

## Hydrophobically Modified Acrylamide Based Hydrogels

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### ABSTRACT

The synthesis of acrylamide based hydrogels incorporating a small proportion of hydrophobic functional groups results in a hydrogel structure with improved mechanical properties. In particular increased mechanical toughness and tensile strength whilst maintaining a relatively high swelling ratio. A method of increasing toughness has been developed by introducing a number of long alkyl chain hydrophobic groups into the hydrophilic structure. These hydrophobic groups create domains of densely clustered polymer chains within the highly swollen hydrogel matrix. Single edged notch tensile tests demonstrate a significant increase in fracture energy when the hydrophobes are able to interact in aqueous solutions compared to gels swollen in organic solvents in which the hydrophobes act independently. Therefore it is speculated that these domains increase energy dissipation around the crack tip during fracture causing an increase in mechanical toughness.

### 1. INTRODUCTION

Hydrogels have many practical biomedical applications, in particular as contact lenses, catheters, drug delivery systems, wound dressings etc. However, the use of these materials in more structural applications is limited by their poor mechanical properties. Hydrogels are composed of swollen crosslinked networks of polymer chains with water filling the interstitial spaces. Due to this highly swollen state, polymer chains are generally quite extended with little possibility for movement or extension when placed under stress. Thus very few energy absorption processes operate during deformation resulting in quite brittle materials.

The strength of hydrogels can be improved by the addition of hydrophobic monomers to the polymer architecture thereby creating regions of more densely coiled or entangled chains which would contribute to an overall increase in modulus and strength. However it should be noted that the presence of hydrophobic components will always reduce the equilibrium water content of the gel.

There are numerous ways of incorporating hydrophobic monomers into a hydrogel structure the most common being grafting, copolymerisation or the formation of interpenetrating networks. The present work focuses on the use of the monomer N,N-dimethylacrylamide (DMAM) which is unusual because both the monomer and polymer are soluble in aqueous and various organic solvents<sup>1</sup>. This makes the polymer suitable for simple copolymerisation reactions with hydrophobic monomers in organic solvents.

The synthesis of hydrophobically modified hydrogels of PDMAM has been reported previously by numerous workers. Copolymer macromers of PDMAM and poly methyl methacrylate (PMMA) were synthesized by graft copolymerisation by Muratore and Davis,<sup>2</sup> and by a combination of copolymerisation and graft polymerisation with PMMA by Liu et al.<sup>3,4</sup>. Although the water content is found to be sufficient and high strength gels can be formed, copolymer grafting is complex and involves numerous steps. Alternatively, DMAM has been used to form semi-interpenetrating networks

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with PMMA with demonstrated success as the tensile strength increased with PMMA content without significant reduction in equilibrium water content<sup>5</sup>.

Undoubtedly the simplest approach would be to produce statistical copolymers of DMAM with a suitable hydrophobic co monomer. The key to suitability is that the hydrophobic monomer contains long alkyl chains which are capable of forming entangled hydrophobic aggregations between the hydrophilic chains. To this end, hydrophobically modified copolymer hydrogels based on DMAM have been synthesized by a homogeneous free radical solution polymerisation method using the hydrophobic co monomer dodecylacrylate (DA) in DMF. The co monomer was incorporated into the polymer in a random manner simply determined by the reactivity ratios of the monomer components. Crosslinking agent, methylene bis acrylamide (MBAM) was added in various amounts to introduce chemical bonds between the hydrophobic domains and the hydrophilic matrix. Once the gels have been formed the organic solvent can be exchanged with water to produce a hydrophobically modified hydrogel.

Even though hydrophobically modified PDAM hydrogels have been described previously and the effect that the hydrophobic component has on the strength of the gel often reported, the influence that these copolymers have on the toughness of the gels has not been published. Indeed a review of relevant literature shows that a quantified assessment of the toughness of hydrogels is infrequently reported. This is probably due to the difficulty of preparing hydrogel samples in a suitable form for standard toughness measurements, such as the notch test, due to the fragile state of unmodified gels. The present work however reports the findings of single edged tensile notch tests of the modified hydrogels compared to unmodified gels of the same swelling state to provide indisputable evidence of the effect of hydrophobic modification on the toughness and fracture behavior of hydrogel structures.

