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Parametric study of factors affecting melamine-resorcinol-formaldehyde xerogels properties.

Ivan A. Principe and Ashleigh J. Fletcher

Department of Chemical and Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK.

Highlights

- Systematic study of three main synthesis variables: R/C, R/F and melamine content.
- Successful incorporation of nitrogen onto resorcinol-formaldehyde xerogels.
- Optimum R/F ratios determined as 0.25 and 0.5.
- Increasing R/C ratios, decreases surface area, pore volume and microporosity.
- Increasing melamine concentration has same effect as increasing R/C ratio.

Abstract

Resorcinol-formaldehyde (RF) xerogels are organic materials have been widely studied due to their industrially relevant characteristics, through which, RF gels have significant potential to be tailored to specific applications. Xerogel properties have been tailored, within this study, by altering the synthesis procedure with a focus on monomer concentrations, catalyst to monomer ratio, and the introduction of a nitrogen-rich precursor, thereby incorporating nitrogen into the structure to additionally affect the chemical properties of the final gel. Melamine (M) is used as the source of nitrogen, partially replacing the resorcinol (R) typically used, and resulting in a melamine-resorcinol-formaldehyde (MRF) gel; synthesis was facilitated by a sodium carbonate catalyst (C), as often used in RF gel production. R/C and R/F molar ratios, and M concentration ([M]), were chosen as parameters to study in-depth, as they have previously been shown to markedly influence sol-gel formation. The MRF gels produced were subsequently characterized to determine porous structure and chemical functionality. The results indicate that, texturally, increasing [M] produces a similar effect as increasing R/C values: increasing pore size, while decreasing surface area. Pore volume tends to increase when R/C or M increase individually but pore volume and surface area decrease drastically when both variables increase concurrently. Microporosity also tends to increase as R/C decreases, and as the concentration of M is decreased. Altering the gel matrix, by replacing M for R, results in a weakening of the gel structure, as the bridges formed during curing are reduced in quantity, which indicates a maximum level of substitution that can occur within these materials. Combined, these results suggest that nitrogen can be successfully incorporated into organic gel structures but that the interplay between process variables is crucial in determining final gel characteristics for specific applications.

Keywords

Catalyst; FTIR; surface area; pore size; microporosity.

1. Introduction

The design of materials for applications such as carbon capture, solid sorbents, catalyst supports, membranes and hydrogen storage require the control and capability of tuning the porous structure of such systems, including surface area, pore size and distribution, microporosity, and pore volume. Such materials may be formed from gels, including Resorcinol- Formaldehyde (RF) resins, which are a type of organic material that have attracted attention due to their potential application in many processes, such as, catalysis, thermal insulation, carbon capture, filtration, energy storage and as precursor of electrically conducting carbon materials. RF gels, generally, exhibit a high pore volume, low density, large surface area and an amorphous structure. These parameters can be controlled and tailored as a function of the synthesis procedure [1], thereby making RF gels very attractive for a number of applications. Several factors, such as solvent, temperature, chemical reaction, time, catalyst (C), and agitation, influence sol-gel chemistry, however, base catalysed synthesis is most affected by the concentration of monomers and catalyst, and the initial pH of the sol.

Primary studies produced RF gel by polymerization of R and F, using sodium carbonate as catalyst (C) [2-4], while several other researchers studied the analogous production of aerogels from phenol (P) and F [5, 6] in PF gel synthesis. Methylene ether (-CH₂OCH₂-) or methylenes (-CH₂-) are the two main typical groups bonding the aromatic moieties in the synthesis of phenolic resins. Similarly, for RF gels, the linkages of the different aromatic groups are facilitated by the presence of the aforementioned groups. The concentration of those groups depends on a number of parameters, such as pH, catalyst and monomer concentration. RF gels can be synthesized under either basic or acid conditions and R reacts with F, via a similar route as P does. However, the ability of R to crosslink, forming clusters, is higher than for P because R can bond up to three F groups; with these additions producing mainly ether bridges.

The RF reaction generally occurs in aqueous system at room temperature, the reaction of R and F is favoured, however, it is very slow. For this reason, a catalyst is typically added to accelerate the rate of reaction, where it is consumed and not recoverable after the reaction. For basic catalysis, sodium carbonate is most commonly used as C, which is representative of Group I species (Li, Na, K and Cs) [7]. For gels synthesised under basic conditions, gelation is slow and requires a high temperature. Instead, for gels created under acidic conditions, gelation occurs at room temperature and is faster, often only a few hours [8]. The catalyst used in acidic synthesis is usually acetic, perchloric or hydrochloric acid. Base-catalysed gelation was used exclusively throughout this study, for several reasons, including the fact that acid catalysed gel often exhibit reduced porosity (higher density), which is an important parameter in gas treatment [9]; also industrially, it is usual to avoid the use of acids to reduce risks, and associated costs. RF gel formation has been well studied [10, 11]; as mentioned above, in a basic environment, R is deprotonated to its anionic form and the increased electron density at the 4 or 6 position enhances attachment of a -CH₂OH group [10]. The addition of one molecule of F results in hydroxymethylation, activating a second position to add another -CH₂OH group, giving rise to the dihydroxymethyl (8). Subsequently, the basic catalyst allows formation of the o-quinone intermediate due to deprotonation of hydroxymethylated R to form a methylene bridge (-CH₂-) with another R molecule, via condensation reaction, which results in the formation of nanometre-sized clusters that undergo crosslinking within the structure to form the final gel [12]. In any sol-gel process, the formation and growth of clusters is influenced by typical sol-

gel parameters such as solution pH, temperature and monomer concentration [3, 13], as outlined below.

Initial sol pH: It is generally understood that increasing pH increases surface area [2, 14-16]. For higher values of pH, the formation of hydroxymethyl derivatives of resorcinol is favoured, producing highly branched clusters. This leads to more unstable structures, which produce a larger number of particles and smaller interconnections between them [10]. In contrast, when the pH is lower the effect is reversed. Thus, the formation of resorcinol anion is less favoured which, as a consequence, leads to fewer branched structures, therefore polymerization would take longer and the particles formed would be larger. Consequently, the nucleation regime controls the size of the pores and voids in between the particles of the polymer, thus controlling the mesoporosity of the gel; therefore, lower pH tends to produce larger pore sizes, while higher pH favours crosslinking of the gel, reducing the pore size [15].

Resorcinol–Formaldehyde (R/F) molar ratio: The stoichiometric ratio for R/F is typically set at 1:2. However, the relative quantities can be varied to affect the degree of crosslinking, hence, the density and structure of the final gel.

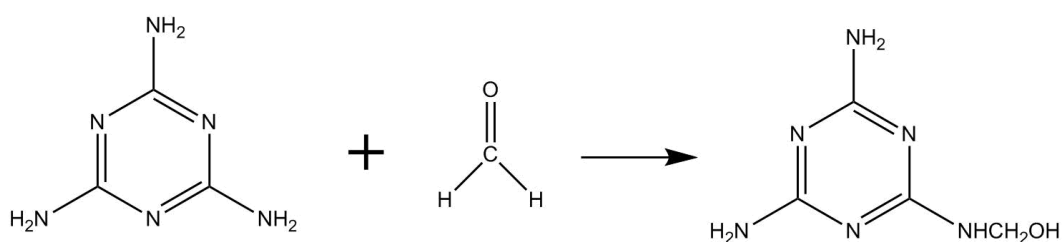
Resorcinol – Catalyst (R/C) molar ratio: The R/C ratio is one of the most important factors dominating gel physical properties. Low R/C values (high catalyst content) lead to the formation of small particles, creating microporosity, while high R/C values (low catalyst content) result in mesoporosity. During the polycondensation reaction between R and F, highly cross-linked particles are formed. The R/C ratio is the main parameter controlling the size of interconnected particles and, consequently, the final pore size [11]. R/C ratio has a direct impact on density, surface area, and mechanical strength of R-F materials. Previous work indicate that using lower R/C values, i.e. higher catalyst content, results in gels with smaller particles (3 – 5 nm diameter) and large neck size (fibrous appearance). On the other hand, higher R/C ratio (lower catalyst content) leads to larger particle sizes (11 – 14 nm) and a ‘string of pearls’ morphology [4, 11]. In general, as R/C ratio decreases so too does pore diameter, while density is increased [4, 17]. This structural difference is related to shrinkage of the gel during the drying stage. For instance, colloidal gels incur little shrinkage during supercritical drying, which affords them with lower monolayer surface areas and weaker structures than polymeric gels [10], which benefit from densification of the gel skeleton. The different shrinkage rates also impact the density of RF gels, for instance, at constant R/F ratio, decreasing R/C ratio increases the density [18]. Despite this, a comparison of gels with similar densities showed that polymeric gels (R/C = 50) were three times stiffer than colloidal material (R/C = 200), demonstrating the impact of neck particles on final mechanical properties [10]. Additionally, other authors have shown that R/C ratio is also the most influencing parameter controlling the surface area, pore volume and mechanical properties [1]. Mirzaeian *et al.* showed, that for the same RF gel system, increasing R/C ratio leads to an increase in the volume of N₂ adsorbed [1]. Additionally, Yamamoto *et al.* showed that the pore size distribution increases with increasing R/C ratio for a constant ratio of R to water (W) [17].

