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Impact-induced gelation in aqueous methylcellulose solutions

Solutions of methylcellulose undergo rapid gelation in response to mechanical impact. This transition is endothermic and provides a route for the uptake of the impact-delivered energy. The resulting attenuation of shockwaves is demonstrated, opening new avenues for various applications.

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Impact-induced gelation in aqueous methylcellulose solutions†

Galit Parvari, [ID] ‡*[a] Yonatan Rotbaum,‡[b] Yoav Eichen [ID] [a] and Daniel Rittel [ID] [b]

Aqueous methylcellulose is an "abnormal" inverse-freezing fluid, which gelates when heated. We ventured to stimulate this phase-transition by mechanical impact, whose resulting shockwaves and local heat could be uptaken by the endothermic gelation. High-speed photography was used to observe this transition in microsecond timescales. This phenomenon enables attenuation of shockwaves.

Inverse-freezing materials have been known for some decades now, and the phenomenon of solidification by heat is observed for several types of molecular systems, including small molecules, polymers, and inorganic materials.[1] Methylcellulose, a linear, partially methylated polysaccharide in wide use in several fields including food, agriculture and pharmacology[2] is among the best studied inverse-freezing, or more specifically reversibly thermo-gelating, polymeric systems.[3] Although the precise structure of the hot methylcellulose hydrogel (MCHG) remains unknown, recent studies show that it includes fibril-shaped components characterized by variable length but a uniform diameter of ϕ = 15 nm.[4] Theoretical modelling suggests that these fibrils are formed by the self-assembly of ring-shaped units of collapsed methyl cellulose polymers.[5] These structures are found after the solutions are annealed at temperatures exceeding their gelation temperature for 30 minutes or longer.[4] To date, the fastest reported formation of MCHG due to sudden temperature rise exceeds 150 seconds.[6]

As is known to chemists from the fields of photo-, sono- and/or mechano- and electrochemistry, heat is not the only form of energy which can drive reactions. As part of our exploration of the inverse-freezing phenomenon, we set out to examine whether the gelation of aqueous methyl cellulose solutions (AMCS) could be induced by mechanical impact. Impacts and their resulting shockwaves have previously been reported to perform chemical transformations, such as the alteration of unit cells and planes in inorganic crystals and ceramics[7] and allotrope conversions from graphene to diamond.[8] Further, shockwaves have been used in astrochemical and more general kinetic studies to carry out reactions between small molecules in the gas phase.[9] Ultrasonic sound waves have been known to induce gelation in metal oxides, known as sonogels for several decades,[10] and more recently gels based on small organic molecules or organic systems incorporating inorganic catalysts are emerging as the promising field of sonochemistry continues to advance.[11] However, to our knowledge, mechanical impacts have not yet been shown to induce solidification in polymeric solutions, particularly not on sub-second timescales.

The reasoning behind our selection of aqueous methylcellulose for these studies, beyond its endothermic gelation,[12] was also its known property of gelation temperature reduction due to increase in polymer concentration. Since impacts provide large local increase of both heat and pressure, we surmised that in this case the two stimuli would induce gelation. This is in contrast to other, "normal" materials, where pressure increase promotes solidification while heat negates it.

Unlike shear thickening fluids, in which large-enough shear forces lead to the emergence of a solid-like response,[13] AMCSs in their liquid state are known to exhibit shear thinning.[14] In many of their common embodiments, AMCSs contain relatively low polymer content ($<20\%$ wt) compared to $>45\%$ wt rigid particles in shear thickening fluids.[13] However, in our recent mechanical studies of MCHGs[15] we found that these gels show considerable stiffening upon dynamic mechanical compression. While MCHGs exhibit almost no strain-rate sensitivity within the quasi static loading regime (strain rates lower than 1 s^{-1}), high strain-rate (>1000 s^{-1}) compression tests reveal significant rate sensitivity and hardening. For instance, at a strain of 15% the flow stress of MCHG submitted to dynamic compression is ~ 20 times larger than its quasi-static counterpart.