## 2. METHODOLOGY

### 2.1. Materials

Monomers, N,N-dimethyl acrylamide (Aldrich) and dodecyl acrylate (Aldrich) were used as received (see table 1).

Hydrophilic monomer	Hydrophobic monomer
$  \begin{array}{c}  \text{H}_2\text{C}=\text{CH} \\    \\  \text{C}=\text{O} \\    \\  \text{N} \\  / \quad \backslash \\  \text{H}_3\text{C} \quad \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{H}_2\text{C}=\text{CH} \\    \\  \text{C}=\text{O} \\    \\  \text{O} \\    \\  (\text{CH}_2)_{11} \\    \\  \text{CH}_3  \end{array}  $
N,N-dimethylacrylamide (DMAM)	Dodecylacrylate (DA)

Table 1 : Chemical structure of comonomers

## 2.2. Preparation of uncrosslinked copolymers

Uncrosslinked copolymers were produced in order to assess the aggregation of hydrophobic side chains by rheology. Copolymerizations were carried out by a free radical mechanism in toluene in a round-bottomed flask fitted with a condenser and nitrogen gas inlet. Various co-monomer ratios were added to toluene in the correct quantity to make 50 ml of 1.0 molar solutions (total monomer concentration), Table 2. The solution was purged for 1 hour before raising the nitrogen gas inlet above solution for the duration of the reaction.

During the purge the solution temperature was raised to the reaction temperature, 55-65°C. After raising the gas purge,  $1 \times 10^{-2}$  mol/L of initiator, 2,2'-azobis-isobutylnitrile (AIBN), was added and the solution was left at temperature for 20 hours. After the reaction, the solution was allowed to cool to room temperature before the copolymers were precipitated in diethyl ether and dried in vacuum for several hours at 30°C.

Sample	$f_B = \frac{[B]_0}{[A]_0 + [B]_0}$	$[A]_0 + [B]_0$ mol/L	$[AIBN]_0$ mol/L
1.25DA	0.0125	1	0.01
2.5DA	0.025	1	0.01
3.75DA	0.0375	1	0.01
5.0DA	0.05	1	0.01
7.5DA	0.075	1	0.01
10.0DA	0.1	1	0.01

Table 2: Copolymer samples, synthesis and characterisation.

$[A]_0$  is the initial molar concentration of hydrophilic monomer DMAM,  $[B]_0$ , the initial molar concentration of hydrophobic monomer and,  $f_B$ , the initial molar feed ratio of hydrophobic monomer. Polymer conversion calculated on a weight by weight comparison with the initial monomer amount was found to be around 90% in all cases.

## 2.3. Preparation of the gel

Plates of gel were synthesised in glass moulds contained within a reaction vessel fitted with condenser and argon gas inlet. A solution of 0.9625 mol/L N,N-dimethylacrylamide (DMAM), 0.0375 mol/L dodecylacrylate (DA),  $1 \times 10^{-2}$  mol/L of initiator, 2,2'-azobis-isobutylnitrile (AIBN) and  $3.65 \times 10^{-2}$  mol/L crosslinking agent, methylene bis acrylamide (MBAM) in N,N-Dimethylformamide (DMF) was purged with argon for 10 minutes before placing in the argon filled chamber. The system was then purged for a further 10 minutes and a low flow rate of argon allowed to continue during the course of the reaction. The reaction chamber was heated in silicone oil to the reaction temperature ( $T \sim 60$  °C) for 4 hours. The gel was removed and rinsed in DMF several times to remove excess monomer and stored in water for one week to allow the gel to reach full equilibrium swelling in water. Samples of fully water swollen gel were dried over a period of one week at room temperature in order to determine the degree of swelling as a ratio of swollen gel weight to dry gel weight.