Catalyst (C): The term catalyst is a misnomer as the role of these species is thought to be one of transition state stabilisation; however, convention of the field means such species are labelled catalyst. The catalyst plays a key role in gel formation, altering gelation time and the physical characteristics of the gel. While the anion is thought to alter the pH to the region for reaction to

proceed, the metal ion is integral in cluster crosslinking. A comparison of group I catalysts showed that Li, Na, K have similar abilities to stabilize RF colloidal suspensions, by destabilizing the oligomers, thereby increasing their solubility and leading to small clusters [7]. By contrast, Cs is less able to stabilize colloidal suspensions, hence oligomers becomes less soluble, which leads to larger clusters, while the use of ammonium carbonate has been shown to prevent cluster crosslinking resulting in a powdered material [7]. This means that gels produced with Li, Na or K as catalyst could be applied to gas phase separations, while gels created using Cs as catalyst are better suited to aqueous phase processes.

Total solid content: Increasing solids content means less solvent in the mix, therefore, the density of the final RF gel is increased, as observed by Fairen-Jimenez *et al.* [19]. Increasing density leads to smaller pore sizes due to the increase in reactant quantity for a given volume [13], which also influences the pore size distribution where high solids content results in monodisperse pores, while low solid content exhibits a heterogeneous polydisperse porosity [11].

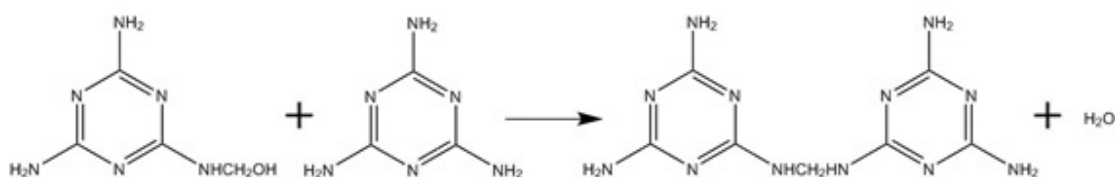
M has previously been used to incorporate nitrogen into RF gels by substituting R, in order to provide chemical moieties useful for applications including carbon capture. M and F undergo a reaction similar to R and F, with the production of stable polymeric resins, which indeed have a very similar synthesis procedure and chemistry compared to phenolic resins [20]. The reaction of M and F produces six possible products, of which the most stable is the hexamethylolmelamine [21]. Hoodgind *et al.* stated that this compound can be produced in two ways, either by heating M with an excess of neutral F at 90 °C or by allowing M to react with F at room temperature for a prolonged period of time (15 to 18 h) [21]. The first of those options is similar to the conditions used in this research. MF gel production, and the properties of the resulting materials, is controlled by the same parameters as for RF gels, i.e. ratio of monomers, catalyst, time of reaction and temperature [21, 22]. The MF reaction can be divided into two stages: formation of methylolmelamines (Scheme 1) and condensation (Scheme 2). F in the solution reacts with dissolved M, but M has a low solubility at room temperature in water (0.5 g/100 mL at 298 K and 5 g/100 mL at 373 K); hence, the methylolmelamine formed as a result of that reaction is more soluble than M, so the solution rapidly changes from a suspension to a clear solution.



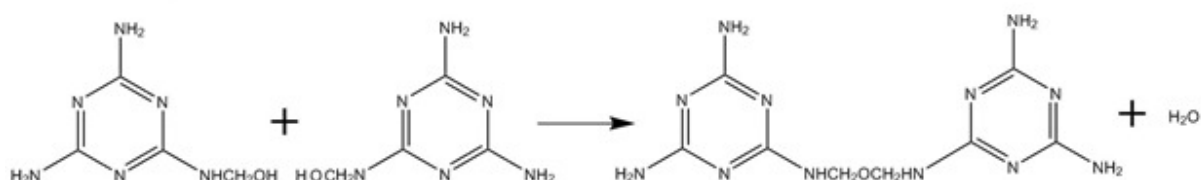
Scheme 1: Formation of methylolmelamines via reaction of melamine and formaldehyde

Crosslinking of methylolmelamines cluster happens by two types of linkages: ether or methylene bridges [22], dependent on solution pH. At low pH (7 – 8) methylene bridges are favoured, while at $\text{pH} \geq 9$ ether bridges are predominant [23], see Scheme 2.

pH = 7 - 8 Methylene Bridge favoured



pH \geq 9 Ether Bridge favoured



Scheme 2: Methylene and ether bridge formation depending on the solution pH during reaction of melamine and formaldehyde.

Zhou *et al.* showed that both systems described above, RF and MF, can produce large polymer microspheres under hydrothermal conditions, even without catalyst [20], and condensation of MF into an RF system can produce a homogeneous MRF microsphere network. The crosslinking reaction between MF and RF microspheres would be facilitated by methylene and ether bridges of hydroxymethyl groups, forming small clusters, which in turn act as nucleation sites trapping inside sufficient unreacted particles to continue the reaction and consequently grow clusters. This process is comparable with the Stöber process, where nucleation is fast before clusters formation, without the need of new nucleation sites [24, 25].

Melamine content (M) is less well studied than other process variables, however, previous work shows that increasing M/R ratio decreases particle size significantly [20]. Given its basic character, increasing [M] should accelerate the polymerization reaction between R and F, thereby increasing crosslinking density and the molecular weight of polymers. However, the steric hindrance observed for larger chain structures increases their incompatibility with water, which, in turn, increases nucleation rates but decreases the time for cluster growth; overall, increasing [M] results in smaller microspheres [23].

The RF gels discussed here can be applied to a variety of applications, for example gas/liquid purification, insulation or as catalyst supports, but this is highly dependent on their final properties. Controlled variation of the parameters discussed above allows a range of gel materials to be created, each with a specific combination of textural and chemical character; this latter property can be further altered by the inclusion of modifying chemicals, such as melamine. In this study, we focus on the interplay between the parameters outlined above and the effect of substituting resorcinol by melamine in the synthetic matrix; the results of which will provide a basis for materials tailoring for specific applications.

2. Experimental

Materials and Synthesis. Resorcinol (ReagentPlus, 99%), aqueous formaldehyde solution (37 wt% F, stabilized with 10 – 15 % methanol, pH 2.8 – 4.0), sodium carbonate (anhydrous, \geq 99.5%), melamine (99%) and acetone (ACS reagent, \geq 99.5%) were all purchased from Sigma-Aldrich.

Compositions of MRF solutions were calculated using the molar ratios of R/F and R/C, sodium carbonate was used as catalyst for all samples. Solution volume was fixed at 30 mL and total solid content (i.e. R, M, F and carbonate) was fixed at 20% w/v, which corresponds to a solid content of 6 g. The chosen parameters of study, R/C, R/F and [M], were varied as shown in Table 1. Note that [M] refers to the percentage of resorcinol substituted by melamine, therefore R/F denotes (R+M)/F, but for simplification it will subsequently be named R/F. The total number of gels produced is 100, which includes four gels produced using R/F = 1 ([M] = 100 and R=0), for the four R/C levels stated, resulting in MF gels (see Table SI 1 – 4). This allows comparison of MF gels as the direct opposite of MRFO gels (RF).

Table 1: Melamine-Resorcinol-Formaldehyde synthesis variables studied in this work (Resorcinol/Catalyst ratio, Resorcinol/Formaldehyde ratio and melamine content) and levels selected for each.

R/C	50	100	200	400		
R/F	0.25	0.5	0.75	1.0		
[M] %	0	1	10	20	30	40

For each chosen R/C, R/F and [M], the required M was weighed out and placed in a sealable 500 mL jar with 25 mL of deionized water, produced in house (Millipore Elix 5 system). The M solution was heated up to ≈ 323 K and stirred magnetically until completely dissolved. Then, the required R and carbonate were weighed out and added to the solution while it was continuously stirred, until completely dissolved. The required volume of F solution was added to the jar, together with the additional water make the volume up to 30 mL, the jar was sealed and stirred for 30 min. Once the stirring period was complete, the pH of the solution was recorded using a Hanna pH 20 meter, fitted with an H1-1110B pH electrode, before sealing the jar and placing it in a pre-heated oven at 358 ± 5 K, as used in previous works [3]. The solution was left to gel for 3 d. Upon gelation, water contained within the pores of the network was removed through solvent exchange. The cured gel and 90 mL of acetone were shaken for 3 d at room temperature. The wet gel, after solvent exchange, was placed in a vacuum oven at a temperature of 363 K in order to remove any remaining solvent from the gel pores.