[a] Schulich Faculty of Chemistry, Technion – Israel Institute of Technology,
Haifa 3200008, Israel. E-mail: galitpar@technion.ac.il
[b] Faculty of Mechanical Engineering, Technion – Israel Institute of Technology,
Haifa 3200008, Israel
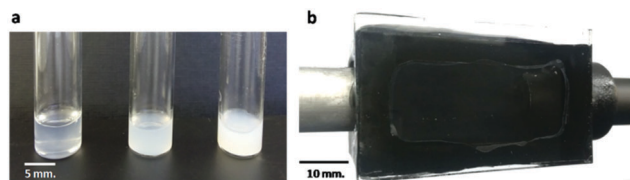
Fig. 1 (a) View of 5.6% wt aqueous methylcellulose in glass vials, from left to right: AMCS ($<T_g$, 26 °C), AMCS transition to MCHG ($\sim T_g$, 42 °C), MCHG ($>T_g$, 50 °C). (b) Side view of the AMCS-filled impact chamber, with blackened walls for background and a front transparent plate. The impacting bar is on the right, and advances into the chamber upon impact.

One explanation for this could be that in the liquid, solvent-rich moieties within the polymer network, there are still enough non-interacting methylcellulose molecules, which upon dynamic compression were induced to associate and add to the load-bearing structures. This motivated further research aimed at exploring the behavior of these materials in their liquid state, especially their ability to respond to fast mechanical impacts.

Previous studies have shown that as AMCSs are heated to their gelation temperatures, they transition from a transparent, colorless liquid to an opaque, white gel (Fig. 1a). The onset of this opacity is known as the "cloud point" and is correlated directly to the gel formation.[16] Utilizing this property, we applied high-speed photography to follow the AMCS as it responds to impact. A custom-made low reflectivity chamber, equipped with a transparent window and an orifice for the insertion of the Hopkinson (Kolsky) impacting bar,[17] was filled with the 5.6% wt AMCS, Fig. 1b. This metal bar transmits shockwaves from the impact by a projectile fired from a pressurized gas gun on its farther side. Verification that this system is suitable for observation of heat-induced gelation in AMCS was performed.[18] Control experiments were performed on water and on 5% wt ballistic gelatin (BG) using the same cell, setup, and impact profiles.

Fig. 2 frames a–d depict time-lapse pictures of the AMC gel following impact (see Movie S1, ESI†). Volume oscillations (pulsations) of air bubbles, trapped inside the gel, indicate the recurrent passage of stress-waves across the sample. An optically opaque front develops on the edge of the bar ~50–100 microseconds after

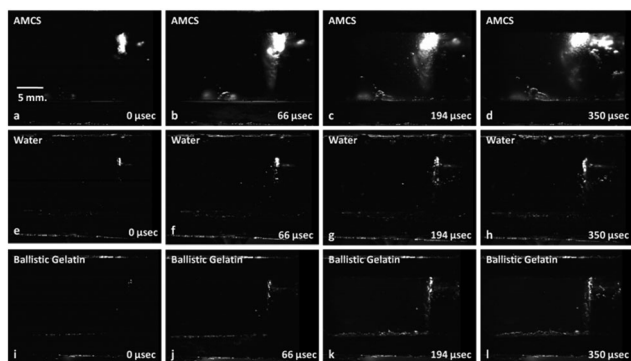**Fig. 2** High speed camera impact-response time-lapse pictures of: (a–d): AMCS 5.6% wt; (e–h): water; (i–l): ballistic gelatin 5% wt. In all cases, t_0 = time of impact on the liquid, sample temperature is 23 ± 2 °C. The impact proceeds from the right.

the impact, and propagates to 3–5 mm depth within the following ~300 microseconds. This front progresses at a velocity of ~50 m s^{-1}, which is much slower than the AMCS bulk wave velocity, which is approximately 1600 m s^{-1}.[15]

In order to rule out reasons for the impact-induced opacity other than gelation, two control experiments were carried out. An experiment with near identical loading conditions was performed on pure water, as they compose 94.4% wt of the AMCS. A second control experiment was carried out on 5% wt 300 bloom ballistic gelatin, the most extensively studied organic aqueous gel material in impact experiments. However, in both control experiments only the formation of trapped oscillating air bubbles was observed, Fig. 2, frames e–h and frames i–l respectively (see Movies S2 and S3, ESI†).

Cavitation as a possible cause for opacity[19] is also excluded since the air bubbles, present throughout the samples, clearly "pulsate" in size. This volume oscillation originates from reflections of the faster travelling elastic stress-waves within the medium, and is incompatible with conditions required to form a cavitation-induced advancing front.

