#### ABSTRACT

## Title of Thesis: Probing the Ability of Flexible Hydrogels to Protect Fragile Objects Sairam Ganesh, Master of Science, 2021

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Hydrogels are networks of polymer chains that are swollen in water. In recent years, several routes have been devised to make hydrogels that are flexible and bendable. This thesis investigates whether such flexible gels can be wrapped around brittle or fragile objects (such as an egg or a fruit) and protect against impact. We study gels made by either physical crosslinking (e.g., gelatin) or chemical crosslinking (e.g., acrylamide) and also the same gels with various particulate additives. None of the bare gels are protective, and nanoparticles like iron oxide or silica do not help. However, the addition of starch granules to the above gels greatly enhances their protective abilities. When a load strikes a gelatin gel with 20 wt% starch, the peak impact force is reduced by 25% when compared to a bare gel without the starch. Correspondingly, the coefficient of restitution (COR) is also lowered by the presence of starch (i.e., a ball bounces less on a starch-bearing gel). We correlate the protective effects of starch granules to their ability to shear-thicken water. When starch granules are gelatinized by heat, they no longer give rise to shear-thickening, and in turn their protective ability in a gel is also eliminated. Our research can guide the rational design of protective coatings or armor for fragile objects, which could be applied in the sports, defense, and consumer sectors.

# Probing the Ability of Flexible Hydrogels to Protect Fragile Objects

By

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# **Dedication**

This thesis is dedicated to my family, for their eternal love and support throughout good times and bad. For without them, I would not be here.

To my mom and dad. Thank you for always encouraging me and motivating me to be better. I will always be thankful to you for making me independent and instill so much confidence that I can take on any challenge with no fear. I know you will be there to back me up as my pillars of strength. Without your sacrifices and never-ending love, I wouldn't have been the person that I am and that I will be. These words are not enough to justify the love and gratitude that I have for you.

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Polymer hydrogels are water-swollen materials formed by crosslinking polymer chains through either physical or chemical bonds.<sup>1</sup> A gel of gelatin (Jell-O) is an example of a physical gel – the protein chains in this gel are connected by physical crosslinks.<sup>2</sup> Chemical gels are formed by free-radical polymerization of water-soluble monomers such as acrylates, and in this case the polymer chains are connected by chemical (covalent) bonds at crosslink points.<sup>3,4</sup> Our laboratory and/ many others around the world have had a long-standing interest in making gels that are flexible, stretchable, and tough.<sup>5-8</sup> For example, we have synthesized gels that can be stretched more than 10 times their original length before breaking.<sup>9</sup>



**Figure 1.1 Concept of the thesis:** A brittle material such as an egg (a), is covered with a flexible hydrogel (b). Can the gel protect the egg? That is, can the gel-covered egg withstand impact onto a hard surface, as shown in (c)? Can the properties of the gel be tuned to maximize protection?

The studies in this thesis were motivated by the question shown in Figure 1.1: can a flexible gel protect a fragile object? As a prototype for a fragile object, we consider a raw egg, which has a thin, brittle shell. If this egg is dropped from a height of about 30 cm (1 foot) onto a hard surface (the ground or a tabletop), the shell will crack. Now, consider a hydrogel that is 2-5 mm thick and flexible enough for it to be wrapped around the egg, as shown in Figure 1.1b. Could we drop this gel-covered egg onto a hard surface from the same height and have the egg withstand the impact? Similarly, could one drop a heavy object onto the gel-covered egg (or hit it with a hammer) and still have the egg remain intact?

The above questions have practical relevance and importance. Specifically, there is a need to protect people (especially their heads) from hard impact. For example, football players wear helmets to protect against the violent impacts they suffer while playing the game. Still, there has been an increase in the concussions suffered by these players in recent years.<sup>10</sup> Football players are also increasingly at risk for brain damage or the early onset of neurodegenerative diseases.<sup>11,12</sup> A better understanding of impact-absorbing materials could pave the way for improved helmet designs to protect these players. Apart from humans, there is also a need to ensure that soft or fragile goods, both natural and manmade, are protected from breaking or being crushed. An example in this regard are Smartphone cases, which have to be as thin as possible and yet protect an expensive device. Currently, in the market, there are commercial products such as Sorbothane® and D3O® that claim to offer superior resistance to impact. These claims seem to rest in patents<sup>13,14</sup>, but there is very little systematic discussion in the scientific literature. Moreover, the above materials seem to be mostly elastomers or foams. We have not found any papers that have explored the use of hydrogels for impact protection.