Xerogel Characterization. A Micromeritics ASAP 2420 system was used to obtain surface area and porosity by nitrogen adsorption/desorption equilibrium measurements at 77 K, using ~ 0.5 g sample. The sample was first degassed, at 393 K for 120 min, before testing the nitrogen adsorption capacity. Surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) theory [26] combined with Rouquerol correction for BET application to microporous materials [27]. Pore volume was calculated from the equilibrium measurement of nitrogen adsorbed at ~ 0.98 bar (i.e. the saturation vaporous pressure of N_2 at 77K). The pore size distribution and average pore size were obtained by application of the Barret-Joyner-Halenda (BJH) method [28], while the t-plot method [29] was used to calculate the micropore volume and micropore surface area of samples. Elemental analysis was used to quantify the concentration of carbon, nitrogen and hydrogen. CHN analyses were performed using a Perkin Elmer 2400 Series II CHNS Analyser. Results were obtained as percentage weight, and were measured as a function of thermal conductivity; sample sizes were ~ 1 -2mg of xerogel. All samples were analysed by Fourier transform infrared spectroscopy (FTIR) for surface moiety characterization. Xerogel samples were fully ground prior to FTIR analysis using a pestle and mortar assembly to obtain a homogeneous particle size.

3. Results and Discussion

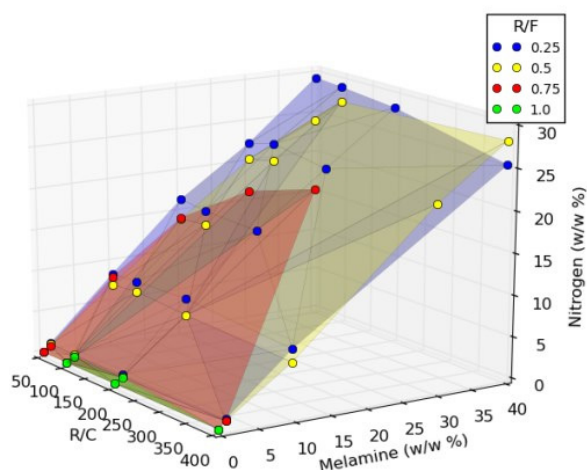


Figure 1: Nitrogen contents for Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 50-400; Resorcinol/Formaldehyde ratio of 0.25-1 for melamine content of 0-40 w/w%.

Textural and chemical properties were determined for all 100 gels produced from the possible synthetic parameter combinations used in this study. Results obtained for CHN analysis were as expected (see Figure SI 1). Due to their chemical compositions, both R and M contribute to the total carbon content of each sample but the relative contributions vary due to their individual carbon proportions (carbon contents of 65.5% and 28.6%, respectively). Therefore, as R is substituted by M, the C content decreases, while N comes only from M, therefore, N content increases linearly with [M] [20], as can be seen in Figure 1. Similar results were observed for all series of MRF xerogels studied (see Supporting Information) and the trend of %N with [M] is shown for an example suite of materials in Figure 2. H content is not significantly different for R and M, only a small decrease is observed as M substitutes R and these results are confirmed by CHN analysis for all samples produced in this study. Of these combinations 36 systems failed to produce a viable gel material, hence, the results presented are for the 60 gel combinations that were successfully synthesised (see Supporting Information).

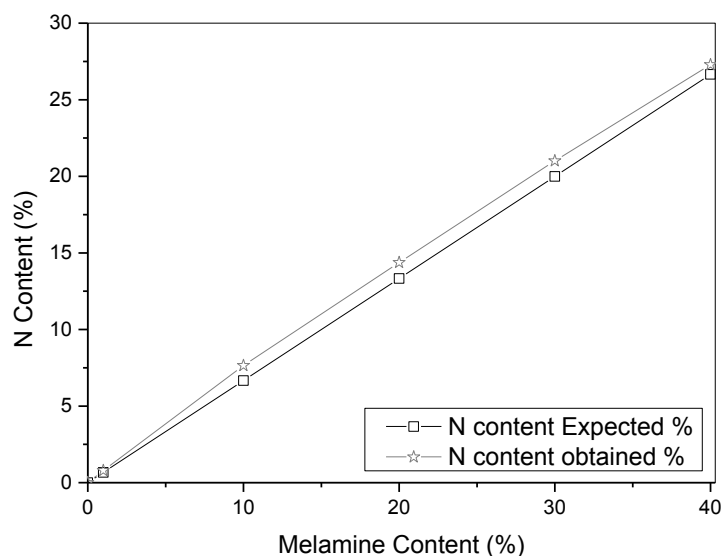


Figure 2: Nitrogen contents for Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 100; Resorcinol/Formaldehyde ratio of 0.5 for melamine content of 0-40 w/w%.

FTIR analysis was used to gain information regarding surface functionalisation of the synthesised gels as FTIR spectroscopy has been routinely applied to probe the chemical structure of carbon materials [30]. In this work, the effect of altering R/C, R/F and [M] on surface group development was examined. The suite of MRF materials were analysed by FTIR; Figure 3 shows a selected group where [M] is increased at constant R/C (50) and R/F (0.50). Comparison of O-H bond peak (3200-3500 cm^{-1} [31]) depth relative to other peaks across the spectra gives an indication of the concentration of the species. For example, it can be seen that as [M] increases, the proportionality of the peaks in the fingerprint region compared to the O-H peak increases considerably. This suggests that the concentration of O-H groups in MRF40 is lower compared to the concentration of the structural bonds (observed in the fingerprint region) than for the MRF0 sample, for which, the intensities of the O-H peak and fingerprint region are very similar, suggesting as many O-H bonds as C-O or C-H structural groups. Therefore, it can be concluded that an increase in [M] results in fewer OH⁻ bonds, from phenolic groups, in the final solid. It is worth noting that for pure RF gels, or gels with lower concentrations of M (up to 10%), the O-H peak is wider than for materials with higher [M]. This indicates that, due to the higher concentration of O-H groups, the electrostatic interactions to surrounding hydrogen atoms become more important and these vibrations occur at wavenumbers close to the O-H bond, but sufficiently shifted to result in a wider peak (Figure 4). Conversely, increasing [M] reduces the concentration of O-H groups, therefore, the interactions between them weakens resulting in a narrower peak (Figure 4).

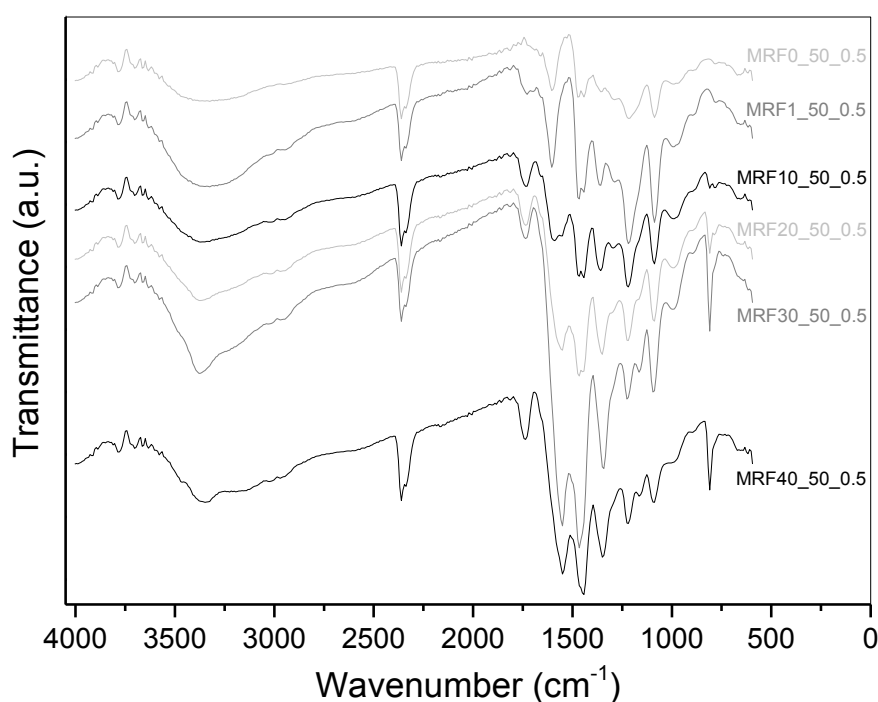


Figure 3: FTIR spectra of varying melamine content of 0-40 w/w% for a constant Resorcinol/Catalyst ratio of 50 and Resorcinol/Formaldehyde ratio of 0.5.

