analysis of the number of papers on the "aerogels" topic (data retrieved from Clarivate

Figure 1 Synthesis steps in the formation of the resole-formaldehyde gel.

Figure 2 **a**: Variation in the number of citations for Pekala's paper on organic aerogels [1] and **b** cumulative number of articles published in the domain of aerogels and organic aerogels

(Clarivate Analytics Web of Science database, search date: 20.04.2020. For **b** search terms: "aerogels"; "organic aerogels").

Analytics Web of Science) has revealed an inflection point in 2000, following the same slow onset as the citations from Pekala's *J Mater Sci* paper (Fig. 2b). This particular dynamic could be due to the lower practical interest of the scientific community for the

research field of aerogels. Anecdotally, the February 1993 issue of the magazine *Popular Science* featured the materials, stating that "a new class of materials that are the lightest solids known could be used for everything from silencing submarines to insulating

refrigerators. Some of them are even 90% effective against cockroaches" [6]. The material is not toxic but can stick to the insect's body and dehydrate it through capillarity.

An article from the middle of the decade following publication stated that aerogels (especially the newly reported organic ones) could serve as enabling material in many new applications (e.g. energy storage, gas filtration, catalyst supports, thermal insulators), but are uncompetitive over activated carbons, carbon blacks or polymer foams in terms of cost (a piece of aerogel the size of an average brick cost more than 1000\$), production time (typically more than a few days) and safety (several occupational accidents occurred in the early 1990s from working with solvents in supercritical conditions) [7].

In four years from its publishing, Pekala's report gathered only 17 citations, mostly papers from the group working at the Lawrence Livermore National Laboratory and few other independent research groups. During this period, intensive research was undergone to study the properties of organic aerogels in comparison with their inorganic counterparts. It was established that organic RF aerogels present lower densities and thermal conductivities than silica aerogels obtained under similar pH conditions and precursor ratios.

Interestingly, only a few months after the first organic aerogel synthesis report, a new type of material was reported: the carbon aerogel. This material could be obtained through the controlled pyrolysis (400 to 1800 °C) of the RF aerogels or other organic aerogels [8].

Carbon aerogels are unique materials because they not only have surface areas ranging from about 500 to 2500 m²/g (even higher than activated carbons), but they are also electrically conductive. The electrical conductivity of carbon aerogels is density dependent, so it is linked to its RF aerogel precursor's structure [8]. The advent of these materials enabled the mass production of miniature-sized supercapacitors in the late 1990s (or "aerocapacitors", as Pekala named them) with capacitances of 50 to 100 F. That is more than 500% improvement in capacitance, compared to the devices available at the beginning of the 1990s, or as an analogy, it is like buying a new 300-horsepower car, only to find out that days later a 1500-horsepower version is available but much cheaper!

By activating carbon aerogels with CO₂ or concentrated alkali solutions, these materials can reach a

whopping 3300 m²/g surface areas and specific capacitances of 250 F/g [9].

It was practically due to these carbon aerogels that Pekala's paper saw a revival starting with 2000. Since this year, the number of citations increased steadily, a trend that has maintained to date. Nearly 70% of the citations that Pekala's paper attracted in the 2000–2020 period report on synthesis procedures and applications for organic aerogels.

Also, in 2000, the synthesis of the first "true" hybrid organic–inorganic aerogel composites was reported, through co-polycondensation of resorcinol, formaldehyde and surfactant-stabilized silica sol particles. The term "true" is emphasized here, implying that this hybrid material was obtained entirely from small-molecular organic and inorganic building blocks, not through pressure impregnation of a pre-existent inorganic aerogel with a polymer.

Organic aerogels present another exciting feature: unlike activated carbons and metal–organic frameworks (MOFs), their pore network is highly available even to their narrowest pores [4, 8].

It came only naturally that in 2000 and in the following years, organic aerogels served to obtain the first metal–organic framework (MOF) aerogel structures. Another research direction opened up this year was directed to the environmental remediation of wastewaters containing industrial dyes with activated pyrolyzed RF aerogels [8, 10].

Since the polycondensation of R and F occurs in an aqueous environment, various water-soluble additives can be added to the reaction mixture, enabling the incorporation of heteroatoms in the organic aerogel's framework. Organic and carbon aerogels with controlled microporosity were reported to be obtained by doping Ce or Zr into the resorcinol–formaldehyde reaction mixture (while the un-doped aerogels are usually mesoporous). Following a similar approach, graphitized glassy aerogels were obtained in the presence of Cr, Fe, Co and Ni [11].