The focus of this thesis is on hydrogels and their ability to absorb impact and thereby provide protection to underlying objects. Hydrogels are a convenient class of materials for our studies because our laboratory has a lot of experience with them, and we know how to systematically change their properties. The ideal gel should be thin, flexible, and robust. We should be able to wrap it around a fragile object of arbitrary shape without the gel tearing or breaking. Ideally, such a robust gel should be easily synthesizable in the lab from inexpensive precursors, and even better would be if the gel were biocompatible and biodegradable. From a scientific standpoint, we are interested in probing the following questions:

- (1) Are some gels better than others at absorbing impact? If so, what is the distinguishing property (nanostructure) of these gels?
- (2) Are the above differences reflected in the rheological properties of the gels? If so, how? Is it better for a gel to be more elastic or should it be viscoelastic?
- (3) Are there additives that can alter the rheology and/or nanostructure of gels and thereby enhance the gels' ability to absorb impact?

We have conducted systematic studies to answer the above questions. Our studies show that typical gels on their own fail to provide protection against impact. However, our striking discovery is that the addition of starch granules greatly enhances the protective abilities of gels. We show that starch-bearing gels are able to protect fragile objects such as eggs, fruits, and vegetables from hard impact. The impact absorption is quantified in several ways during the course of our studies. Starch granules, when suspended in water, induce a type of non-Newtonian behavior called shear-thickening or dilatancy – this involves the viscosity of the suspension increasing with shear-rate.<sup>15</sup> We hypothesize that this shear-thickening property is related to the gels' ability to absorb impact. Collectively, our studies offer a new paradigm for designing gels to protect underlying fragile objects.

#### 2.1 Impact-Absorbing Materials

Impact-absorbing (also called impact-dissipating, impact-dampening, or shockabsorbing) materials are used for their ability to absorb energy at the moment of impact.<sup>16</sup> They are particularly useful for withstanding "blunt trauma", which is the medical term for injuries afflicted by blunt (rather than sharp) objects such as a heavy weight. At the moment of impact, the incident energy is transferred to the material by making it undergo viscoelastic or plastic deformation.<sup>17</sup> Thus, to absorb impact, the material must be flexible or deformable. In this context, several researchers have been looking at thermoplastic elastomers as potential impact absorbing materials.<sup>18,19</sup> The impact absorbing property of these materials has been primarily attributed to their viscoelastic nature.<sup>20,21</sup>

Viscoelasticity is a property of material which has both viscous and elastic characteristic when deformation is induced.<sup>22</sup> Viscous materials flow when shear is applied (e.g., honey resists shear flow when stress is applied.). Whereas elastic materials stretch when stress is applied and return to original configuration when stress is removed(e.g., a rubber band returns to original shape after it is released from stretching). Viscoelastic materials show both these properties. Purely elastic materials don't dissipate energy when force/load is applied<sup>23</sup>, but viscoelastic material loses energy due to plastic deformation.<sup>24</sup> This makes them suitable for applications involving impact absorption and vibration damping.

In addition, impact-absorbing properties have also been associated with materials like foams, which have a cellular matrix<sup>25</sup> that helps in distributing energy evenly and quickly.<sup>25,26</sup> In this case, the structure of the cellular matrix determines the impact absorbing capabilities of the foams. Studies have also shown that elastomers-based foams have been used as impact absorbing materials used in transporting precious cargo.<sup>27,28</sup> These foams have force dissipating qualities due to their unique structure. Although the size of these foams that are too big and hence cannot be used as flexible protective layer around fragile objects.

In biology, impact absorption is associated with the spine, and with the spinal discs in particular.<sup>29</sup> The spinal or intervertebral discs are composed of two gel-like materials, one that forms a soft core and the other a stiffer shell. This gel-like discs are responsible for absorbing any shock on the spine from different activities such as walking, sitting, or running. There also are examples of hard materials in biology that are still able to absorb impact, and one example is the armor or shell of armadillos.<sup>30</sup> This hard armor contains scales that allow it to dissipate the energy of impact.

#### 2.2 Physical and Chemical Hydrogels

Hydrogels are crosslinked networks of polymer chains that are swollen with water.<sup>31,32</sup> They have myriad applications ranging from tissue engineering to consumer products.<sup>5,33</sup> They can be classified into two categories based on the types of bonds that constitute their crosslinks: physical gels, where the bonds are physical, i.e., non-covalent, and chemical gels, where the crosslinks are covalent. Chemical gels are formed by the free-

radical polymerization of a water-soluble monomer and a crosslinker.<sup>34,35</sup> For example, a monomer with one double bond such as acrylamide (AAm) is mixed in water with a crosslinker such as N,N'-methylenebisacrylamide (BIS), which has two double bonds. In addition, an initiator like ammonium persulfate (APS) and an accelerant like tetramethylethylenediamine (TEMED) are added to the water. When this mixture is heated, APS thermally decomposes into free radicals. AAm molecules capture the free radicals and start to grow AAm chains. BIS molecules can also capture the free radicals, and these will connect to more than one growing AAm chain, i.e., crosslink the AAm chains into a network. The net result is the hydrogel, i.e., a 3-D network of chains, with the water entrapped in the network.