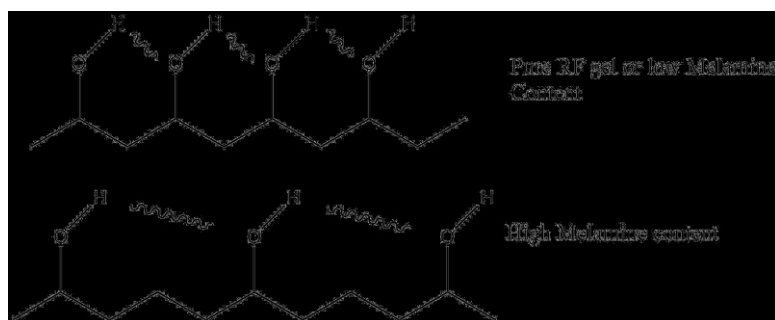


Figure 4: Schematic of hydrogen interactions with OH groups at low (high resorcinol) and high (low resorcinol) melamine content.

As detailed above, the peak at $3550\text{-}3200\text{ cm}^{-1}$ corresponds to strong O-H bonding, related to R concentration and intermolecular O-H bonds, while O-H bending ($1410\text{-}1260\text{ cm}^{-1}$ (s)) and C-OH stretching ($1150\text{-}1040\text{ cm}^{-1}$ (s)) can be observed in the fingerprint region [31]. The O-H stretch can mask weaker -NH_2 or =NH stretching vibrations ($3500\text{-}3300\text{ cm}^{-1}$ (m)); these groups also absorb around 2360 cm^{-1} but, as this peak is also present for MRF0, which has no nitrogen content, it is more likely to correspond to CO_2 which vibrates at 2349 cm^{-1} , with a stronger intensity [31]. While the peak at 1743 cm^{-1} could be ascribed to carbonyl functionalities, this peak is not present in MRF0 and its intensity increases as nitrogen content is increased. This suggests that the peak more likely results from imide functionalities (1697 cm^{-1}), formed by nitrogen bonding to two acyl groups via combination with F [31]. Conjugated C=O bonds appear at $\sim 1640\text{-}1595\text{ cm}^{-1}$, and C-H stretching of saturated bonds ($1470\text{-}1430\text{ cm}^{-1}$), can be related to methylene bridge formation (Scheme 2) [31]. Additional peaks in the fingerprint region can be ascribed to C-O ($1300\text{-}1020\text{ cm}^{-1}$ (s)), and aromatic group C-H peaks at $850\text{-}700\text{ cm}^{-1}$ (s) [31]. The key changes observed for increasing [M], at constant R/C and R/F ratio, are the reduction of O-H stretching vibrations ($3550\text{-}3200\text{ cm}^{-1}$), as a consequence of reducing R concentration, and an increase in imide functionalities (1697 cm^{-1}).

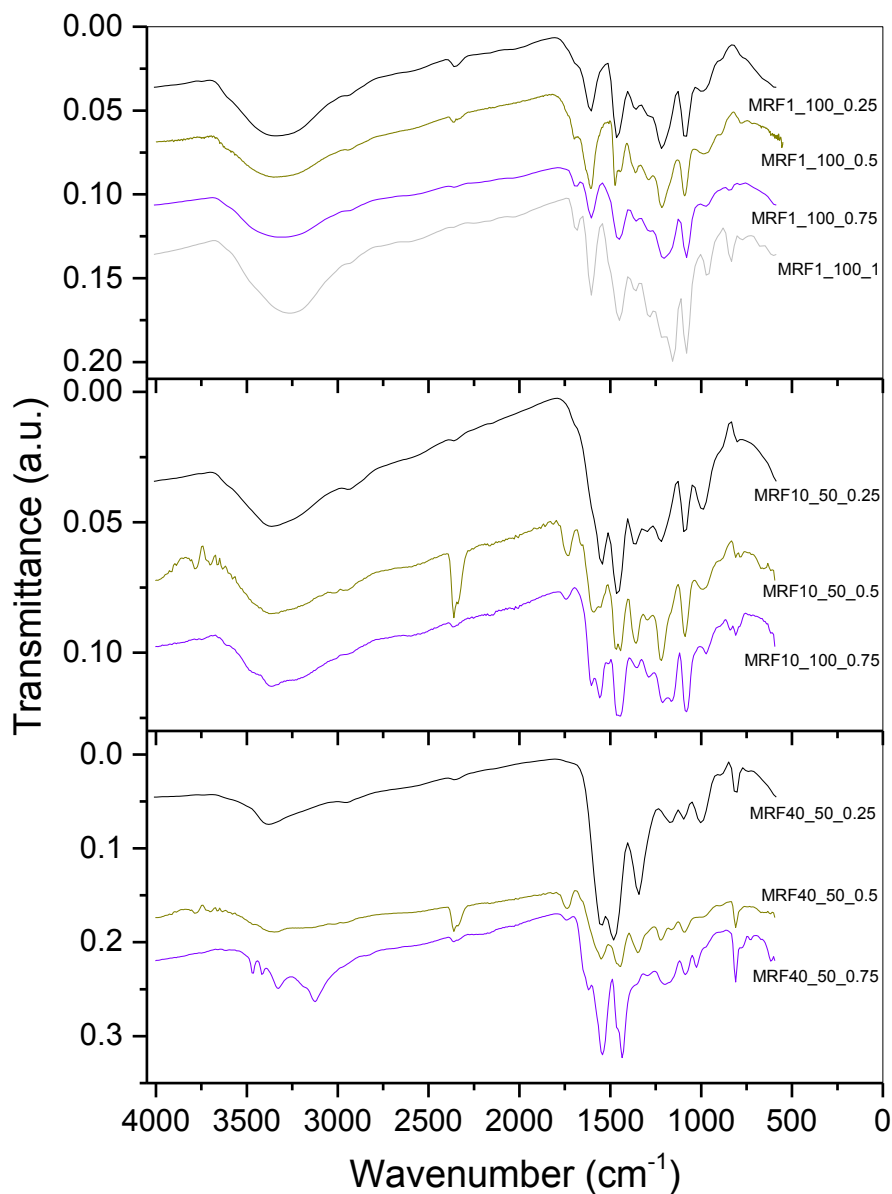


Figure 5: FTIR spectra of varying Resorcinol/Formaldehyde ratio for three sets of constant (low, medium and high) Resorcinol/Catalyst ratio and melamine content.

Figure 5 shows the effect of increasing R/F ratio for a system with constant [M] and R/C ratio. The data represents suites of low, medium and high [M] materials. It can be seen that while O-H stretching ($3550 - 3200 \text{ cm}^{-1}$) is little affected at high [M]; peaks at $1600-1400 \text{ cm}^{-1}$, ascribed to C=O groups, seem to reduce in intensity as R/F increases. Data suggest that C=O bonds concentration increases also with R/C increasing (see Figure SI 2). This decrease may be attributed to the higher degree of cross-linking at low R/F, as ring substitution increases with higher relative concentrations of F. As detailed above, the $1600-1400 \text{ cm}^{-1}$ peak can also result from methylene bridge formation; hence, at low R/F such bridging should be favoured, particularly at initial solution pH 7-8. Similar results are observed for increasing R/C ratio for constant R/F and [M], with more evident changes at higher [M] (see Supporting Information). Increasing R/C impacts more markedly on the region $1600 - 1250 \text{ cm}^{-1}$, with higher intensity peaks as [M] increases, but generally affects the entire fingerprint region. As R/C increases, more R is present in the initial solution, therefore, crosslinking is enhanced

with increased intensities for associated peaks at 1640-1595 cm^{-1} (C=O), 1470-1430 cm^{-1} (C-H methylene bridge), 1300-1020 cm^{-1} (C-O) and 850-700 cm^{-1} (C-H). It is also worth noting (Figure 5c) that as [M] increases, and [R] decreases, N-H vibrations can be detected in the region 3500-3200 cm^{-1} , as O-H concentration reduces.