## 2.4. Rheological Study

In order to assess the effect of hydrophobic modification on the rheological properties of uncrosslinked copolymers a reference material is required from which enhancement is measured. The best comparison of rheological behavior and hence example of the effects of hydrophobic attachments can be obtained if rheology of exactly the same polymer is compared in a good organic solvent (DMF) and in water. This allows effects due to differences in molecular weight, polydispersity, co-monomer ratios or contaminants to be eliminated. This comparison would be as explicit and indeed more accurate than a comparison to an unmodified polymer.

The prepared copolymers were dissolved in water or DMF in a range of concentrations from 0.1 wt% through to 16 wt%. Solutions were mixed gently for at least 24 hours before viscosity measurements were made. The more viscous solutions were then left to stand for at least 24 hours to allow bubbles to escape before measurements.

The viscosity of each polymer solution in water and DMF was measured as a function of shear rate. Two rheometers were required in order to cover the range of rheological behavior observed. For low viscosity samples a 'Low Shear 30' rheometer (Contraves) was used. This instrument utilizes a couette cell with co-axial geometry. For more viscous samples, measurements were performed on a controlled strain rheometer, Rheometric RFSII (Rheometrics) equipped with cone-plate geometry. The diameter of the cone-plate was 25 or 50 mm as required. All measurements were conducted at 25 °C and samples were covered to prevent evaporation during the tests.

The measured viscosity was normalized with respect to the solvent used, hence, the results are represented in terms of specific viscosity which is defined as;

$$\eta_{sp} = \left( \eta_{solution} / \eta_{solvent} \right) - 1 \quad (1)$$

The specific viscosity as a function of shear rate was extrapolated to zero shear rate in order to determine the *zero shear rate viscosity*, which was plotted as a function of polymer concentration to compare the viscosity profile of each copolymer over a wide range of concentrations.

## 2.5. Mechanical Testing

In a similar manner to the rheology study the effects of hydrophobic modification on the mechanical properties were assessed by comparing the gels fully swollen in water with the gels swollen to an equivalent extent in DMF because this allows comparison of exactly the same polymers either with or without hydrophobic aggregation.

The mechanical properties of the hydrogels were assessed by tensile testing and single edged notch testing under tension in a TA Instruments DMA Q800 instrument. The fully water swollen gel was cut into strips approximately 20 mm in length x 3.5 mm wide x 1.5 mm thick. A portion of these were tested immediately under tension at a rate of 1mm/min to failure. Others were notched with a razor and tested under tension at a rate of 1 mm/min to failure.

Approximately half of the strips were retained and carefully weighed before placing in DMF for a period of at least a week to allow the solvents to exchange. The solvent was changed several times to ensure complete removal of water. It was noted that the samples swelled considerably once placed in DMF. After one week the fully swollen gel samples in DMF were removed from the solvent and allowed to dry in the fume hood on teflon plates. The weight of each sample was monitored closely as the samples dried and subsequently shrank due to loss of solvent. When each sample reached

its equivalent fully water swollen weight it was either tested under tension at a rate of 1mm/min to failure or notched and tested under tension at a rate of 1mm/min to failure.

To allow the soft gels to be gripped in the clamps, pieces of balsa wood were glued to each end of the strips to be tested using a cyanoacrylate adhesive as described previously by Temenoff et al. <sup>6</sup>. This technique is acceptable provided that the bond between the gel and the wood is stronger than the fracture strength of the hydrogel.