The above AAm-BIS networks tend to be stiff and brittle. One simple way to improve the flexibility of chemical gels is to substitute the BIS crosslinker with laponite (LAP) nanoparticles.<sup>36</sup> Laponite is a type of synthetic clay and the particles are in disk shape with a diameter of 25 nm and a thickness of 1 nm. The particles carry a negative charge on their surfaces. When a monomer like AAm is combined with LAP particles along with APS and TEMED, the resulting polymerization gives rise to an AAm-LAP gel that is much more flexible and stretchable than a AAm-BIS gel. The crosslinks in this gel are the LAP particles, i.e., the AAm chains grow from the particle surfaces. The interaction between the chains and the particles has a covalent character and thus the gel is still a chemical gel and will not dissolve when placed in water. Note that a gel is not obtained if either the AAm or linear polymer chains are simply mixed with the particles.

Physical gels are typically obtained by physical crosslinking of polymers in water. A major focus of this thesis is on gels of gelatin. Gelatin is synthesized by alkaline or acidic hydrolysis of the native protein collagen; note that the chains of gelatin are in a denatured form.<sup>37</sup> A gelatin gel is generally formed by dissolving gelatin powder in water at a temperature above  $\sim 40^{\circ}$ C and cooling to room temperature.<sup>38</sup> Upon cooling, strands of gelatin aggregate and bind to each other at junction points. At these junctions, the strands form triple-helices by non-covalent interactions.<sup>38-40</sup>

#### **2.3 Starch and its Properties**

Starch is a polysaccharide produced by plants such as rice, wheat, corn and potato.<sup>41</sup> Commercial starch is a white powder with a granular structure, with the granule size ranging from 2 to 150 µm depending on the type of starch.<sup>15,42</sup> Starch granules are composed of two polymers of glucose: amylose and amylopectin. Chains of amylose are mostly linear while those of amylopectin are highly branched.<sup>43,44</sup> The higher the amylopectin content, the more 'waxy' the starch appears. Starch granules are insoluble in water at room temperature. Upon heating beyond their 'gelatinization temperature', the starch granules swell in water (Figure 2.1) and the viscosity of the suspension increases. With further heating, the swollen granules break and lose their shape, with the amylose and amylopectin leaching into solution as dissolved chains.<sup>45,46</sup> The viscosity continues to rise and eventually the suspension is converted into a gel (paste-like material)<sup>47</sup> and it remains a gel upon cooling.<sup>48</sup> In this gel, starch chains are connected to each other by physical bonds. The use of starch as a thickener for soups and sauces in cooking is because of its ability to gelatinize upon heating. The value of the gelatinization temperature depends upon the type of starch and can range from 55 to 85°C.<sup>49</sup>



Figure 2.1 Schematic showing the gelatinization of starch granules upon heating.

Suspensions of starch granules in water (termed 'Oobleck' in a children's story by Dr. Seuss) exhibit non-Newtonian properties.<sup>50</sup> For example, a person can walk rapidly on a pool containing a corn-starch suspension (i.e., the fluid transforms into a solid). The property referred to here is shear thickening<sup>51</sup>, where a material transitions from fluid to solid (i.e., its viscosity sharply increases) as the shear imposed on it is increased. Shear thickening of a suspension of particles is attributed to the creation of transient hydrodynamic clusters ('hydroclusters') by the jamming of particles.<sup>52,53</sup> This clustering leads to an increase in viscosity. When the shear is ceased, the clusters dissipate away into individual particles and the viscosity reverts to a low value. Incidentally, when starch is gelatinized, the sample will cease to exhibit shear-thickening and instead will show shear-thinning (decrease in viscosity with increasing shear-rate). This is because, upon

gelatinization, the granules will be partly or completely dissolved, and thus the sample will no longer be a suspension of particles.