Surface areas and porosities were determined for all samples; selected N_2 adsorption/desorption isotherms with associated pore size distributions, calculated using the desorption branch, are shown in Figure 6 and 6. In general, it can be seen that increasing R/C significantly reduces the adsorption capacity of the gels, as in the case of conventional RF xerogels [32]. Increasing [M] in MRF gels also produces a decrease in adsorption capacity [33]; however, as R/C is increased the onset of this reduction occurs at lower [M], suggesting that, for a given R/C (and R/F), there is a maximum level of [M] that can be successfully incorporated into the gel matrix before the pore size becomes so large that surface area falls drastically and adsorption capacity is notably reduced. The isotherms obtained can be classified as Type IV, indicative of mesoporous adsorbents; initial monolayer coverage and micropore filling is followed by multilayer adsorption and capillary condensation in pores. The latter phenomenon is often accompanied by a hysteresis loop, the closure point of which, in the case of N_2 adsorption at 77 K, occurs for pores wider than 4nm [34]. Data obtained for samples made using R/C 50 and R/F 0.25 (Figure 6) show an increase in average pore size from 2.4 to 9.5 nm, and the gradual opening of the hysteresis loop across this same series. Similarly, in the series with R/C 50 and R/F 0.5, the loops become appreciably open as [M] increases (see Figure SI 3 - 6).

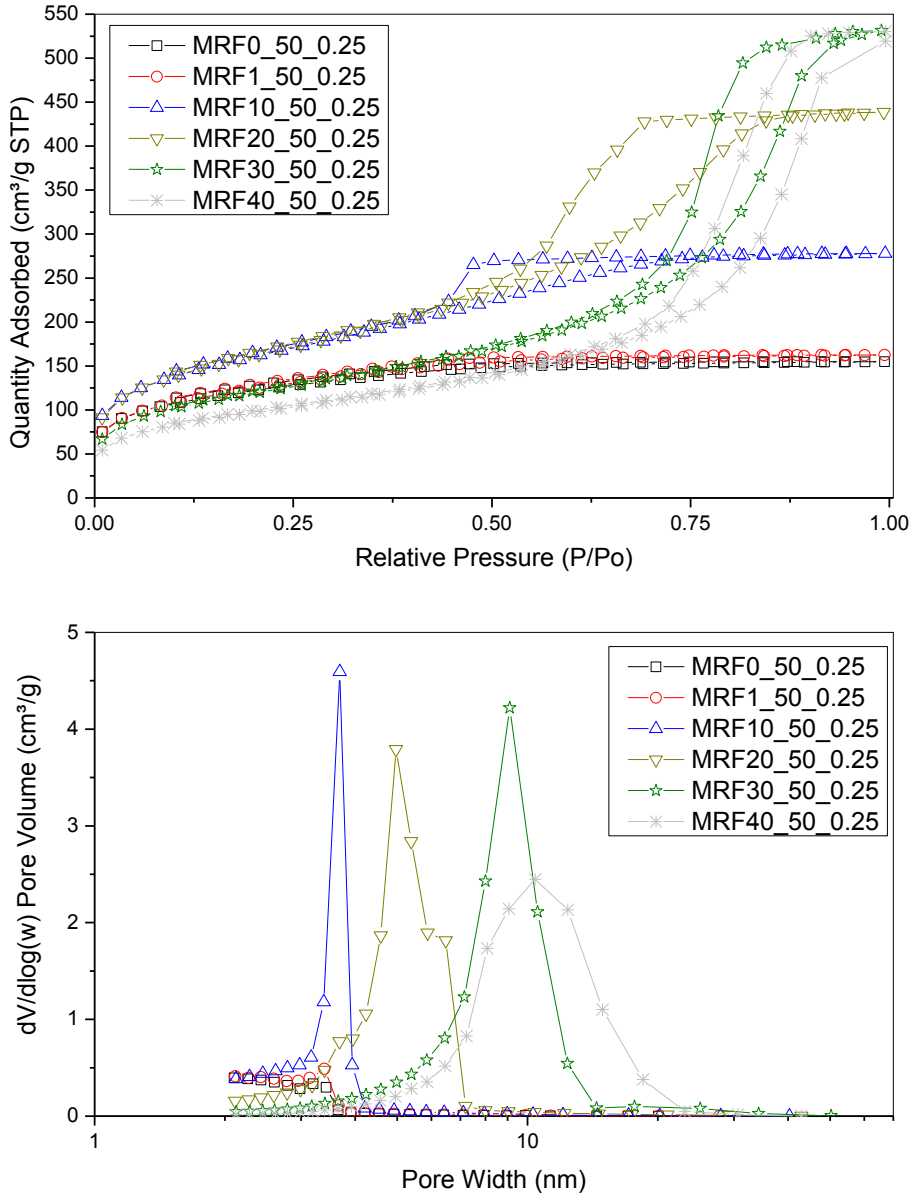


Figure 6: (a) Nitrogen adsorption isotherms and (b) Pore size distributions for a family of Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 50, Resorcinol/Formaldehyde ratio of 0.25 and melamine content of 0-40 w/w%.

The hysteresis loops observed can be classified as Type H1 or H2 depending on the synthetic parameters; at low [M], the hysteresis loops tend to be Type H2(a) before shifting to Type H2(b) for intermediate [M] and, finally, to Type H1 for higher [M]. Type H2 loops indicate complex structures where network effects becomes important, the steep desorption branch is associated with pore-blocking or percolation in narrow pore necks or to cavitation due to the effect of lowering the pressure, therefore, suggesting ink bottle like pores (narrow neck and wide body). Type H1 loops, on the other hand, are often found for ordered mesoporous carbons [34]. This suggests a transition from pores with restricted access to open mesopores as [M] increases, potentially the result of a decrease in crosslinking [33]. Such changes are not observed for all gel series, however, and for higher values of R/F there is only a transition from H2(a) to H2(b), likely due to the lack of F and again the associated impact this has on crosslinking of the materials. The widening of the pores is

evident across all R/C values as [M] increases; however, as R/C increases, the shift from H2(a) to H2(b) loops occurs at lower [M], which indicates that the influence of [M] is greater when less catalyst is present in the system (Figure 7).

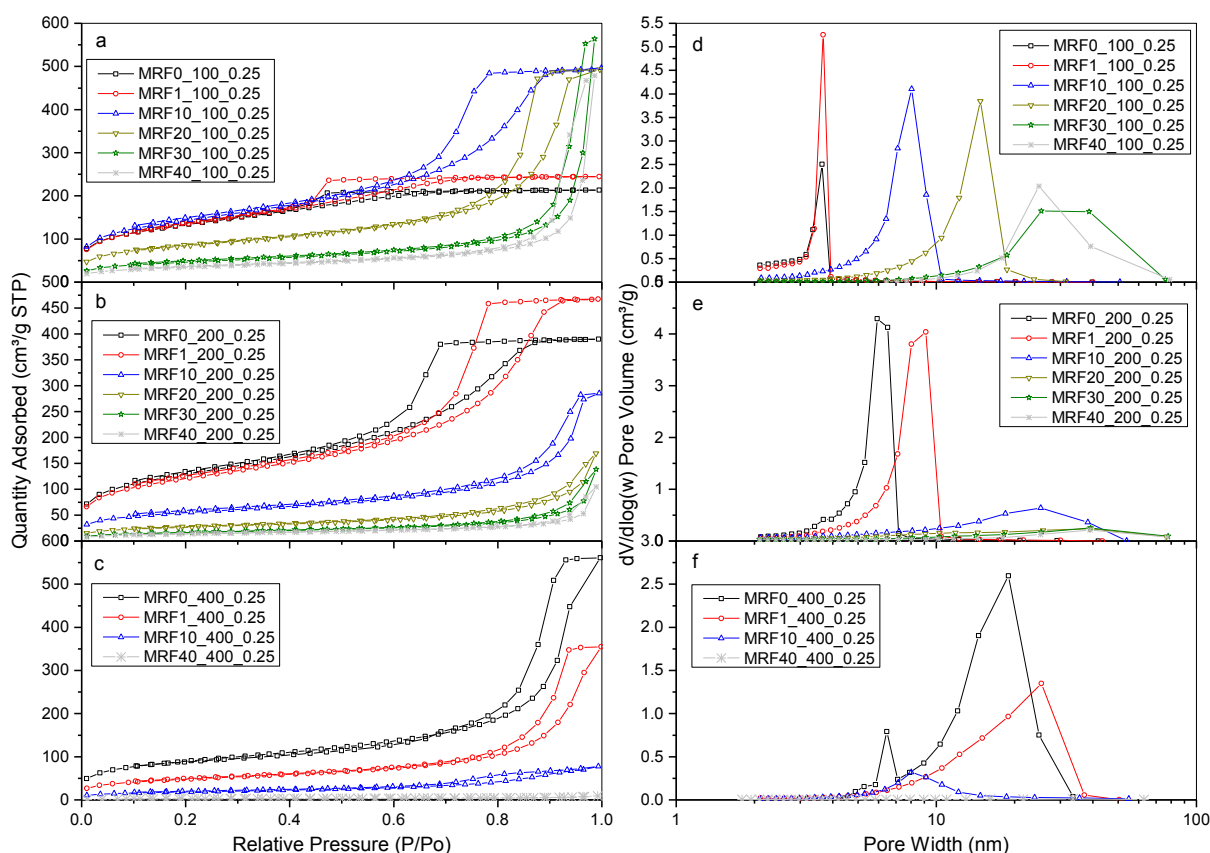


Figure 7: (a) Nitrogen adsorption isotherms and (d) Pore size distributions for Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 100, Resorcinol/Formaldehyde ratio of 0.25 and melamine content 0-40 w/w%; (b) Nitrogen adsorption isotherms and (e) Pore size distributions for Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 200, Resorcinol/Formaldehyde ratio of 0.25, and melamine content of 0-40 w/w%; (c) Nitrogen adsorption isotherms and (f) Pore size distributions for Melamine-Resorcinol-Formaldehyde xerogels synthesised using Resorcinol/Catalyst ratio of 400, Resorcinol/Formaldehyde ratio of 0.25, and melamine content of 0-40 w/w%.