The interest sparked by the vast application potential of carbon aerogels was also focused on improving Pekala's original recipe. Lighter aerogels were obtained by supercritical methanol drying combined with freeze-drying, and the obtaining duration was reduced from more than one week to one day when using acetone as solvent instead of water.

Over the years, various cost-efficient hydroxyl compounds (cresol, tannins, lignin, furfuryl alcohol,

poly(vinyl alcohol), polysaccharides) and carbonyl compounds (furfural, melamine, dialdehydes) were used as building blocks for organic and carbon aerogels [10, 12].

Pekala's materials could be tuned to present fractal structures and bimodal pore size distributions (micro- and macropores), by switching water for acetone and sodium carbonate for perchloric acid. This feature is difficult to achieve in other synthetic organic materials [13] and allows for their more efficient use as catalysts.

Starting from Pekala's core concept, new "flavours" of organic and carbon aerogels emerged, as well as new application domains. Interestingly, the inflection points of the cumulative citation dependency variation revealed by the first derivative curve (Fig. 2a) coincide with the years in which these materials were first reported (2005, 2008 and 2012).

At nearly 15 years since their first report, the carbon aerogels "went nano". That is much faster than for any other type of material! The year 2005 signalled the first successful attempt in obtaining a nanocomposite aerogel material. Carbon nanotubes were grown by chemical vapour deposition (CVD) directly inside the pores and on the surface of a Ni- and Fe-doped carbon aerogel [14].

Even further, in 2012 (and developed the next years), through controlled pyrolysis and activation of chitosan and poly(vinyl alcohol)-based organic gels, carbon aerogels entirely consisting of a graphene or carbon nanotube honeycomb matrix were successfully obtained [15].

On the subject of nanocarbons and carbon allotropes, the transformation from an amorphous to a crystalline phase in carbon aerogel materials has remained a challenge until 2011, when the high-pressure, high-temperature synthesis of a polycrystalline nanodiamond aerogel from a RF precursor was first reported [16].

In 2008, a modified aerogel was used for hydrogen chemisorption and storage applications, and in 2012, a high-ionic conductivity thin-film RF organic aerogel was reported [12].

Interestingly, it seems that the cumulative number of papers on organic aerogels in the 1992–2020 period (Fig. 2b) matches the cumulative number of citations for Pekala's *J Mater Sci* paper for the same period closely. This trend could imply that practically the majority of the studies on organic aerogels and related materials recognize the importance of the original

idea contained in Pekala's work and that this study had a profound influence on all future research in this domain.

So, the question that remains is: will the impact of Pekala's paper from *J Mater Sci* still echo in future research? If the Crossref data of Kistler's reference paper on silica aerogels from 1931 [2] are taken into the analysis, it could be observed that since 2018 the number of yearly citations has followed a downward trend. Considering that practically Kistler's method has been rendered obsolete since the 1970s, this paper currently presents an impact from a historical point of view.

If one analyses the trend in the cumulative citations for Pekala's paper until 2019, it could be seen that the cumulative citation trend could be modelled by a logistic power fitting model (coefficient of determination, $R^2 = 0.999$). If this model is to be considered, the number of citations will continue to steadily increase at least 50 years from now, which accounts for over 80 years since the paper's publishing date, in a similar trend to Kistler's. Can this model be accurate, that is, will Pekala's article from *J Mat Sci* still have a significant influence in shaping the research in the domain of aerogels in the near future? The answer will be most probably "yes" if one looks at the recent papers that cite it in the last two years.

In 2019 and 2020, research was focused on templating the porosity of doped and un-doped resorcinol-formaldehyde aerogels by using biopolymers, deep eutectic solvents and ionic liquids for energy conversion, catalysis and CO₂ sequestering applications. Various surface activation procedures were studied to tune the batch adsorption capability of RF aerogels towards typical water pollutants (heavy metal ions, dyes). Bio-sourced phenols (tannins) were researched as alternatives for resorcinol, and alternative ambient pressure-dried flexible RF aerogels are synthesized through modifications of the traditional sol-gel synthesis route. These continuing research directions continue to build on the core Pekala's original idea published in *J Mater Sci* and stem new research directions that shape the domain of materials science on their own.

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