### 3. RESULTS

#### 3.1. Rheology of uncrosslinked copolymers

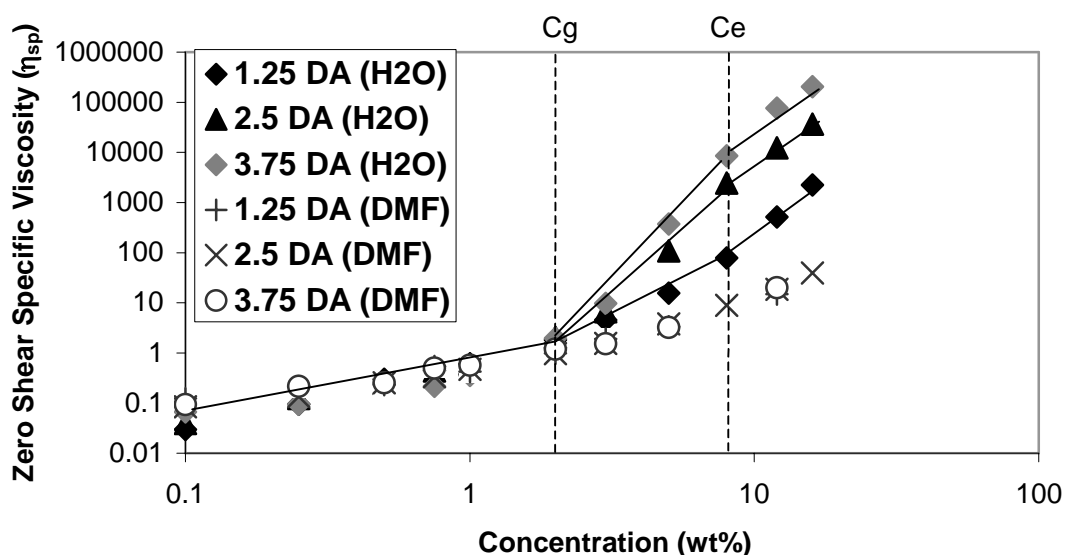


Figure 1 – Zero shear specific viscosity of various copolymers with different DA contents as a function of copolymer concentration in water and DMF.

The viscosities as a function of shear rate were extrapolated to zero shear rate and plotted as a function of polymer concentration, Figure 1. It is apparent that the viscosity of the copolymers in water is much higher than the viscosity of the same copolymer in DMF. Also the rate of increase of viscosity with polymer concentration increases as the hydrophobic content of the copolymer increases.

### 3.2. Mechanical testing of hydrogels

Samples fully swollen in water were weighed and then dried over a period of one week in order to determine the dry polymer weight content. It was found that three separate samples had a polymer content between 30.6 and 32.4 wt% polymer.

Tensile test results are shown in Figure 2, all of the samples tested failed well within the bulk of the sample verifying the assumption that the cyanoacrylate bond had no effect upon the measured mechanical properties. It can be seen that the samples tested in DMF have a tensile strength varying between 12 and 44 kPa and a percent elongation at fracture between 3.5 and 10.5 %. In comparison the samples tested in water demonstrated a tensile strength between 61 and 144 kPa and a percent elongation at failure between 16.4 and 40.8 %.