As outlined in the introduction, initial solution pH can markedly affect gel formation; in this study the pH tends to decrease as R/C is increased, as a result of decreased basic catalyst concentration, and also tends to decrease slightly as R/F decreases. In support of the first observation, the lower pK_b for sodium carbonate (3.67) means it will have the greatest impact on pH but it is imperative to remember that the concentration of catalyst is small in comparison to that of R, M or F. In the second case, formalin (F solution) has a pH of 2.8 – 4.0 (as mentioned in Experimental section), therefore, as R/F increases, less formalin is used, and pH is less affected accordingly. As R/C increases, less carbonate is used and, consequently, pH tends to decrease (see Figure SI 7) due to the combined effect of less base and higher R concentration (weak acid, pK_a 9.15). Consequently, for RF gels, R/C ratio is the main parameter that controls initial solution pH [35]. By comparison, M is an organic base, therefore, as its concentration increases so too does pH; hence, for MRF gels the pH is also affected significantly (especially at high R/C) by M (Figure 8).

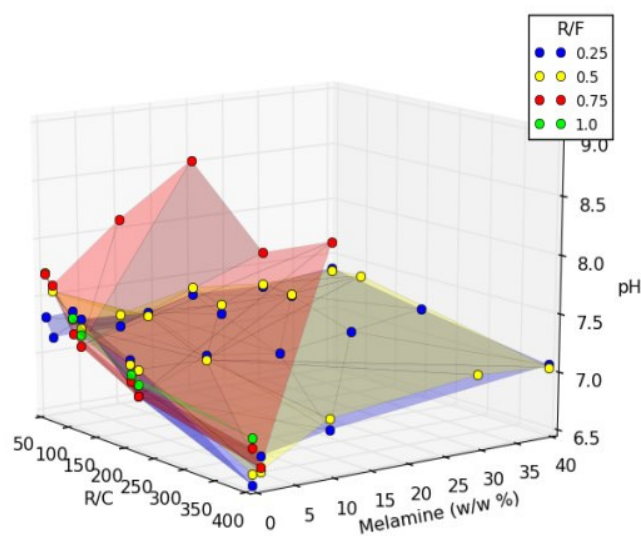


Figure 8: Initial pH of solution as a results of combination of resorcinol, catalyst (sodium carbonate), melamine and formaldehyde.

As R/F is increased, the number of F molecules available to provide linkages decreases resulting in weaker gels, as a consequence of reduced crosslinking between clusters, however, it is the effect of initial solution pH (and R/C ratio) that ultimately controls the pore structure of the final xerogel [15, 36, 37]. As pH approaches 8.0 and 8.5 for [M] of 20 and 10 respectively, pH is generally increased as R/F increases creating weaker porous structures and, in most cases, gelation fails. It can also be rationalised that R/F values of 0.75 and 1.0 would produce weaker xerogels, low surfaces area and pore volume as [22], among other reasons, the high initial solution pH ranges from 7.0 to 8.5 and it is known that initial solution pH has a strong influence on successful gelation. As observed, in this work, for $R/F \geq 0.75$, many gels fail to crosslink sufficiently to make further processing possible; such materials are often amorphous non-porous powders and, as a consequence, only those gels created with R/F 0.25 or 0.5 will be considered in the remainder of the paper.

The total surface area of a material can be divided into external surface area (pores >2 nm width) and micro surface area (pores <2 nm width). For the MRF xerogels synthesised in this work, increasing R/C produces and increasing [M] have a similar effect on surface area, which decreases as either component is increased. It is also notable that if both parameters are increased simultaneously there is a drastic reduction in surface area (Figure 9).

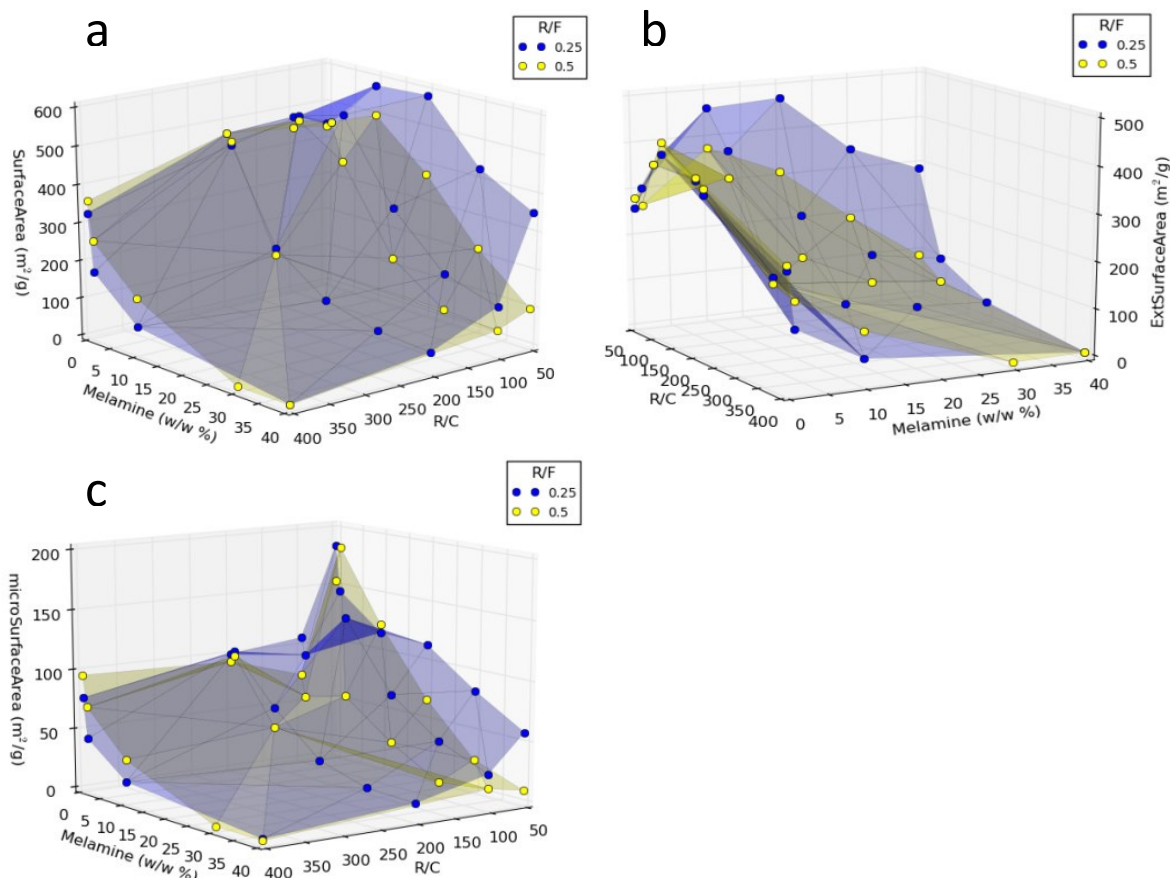


Figure 9: (a) Surface areas, (b) external surface area and (c) micropore surface area obtained for Melamine-Resorcinol-Formaldehyde xerogels produced with Resorcinol/Formaldehyde ratio of 0.25 or 0.5, Resorcinol/Catalyst ratio of 50-400 and melamine content 0-40 w/w%.