We therefore propose that the process occurring within the sample in the area of the leading edge of the bar originates from the rapid shock-induced gelation of the AMCS following impact. Accordingly, and similarly to cloud points in heated solutions, the opacity would arise from heterogeneous structures of large enough size to scatter visible light. This gelation may stem from several sources, among which are the local heating and the large increase, ~150–1500 fold, of local pressures caused by the impact. It has very recently been shown that high pressure (>5000 atm) induces gelation in room-temperature AMCS, in static, equilibrated systems.[20] While in our work such pressures are not achieved, the rapid change in pressures could play a role in gelation-induction at lower pressures. Phase separation, another reported effect in AMCS under static high pressures (>1500 atm)[21] produces opacity and is possible in our case. However, we observe impact-induced opacity starting from the lower pressure ranges (150 atm) and without gelation, phase separation alone is unlikely to account for the observed impact energy attenuation. Regarding heat, it is well known that the energy supplied by impacts to materials, including glassy polymers, is converted into both heat and stored energy of cold (plastic) work.[22] In our system, the energy delivered into the AMCS samples can be calculated based on the difference between impact and reflected elastic waves, recorded using strain gauges on the impact bar.[18] Taking into account the solution's heat capacity[12b] and starting temperature, this supplied energy is insufficient to raise its temperature to the static, equilibrated temperature of gelation (42 °C). However, as extrapolated from literature, the enthalpy of gelation of AMCS is on the order of 0.7 J mL^{-1}.[12] Thus, measurements and calculations reported in Table 1 clearly indicate that in all cases this impact energy delivered to the sample exceeds the energy required to induce gelation in the volume in which opacity is observed, by a factor of at least 1.7, excluding rises in temperature.

By applying statistical analysis on pixel brightness,[18] the kinetics of gelation may be unveiled, Fig. 3. In a typical

Table 1 Energy values provided by the impacting bar compared to those required for AMCS to undergo gelation, in four typical experiments[a]

Exp. no.	Strain energy [Pa]	Depth of observed gel front [mm]	Volume of formed gel [mL]	Impact energy, in volume of observed gel [J]	Energy required for gelation in the observed volume[b] [J]	Ratio of impact energy to gelation energy
1	1.23×10^6	3.0	0.38	0.47	0.27	1.7
2	1.31×10^6	4.4	0.56	0.87	0.39	2.2
3	2.57×10^6	4.4	0.56	1.43	0.39	3.7
4	2.82×10^6	4.3	0.54	1.53	0.38	4.0

[a] The surface area of the bar is constant for all experiments, 12.7 mm. The depth of the observed gel front was measured from the films. [b] Values extrapolated from literature[12] to be 0.7 J mL^{-1}.

impacted AMCS, a delay time of ∼100 microseconds precedes the formation of the opaque front, which presents a rise-time of ∼200 microseconds. The obtained sigmoidal curves are similar to those reported for gel formation by slow heating in rheological measurements, where the storage and loss moduli are plotted as a function of increasing temperature.[23] It is noted that the delay to the rise time can be shortened when the bar is set closer to the rear wall, and that a second gel front may appear on the chamber's hind wall (see Movie S4, ESI†).

To further corroborate our assumption that the impact energy is uptaken into phase transformation, we studied the ability of AMCS to attenuate impact forces. The liquid, 5.6% wt AMCS was loaded into a custom-built aluminium chamber, $L = 20$ mm, fitted with force sensors and the cell was placed in contact with an instrumented Hopkinson (Kolsky) bar,[18] Fig. 4a. This bar transmits the impact energy to the front wall of the cell and the force sensors measure the force amplitudes, both incoming and passing through the solution. In order to distinguish between geometrical dispersion and attenuation of the shockwave in the medium, control experiments were conducted on water using the same setup and the same impact profiles. Another control is the 5% wt BG, whose organic content in water is similar to that of the examined AMCS. Our measurements show that water barely attenuates these impacts, as seen in Fig. 4b. Comparison of the maximal amplitude obtained at the front and rear sensors shows that water reduces less than 4% of the maximal force and even less of the impact impulse, expressed by the positive slope of the curve. BG shows some improvement in attenuation, with about 13% reduction of the maximal force amplitude, Fig. 4c. In sharp contrast, AMCS exhibits a reduction of about 43% of the maximal force amplitude,
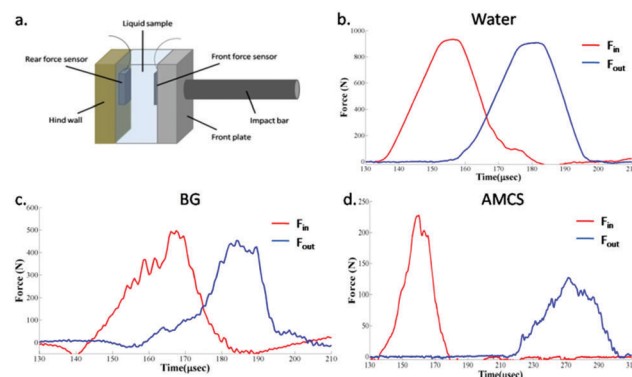
Fig. 4 Impact shockwave attenuation experiments. (a) Scheme of the experiment setup. (b) Impact force attenuation by water. (c) Impact force attenuation by 5% wt ballistic gelatin. (d) Impact force attenuation by 5.6% wt AMCS.