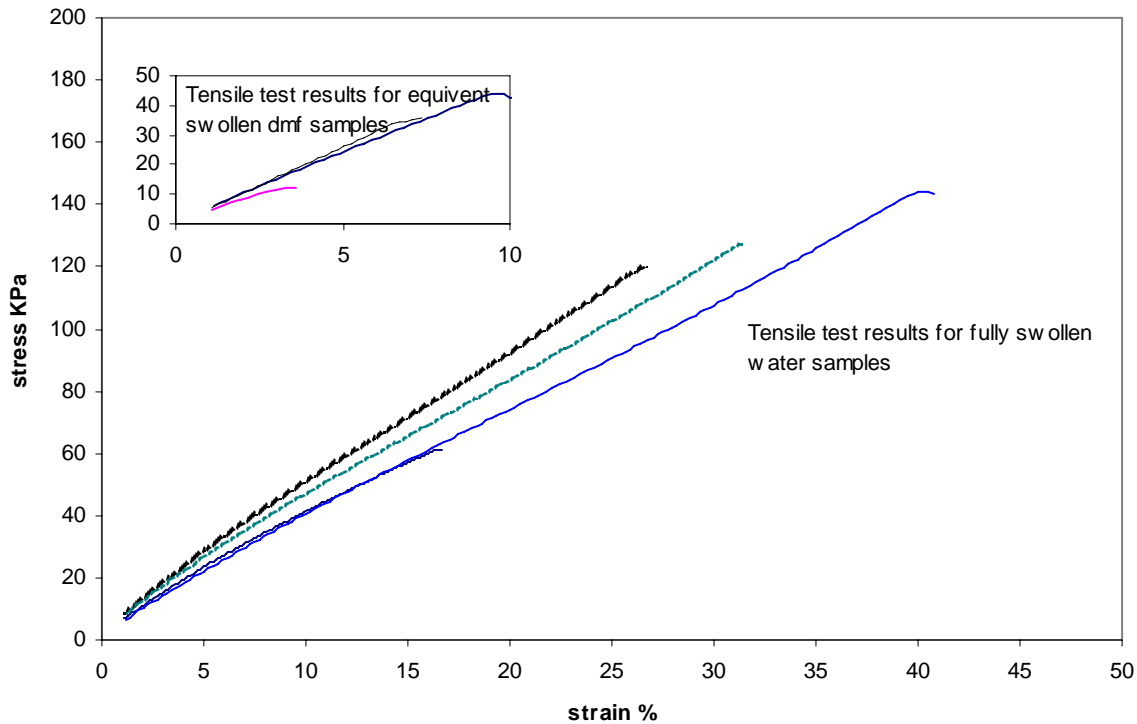


Figure 2 - Tensile test results of hydrophobically modified hydrogels containing 3.75 mol% DA, samples are fully swollen in water (~30wt% polymer) or partially swollen in DMF to ~30wt% polymer.

Typical stress-strain curves from the notch tests are shown in Figure 3. As with the tensile tests it is apparent that the samples swollen in water achieve a much higher tensile strength and elongation before fracture. The notch test results were analysed following standard fracture mechanics equations adapted to behaviour of crack growth in flexible polymers as described in Kinloch and Young <sup>7</sup> which states that crack growth commences at a critical value of the uniform strain energy  $W_c$  (the strain energy per unit volume).

$$\text{And } W_c = \frac{1}{2} \sigma_c e_c \quad (2)$$

Where  $\sigma_c$  is the critical stress and  $e_c$  is the critical strain at crack propagation.

Hence for a sample of single edge crack geometry the fracture energy  $G_c$  can be defined as;

$$G_c = (2\pi a W_c) / (\lambda_c^{1/2}) \quad (3)$$

Where  $a$  is the initial crack length and  $\lambda_c$  is the extension ratio at the critical point where crack growth starts.

$$\text{Hence; } \lambda_c = l_c / l_0 = e_c + 1 \quad (4)$$

Where  $l_c$  is the length of the sample at crack propagation and  $l_0$  is the original sample length.

From equations (2) to (4) the average fracture energy ( $G_c$ ) for the samples tested in the notch test can be calculated. The values used in calculations for a set of at least 3 samples tested in DMF and water respectively are shown in Table 3.