The greatest surface areas (Figure 9) are obtained for MRF 20 and MRF 10; while, MRF 0 and MRF 1 show similar results to each other. After this maximum, surface area drops drastically for melamine contents > 30w/w%. As R/C increases the surface area decreases for all melamine contents, however, this decrease occurs at lower R/C as melamine content increases (see Supporting Information), and this narrows the window available to obtain significant surface areas while incorporating more nitrogen into the material. For MRF 0 and MRF 1, the surface areas determined show little variation in the range of R/C studied (50 to 400), but there is still a notable decrease for R/C >200. As stated above, increasing R/C and melamine content both affect surface area, with marked effects when combined, thereby limiting the working range of values for the three variables studied here. In order to maximise surface area, it is recommended to use R/C of 50-100, R/F \leq 0.5 and melamine content between 0 and 20% (potentially up to 30% for R/C 50).

Microporosity is known to be important when targeting small gas molecules, such as in gas treatment applications. Thus, understanding how varying the synthetic parameters for MRF xerogel synthesis (i.e. R/F, R/C and melamine content) affect the development of microporosity is critical for material optimisation [14, 17]. It can be seen that increasing R/C, melamine content or R/F tends to counteract the formation of microporosity within MRF materials, while also increasing pore size (Figure 10 and Figure SI 8 - 11).

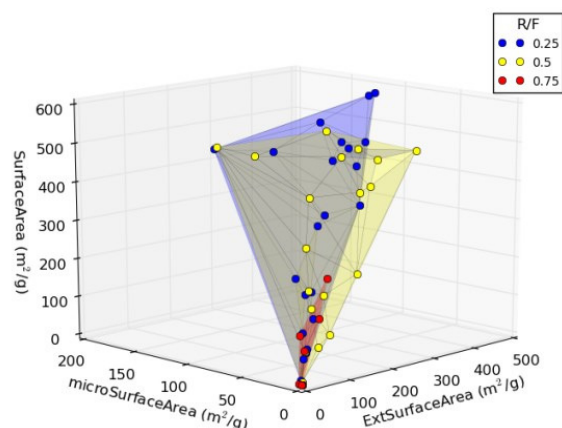


Figure 10: Microporosities obtained for Melamine-Resorcinol-Formaldehyde xerogels synthesised using varying (a) Resorcinol/Catalyst ratio, (b) Resorcinol/Formaldehyde ratio, and (c) melamine content.

As outlined above, R/F values of 0.25 and 0.5 result in better developed gels, offering enhanced control when tuning this type of material by providing improved control of crosslinking during cluster aggregation. R/F directly controls the stoichiometry of the reaction, therefore, the number of substitutions occurring in the ring (R and/or M) and, consequently, the level of crosslinking. Therefore, this affects the formation of voids spaces between the aggregates or clusters, which impact on the pore size and, therefore, the micropore and external surface areas. R/F values of 0.25 or 0.5 result in gels with high internal area and, conversely, higher R/F values result in weak gels with low surface area. As R/C is increased, fewer R molecules are activated to react with F, as less sodium carbonate is available in solution; which weakens the structure, forming larger pore sizes and quelling microporosity in the material. As shown above, increasing [M] affects pore size in a similar manner as increasing R/C, therefore, microporosity is similarly reduced (see Supporting Information) [33].

Total pore volume is calculated from the maximum N_2 uptake observed during BET analysis at the highest pressure (~ 0.98 bar), and micropore volume is calculated using the t-plot method. Higher total pore volumes were obtained for low [M] (0-20%) and low R/C (50-200), see Figure 11. As the t-plot method is used to determine both micropore volume and micropore surface area, they follow the same trend, as expected. Similarly to the results described above, microporosity tends to decrease as R/C and [M] are increased. Notably, samples synthesised using R/C 50 and 100 exhibit high N_2 uptake irrespective of surface area (see Supporting Information), while R/C 200 and 400 demonstrate significant N_2 uptake only for a narrow window at low [M]. This means that increasing [M] does not necessarily mean an increase in N_2 uptake. Surface area is a greater influence on N_2 uptake, which can be tailored by control of R/C and R/F ratio; maximized uptakes are observed at R/C 50-100 and R/F 0.25-0.5 (See Supporting Information).

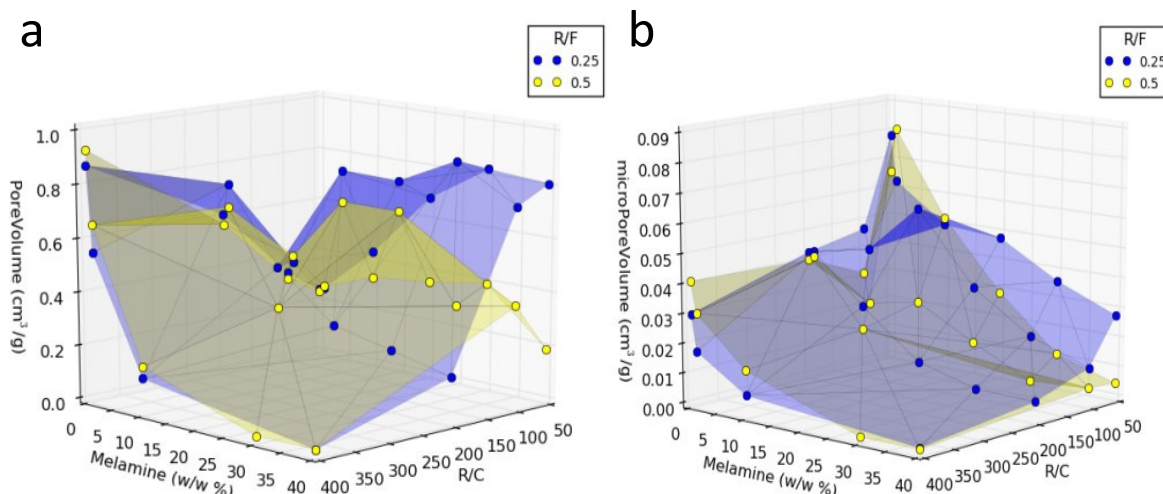


Figure 11: (a) Pore volumes and (b) micro pore volumes obtained for Melamine-Resorcinol-Formaldehyde xerogels synthesised using melamine content of 0-40 w/w%, Resorcinol/Catalyst ratio of 50-400 and Resorcinol/Formaldehyde ratio of 0.25 or 0.5.

Two different behaviours are distinguishable at i) low R/C (50 and 100) and ii) high R/C (400), with regards to both pore volume and nitrogen uptake (Figure 11). At high R/C the largest uptake is seen for low [M] and is decreases progressively as [M] increases, while for low R/C the opposite is observed, where the higher N₂ uptake is for higher [M] with a progressive decrease with decreasing [M]. Highest N₂ uptakes are observed for pore sizes between 5-15 nm, with a few exceptions, e.g. high [M] and low R/C show high uptakes even at 25 nm. While there is incongruity in pore volume (the two maxima are observed, contrarily at low [M]/high R/C, and high [M]/low R/C), micropore volume tends to uniformly decrease as R/C, R/F and [M] increase; for low R/F, the decrease is not as steep (see also Figure SI 12 - 13). The maximum micropore volume for each [M] analysed was observed at low R/C (50).

It is notable that pore size is only controlled for low R/F (0.25 or 0.5), while higher R/F (0.75 or 1.0) results in randomisation of pore size with a tendency to larger diameters as a result of the associated weak crosslinking and interactions between clusters (see Figure SI 14). Smallest pore sizes are obtained for low R/C (50); the amount of catalyst is greatest, which enhances cluster crosslinking, promoting the formation of small voids and pores. For low R/C (50) and R/F (0.25 or 0.5), pore size increases gradually as [M] is increased [38]; in general, low R/C gels results in smaller pore sizes for low [M], while the opposite is observed for higher R/C (Figure 6 and 6).