and an impulse attenuation of about 25%, Fig. 4d. The 5.6% wt organic content within the otherwise water solution reduces the shockwaves more than ten-fold compared to pure water, and more than thrice compared to the similar percentage of the BG organic content. Repeated impacts show that these solutions have no "memory" effect and their response to these "follow-up" impacts produces the same attenuation over more than 20 repetitions with a duty cycle of 2 minutes. As this is the time required to reset the measurement in its present configuration, it is possible that regeneration of the properties occurs at much shorter times.

It is noted that although in the experiments for these three materials the bar delivered the same force of ∼12 000 N into the chamber, the amplitudes recorded on the front force sensor (providing the value of forces entering the material, "F_{in}") are considerably different: ∼950 N for water, ∼500 N for BG and ∼250 N for AMCS. Water and AMCS have very similar acoustic impedances (less than 10% difference), and therefore different impedance mismatches between these materials and the metallic front plate are not a likely explanation for the different F_{in} values observed. A more likely cause is the position of the sensor. It is located on the back side of the impacted wall, in the few millimetres thickness which are seen in the movies to undergo gelation. Thus, the impact-induced gelation causes attenuation on the immediate surface of the shockwave-delivering material, thus lowering the shockwave amplitudes the rest of the bulk solution contends with. Comparison of the entering forces' amplitude between BG and AMCS further supports this: since
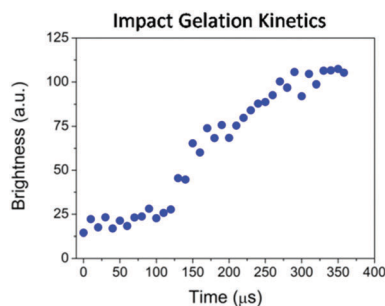
Fig. 3 Gel formation by time from impact (in microseconds), provided by graphical analysis (brightness in arbitrary units), as derived from the high-speed camera films.

BG does not undergo gelation due to impact, its reduction of these forces is considerably smaller than the reduction achieved by AMCS.

In conclusion, AMCS was well-known to undergo gelation in thermally-induced and, recently, in a static pressure-induced process, but to the best of our knowledge this complementary impact-induced gelation is presented here for the first time. While the formation of most complex, supramolecular structures in non-biologically aided chemical systems requires sufficient time for the molecules to sample different mechanistic routes, assume pertinent conformations and orientations, and form the required interactions with their counterparts, in the case of impact-induced gelation such occurrences require only a fraction of the time spans previously under convention. It is noted that the structures of the impact-induced gel are not necessarily as complex, or even contain similar 'building blocks', to those obtained by slow heating. That the process is endothermic can explain the energy uptake and large shock-attenuation observed for impacted, room-temperature AMCS. Because of their unique transition to solids upon heating, this behavior is likely to occur also in other families of inverse-freezing materials. Thus, our findings unfold a new potential to harness these materials for shock mitigation and energy dissipation or storage purposes, as well as for other applications requiring very rapid response of liquid materials.

Conflicts of interest

The authors declare no conflict of interests. G. P., Y. R. and D. R. are the inventors of a PCT application by the Technion, number PCT/IL2018/050606, "Inverse-freezing compositions and use thereof".

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