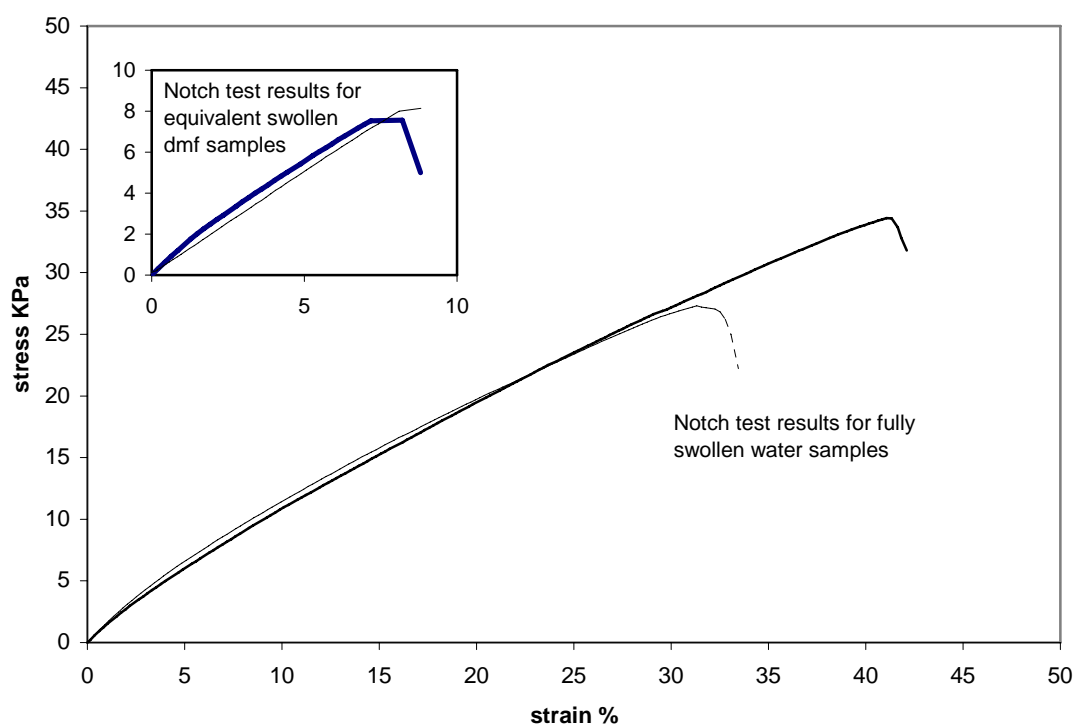


Figure 3 - Single edged notch tensile test results of hydrophobically modified hydrogels containing 3.75 mol% DA, samples are fully swollen in water (~30wt% polymer) or partially swollen in DMF to ~30wt%

Sample	a (mm)	$\epsilon_c$ (%)	$\sigma_c$ (kPa)	$G_c$ (J/m <sup>2</sup> )	Mean average $G_c$	Standard deviation $G_c$
water.1	0.582	20.63	20.08	757.418	1101.977	530.899
water.2	0.4	23.61	25.3	750.630		
water.3	0.561	32.48	31.85	1823.216		
water.4	0.434	20.4	23.81	662.260		
water.5	0.588	31.2	26.31	1516.361		
dmf.1	1.293	8.11	7.99	263.218	196.048	129.968
dmf.2	1.412	7.18	8.75	278.687		
dmf.3	0.361	5.48	7.44	46.239		

Table 3: Values of initial crack length (a), critical strain ( $\epsilon_c$ ), and critical stress ( $\sigma_c$ ) used in calculations for the average fracture energy ( $G_c$ ).

#### 4. DISCUSSION

Before considering the mechanical properties of the hydrophobically modified hydrogels it is useful to examine the viscosity/concentration profiles of the uncrosslinked polymers. The rheological behaviour of the uncrosslinked copolymers as a function of polymer concentration, Figure 1, has three distinct regimes;

- i) *Starting from very low concentrations, we observe a dilute regime,  $C < C_g$ , where the rheological behavior is mainly controlled by intramolecular associations.  $C_g$  is closely related and has a very similar value to the *overlap concentration*,  $C^*$ , for the equivalent unmodified polymers<sup>14</sup> (for an unmodified polymer  $C^*$  is simply determined by the molecular weight of the macromolecular chains). In the concentration regime below  $C_g$ , the hydrophobically associating polymer chains would act independently forming intramolecular associations or possibly forming clusters of limited size unable to percolate the whole volume. Hence the viscosity of the modified polymers would be expected to be either unchanged or lower than that for an unmodified polymer (i.e. polymers in DMF). In Figures 1 this is typically the case for concentrations below 2wt%.*
- ii) *A semi-dilute unentangled regime,  $C_g < C < C_e$ . The transition from the first to the second regime is abrupt, occurring at a critical concentration  $C_g \approx 2\text{wt}\%$ . Considering Figure 1, the polymers which all have very similar molar mass, ( $M_w \sim 100,000$ <sup>8</sup>) show an increasing slope with increasing hydrophobic content, resulting in a set of divergent straight lines. It is apparent that the viscosity of copolymers in water increase significantly with concentration compared to the viscosity of the same copolymers in DMF. This increase in viscosity with hydrophobe content indicates that the hydrophobic side chains are forming interchain aggregations which act as transient physical crosslinks. The greatly reduced viscosity of the same copolymers in DMF further indicates that these physical crosslinks are due to hydrophobic effects because of their absence when the copolymer is dissolved in a good organic solvent. This behavior is in agreement with previous work on micellar polymerized hydrophobically modified acrylamides where the viscosity dependence on concentration increases more dramatically as the hydrophobic content increases and also as the hydrophobic block length increases<sup>9-15</sup>.*