4. Conclusions

Melamine-Resorcinol-Formaldehyde (MRF) xerogels produced using synthesis parameters of Resorcinol/Catalyst ratio (R/C), Resorcinol/Formaldehyde ratio (R/F) and melamine content ([M]) were examined to show the associated effects on initial solution pH, surface area, pore size and volume. For Resorcinol-Formaldehyde (RF) gels (no melamine) R/C is known to rigidly control pH. By contrast, for MRF gels, [M] also impacts pH, with a stronger effect observed for higher R/C where pH increases as [M] increases; at low R/C pH is, instead, noted to fluctuate at ~ 7.5 , which may be a result of the additional basic character afforded by melamine. R/F controls the reaction stoichiometry, therefore, as the value is increased, the final xerogel structure becomes weaker and, in most cases, gelation fails. Low R/F offers better control of final xerogel properties, such as pore size and also enhances crosslinking. Increasing [M] reduces the carbon content of the final xerogel, and, as expected, nitrogen content increases linearly as [M] is increased. FTIR confirmed that the proportion of hydroxyl functionalities decreased as [M] was increased, as a consequence of substitution of R by M in the reaction; additionally the concentration of imide functionalities is also increased. At constant [M] and R/C, increasing R/F is seen to increase the concentration of methylene bridges; similarly increasing R/C, at constant [M] and R/F, also results in an increase in bridging moieties and related vibrations. MRF materials exhibit Type IV nitrogen sorption isotherms, and hysteresis loops shifting from Type H2 to H1 as [M] increases, which is related to narrow necked and wide bodied pores; this effect is diminished with increasing R/F. The most notable effect of increasing [M] in these materials is similar to increasing R/C, this being a reduction in surface area, pore volume and N_2 uptake, as well as an increase in pore size. If both parameters are increased simultaneously the reduction of these structural parameters is drastic, and in order to obtain higher surface areas, pore volumes and control pore size R/F needs to be < 0.5 . In order to optimise microporosity in future materials synthesis, low R/C, [M] and R/F are required as increased levels of each variable increase the tendency toward mesopore formation. This means that, for gas treatment applications, careful consideration of the synthetic variables is required to optimise chemical and textural properties in tandem.

5. Acknowledgements

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6. References

1. Mirzaeian, M. and P.J. Hall, *The control of porosity at nano scale in resorcinol formaldehyde carbon aerogels*. Journal of Materials Science, 2009. **44**(10): p. 2705-2713.
2. Pekala, R.W. and D.W. Schaefer, *Structure of organic aerogels. 1. Morphology and scaling*. Macromolecules, 1993. **26**(20): p. 5487-5493.
3. Pekala, R.W., *Organic aerogels from the polycondensation of resorcinol with formaldehyde*. Journal of Materials Science, 1989. **24**(9): p. 3221-3227.
4. Gebert, M.S. and R.W. Pekala, *Fluorescence and light-scattering studies of sol-gel reactions*. Chemistry of Materials, 1994. **6**(2): p. 220-226.
5. Wu, D., et al., *Low-density organic and carbon aerogels from the sol-gel polymerization of phenol with formaldehyde*. Journal of Non-Crystalline Solids, 2005. **351**(10-11): p. 915-921.

6. Jirglová, H., A.F. Pérez-Cadenas, and F.J. Maldonado-Hódar, *Synthesis and Properties of Phloroglucinol-Phenol-Formaldehyde Carbon Aerogels and Xerogels*. Langmuir, 2009. **25**(4): p. 2461-2466.
7. Taylor, S.J., et al., *Gelation Mechanism of Resorcinol-Formaldehyde Gels Investigated by Dynamic Light Scattering*. Langmuir, 2014. **30**(34): p. 10231-10240.
8. Mulik, S., C. Sotiriou-Leventis, and N. Leventis, *Time-Efficient Acid-Catalyzed Synthesis of Resorcinol-Formaldehyde Aerogels*. Chemistry of Materials, 2007. **19**(25): p. 6138-6144.
9. Merzbacher, C.I., et al., *Carbon aerogels as broadband non-reflective materials*. Journal of non-crystalline solids, 2001. **285**(1): p. 210-215.
10. Mulik, S. and C. Sotiriou-Leventis, *Resorcinol-Formaldehyde*. Aerogels handbook, 2011: p. 215-34.
11. Tamon, H.I., H.; Mikami, M.; Okazaki, M., *Porous structure of organic and carbon aerogels synthesized by sol-gel polycondensation of resorcinol with formaldehyde*. Carbon, 1997. **35**(6): p. 791-796.
12. Pizzi, A.M., K. L., *Handbook of adhesive technology: Second edition.*, ed. I. Marcel Dekker. 2003, New York.
13. Bock, V., A. Emmerling, and J. Fricke, *Influence of monomer and catalyst concentration on RF and carbon aerogel structure*. Journal of Non-Crystalline Solids, 1998. **225**: p. 69-73.
14. Horikawa, T., J.i. Hayashi, and K. Muroyama, *Controllability of pore characteristics of resorcinol-formaldehyde carbon aerogel*. Carbon, 2004. **42**(8-9): p. 1625-1633.
15. Job, N., et al., *Porous carbon xerogels with texture tailored by pH control during sol-gel process*. Carbon, 2004. **42**(3): p. 619-628.
16. Feng, Y.N., et al., *Effects of further adding of catalysts on nanostructures of carbon aerogels*. Materials Science and Engineering: B, 2008. **148**(1-3): p. 273-276.
17. Yamamoto, T., et al., *Control of mesoporosity of carbon gels prepared by sol-gel polycondensation and freeze drying*. Journal of Non-Crystalline Solids, 2001. **288**(1-3): p. 46-55.
18. Fung, A.W.P., et al., *Relationship between particle size and magnetoresistance in carbon aerogels prepared under different catalyst conditions*. Journal of Non-Crystalline Solids, 1995. **186**: p. 200-208.
19. Fairen-Jimenez, D., F. Carrasco-Marin, and C. Moreno-Castilla, *Porosity and surface area of monolithic carbon aerogels prepared using alkaline carbonates and organic acids as polymerization catalysts*. Carbon, 2006. **44**(11): p. 2301-2307.
20. Zhou, H., et al., *Facile preparation and ultra-microporous structure of melamine-resorcinol-formaldehyde polymeric microspheres*. Chemical Communications, 2013. **49**(36): p. 3763-3765.
21. Hodgins, T.S., et al., *Melamine-Formaldehyde Film-Forming Compositions*. Industrial & Engineering Chemistry, 1941. **33**(6): p. 769-779.
22. Okano, M. and Y. Ogata, *Kinetics of the Condensation of Melamine with Formaldehyde*. Journal of the American Chemical Society, 1952. **74**(22): p. 5728-5731.
23. Jahromi, S., *Storage stability of melamine-formaldehyde resin solutions, 1. The mechanism of instability*. Macromolecular Chemistry and Physics, 1999. **200**(10): p. 2230-2239.
24. Van Blaaderen, A.V.G., J.; Vrij, A., *Monodisperse colloidal silica spheres from tetraalkoxysilanes: Particle formation and growth mechanism*. J. Colloid Interface Sci., 1992. **154**: p. 481-501.
25. Liu, J., et al., *Extension of The Stöber Method to the Preparation of Monodisperse Resorcinol-Formaldehyde Resin Polymer and Carbon Spheres*. Angewandte Chemie International Edition, 2011. **50**(26): p. 5947-5951.
26. Brunauer, S., P.H. Emmet, and E. Teller, *Adsorption of gases in multimolecular layers*. Journal of the American Chemical Society, 1938. **60**: p. 309-19.

27. Rouquerol, J., P. Llewellyn, and F. Rouquerol, *Is the BET equation applicable to microporous adsorbents?*, in *Studies in Surface Science and Catalysis*, F.R.-R.J.R. P.L. Llewellyn and N. Seaton, Editors. 2007, Elsevier. p. 49-56.
28. Barrett, E.P., L.G. Joyner, and P.P. Halenda, *The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen Isotherms*. Journal of the American Chemical Society, 1951. **73**: p. 373-80.
29. Lippens, B.C. and J. De Boer, *Studies on pore systems in catalysts: V. The t method*. Journal of Catalysis, 1965. **4**(3): p. 319-323.
30. Smith, B.C., *Fundamentals of Fourier transform infrared spectroscopy*. 2011: CRC Press Inc.
31. Williams, D.H. and I. Fleming, *Spectroscopic methods in organic chemistry*. Fourth edition ed. 1980: McGraw-Hill.
32. Job, N., et al., *Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials*. Carbon, 2005. **43**(12): p. 2481-2494.
33. Salinas-Torres, D., et al., *Effect of nitrogen doping on the pore texture of carbon xerogels based on resorcinol-melamine-formaldehyde precursors*. Microporous and Mesoporous Materials, 2018. **256**(Supplement C): p. 190-198.
34. Thommes, M., et al., *Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)*. Pure and Applied Chemistry, 2015. **87**(9-10): p. 1051-1069.
35. ElKhatat, A.M. and S.A. Al-Muhtaseb, *Advances in tailoring resorcinol-formaldehyde organic and carbon gels*. Advanced materials, 2011. **23**(26): p. 2887-2903.
36. Al-Muhtaseb, S.A. and J.A. Ritter, *Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels*. Advanced Materials, 2003. **15**(2): p. 101-114.
37. Lin, C. and J.A. Ritter, *Effect of synthesis pH on the structure of carbon xerogels*. Carbon, 1997. **35**(9): p. 1271-1278.
38. Rasines, G., et al., *N-doped monolithic carbon aerogel electrodes with optimized features for the electrosorption of ions*. Carbon, 2014(0).