- iii) *A semi-dilute entangled regime,  $C > C_e$ .* According to Rubinstein and Semenov<sup>16</sup>, a different behavior is expected beyond the entanglement concentration ( $C_e$ ), a concentration at which entanglements become elastically effective in an unmodified polymer. From Figure 1, it is clear that this change in behavior occurs above 8wt% in agreement with the related literature which states that  $C_e$  is typically 5 to 10 times higher than  $C^*$  and more particularly with the work of Regalado et al.<sup>14</sup> where a ratio  $C_e/C^* \sim 4$  was reported.

In summary, the rheology studies of uncrosslinked copolymers of the same composition as the hydrophobically modified hydrogels demonstrate a significant increase in viscosity corresponding with the increasing proportion of incorporated hydrophobic side chains. The copolymers were found to have enhanced viscosities in aqueous solutions as compared to their viscosity in an ideal organic solvent (DMF), Figure 1, indicating that the aggregation of the hydrophobic side chains results in transient physical crosslinks<sup>9,14</sup>.

Hydrophobically modified hydrogels of similar composition were formed by simply adding a chemical crosslinking agent during synthesis. The effect of the hydrophobic interactions on the mechanical properties of these gels was evident in the tensile and notch test results.

Hydrogel samples tested in DMF have a tensile strength varying between 12 and 44 kPa and a percent elongation at fracture between 3.5 and 10.5 %. In comparison the samples tested in water demonstrated a tensile strength between 61 to 144 kPa and a percent elongation at failure between 16.4 and 40.8 %. This demonstrates that the hydrophobic aggregation creates regions which act as additional crosslink points allowing the gel to reach higher strength before failure and even more importantly these regions are able to detangle during elongation creating a mechanism of energy dissipation.

The amount of energy adsorption during deformation was quantified during the notch tests in which the average fracture energy ( $G_c$ ) for a set of at least 3 samples tested in DMF and water respectively were 200 J/m<sup>2</sup> and 1100 J/m<sup>2</sup> verifying a significant increase in fracture toughness by hydrophobic modification. This quantifies the amount of energy absorbed in the process of breaking up aggregations of hydrophobic side chains<sup>9,14</sup> ahead of the crack tip before fracture can occur. Conversely, when the samples are swollen with organic solvent, hydrophobic aggregations are not present, as demonstrated in the rheological studies, allowing the gels to fracture with minimal energy absorption.

To remove the speculation that these results are simply due to different swelling ratios, care was taken to ensure that the samples were either tested fully swollen in water (containing approximately 30wt% polymer) or partially swollen in an organic solvent (DMF) at a carefully determined equivalent swelling ratio to ensure that the samples also contained approximately 30 wt% polymer.

## 5. CONCLUSION

Hydrophobically modified poly (N,N-dimethyl acrylamide) PDMAM hydrogels have been synthesised by a statistical copolymerisation reaction with dodecyl acrylate (DA). The long alkyl hydrophobic side chains of DA interact resulting in transient physical crosslinks evidenced by increasing viscosity in uncrosslinked systems of similar composition to the hydrogels. The hydrophobically modified hydrogels on the other hand show significant improvement in tensile strength and toughness when compared to gels with no active hydrophobic aggregation but the same swelling ratio.

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