#### 2.4 Rheology:

One technique used in this thesis is rheology. Rheological measurements are used to study how materials flow or deform under stress. This can reveal the relation between the micro/nano structure of the material and its macroscopic properties. Rheological studies on gels are usually conducted under dynamic oscillatory shear, where the sample is deformed using a sinusoidal strain  $\gamma = \gamma_0 \sin(\omega t)$ . In this equation,  $\omega$  and  $\gamma_0$  are the frequency and the amplitude of the strain, respectively. The stress response will also be a sinusoidal function  $\sigma = \sigma_0 \sin(\omega t + \delta)$  where  $\delta$  is the phase angle. This equation is rewritten in the following way:

$$\sigma = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t)$$
(2.1)

In this equation, G' is the *storage* or *elastic* modulus and G" is the *loss* or *viscous* modulus. For these values to be representative of the material, the measurements must be done in the *linear viscoelastic* (LVE) *regime*. In the LVE regime, G2 and G" are only functions of  $\omega$ , and a log-log plot of the moduli vs. frequency (called the frequency spectrum) is used to characterize the material. A gel will have an elastic response, and hence its elastic modulus G' will be nearly independent of  $\omega$ , and moreover, G' will be higher than G". The value of G' quantifies the *stiffness* of the gel. The fact that G' is independent of  $\omega$  implies that the network structure in the gel is permanent, i.e., it does not relax, regardless of the time scale. Another parameter to characterize viscoelastic materials is the loss tangent tan  $^{TM}$ , which is the ratio of G''/G2. The higher the tan  $^{TM}$ , the more the viscous contribution to the rheology.

# **Chapter 3:** Starch-Bearing Gels and Their Ability to Protect Fragile Objects

#### 3.1 Introduction

In this chapter, we will present our results on a new class of impact-absorbing hydrogels. We will show that starch granules are a key additive that can enhance the ability of gels to absorb impact, and this is shown to work with both physical gels (specifically gelatin) as well as chemical gels (specifically, acrylamide). Both sets of starch-bearing gels are flexible and robust and can be easily wrapped around a fragile object of arbitrary shape. Both gels are synthesized easily in the lab from readily available and cheap precursors. In addition, the gelatin gel is both biocompatible and biodegradable.<sup>54</sup> We have conducted a series of systematic experiments using a custom-built load cell to investigate the impact-absorbing properties of various gels. Two measurable parameters are identified that correlate with superior impact absorption. We also confirm that impact-absorbing gels are able to protect fragile objects such as eggs and fruit against hard impact.

Why do starch granules enhance the ability of gels to dissipate impact? To clarify this aspect, we have studied the dynamic rheology of gels with and without starch. Gels generally display elastic rheology, i.e., their elastic modulus G2 far exceeds their viscous modulus G3. Nevertheless, they do have some viscoelastic character and we find that starch granules enhance the viscoelasticity, i.e., the viscous (dampening) character of the gels. This is reflected in a higher loss tangent tan  $\frac{7M}{7}$ , which is the ratio of G3/G2. Starch granules are known for their ability to shear-thicken water.<sup>55</sup> Shear-thickening is a property associated with flowing suspensions, whereas in a gel, the starch granules are expected to be immobilized. Nevertheless, we show that if the shear-thickening of starch in water is eliminated (by heat-induced gelatinization), so are the protective abilities of the starchbearing gel.

#### **3.2 Experimental**

**Materials.** The monomers acrylamide (AAm), N,N'-methylene-bis(acrylamide) (BIS), gelatin from porcine skin (type-A), N,N2-dimethylacrylamide (DMAA); the initiator ammonium persulfate (APS); and the accelerant N,N,N',N'-tetramethylethylenediamine (TEMED) were all purchased from Sigma-Aldrich. The inorganic clay Laponite® XLG (LAP) was obtained from Southern Clay Products, while nanoparticles of iron oxide and carbon black were purchased from LanXess Chemicals. Cornstarch granules (product name: HYLON®VII) were purchased from Ingredion. The granules have an amylose content of 70% and the size range of the granules is from 10-30 µm. Potato starch granules were purchased from Sigma-Aldrich with the granules having a size range of 10-50 µm.

**Gel Preparation.** To prepare gelatin gels, gelatin powder (with starch granules) was mixed vigorously with deionized (DI) water using a stir bar at a temperature of 60°C. The resulting solution was poured into a container (Petri dish or vial) and cooled to room temperature to form the gel. Typical concentrations were 10 wt% gelatin and 10 wt% starch, unless otherwise specified.

To prepare chemical gels, a solution of the monomer AAm (10 wt%, equivalent to 1 M) was made in DI water that had been degassed by bubbling nitrogen. For BIS-crosslinked gels, 2.2 mol% of BIS with respect to monomer was added to the AAm solution. For LAP-crosslinked gels, 2 wt% of LAP particles were first suspended in DI water and mixed vigorously with a stir bar, and then the AAm was added to it. Starch granules (typical concentration 10 wt%) were also suspended in the monomer solutions for some of the experiments. Then, the initiator APS (200  $\mu$ L of a 0.1% solution) and the accelerator TEMED (30  $\mu$ L) were added and vortex-mixed. Different volumes of the above mixture were poured into a container (Petri dish or vial) and allowed to polymerize at room temperature to achieve gels of different thicknesses.

**Rheological Studies.** The rheological experiments were done on an AR2000 rheometer (TA instruments) at 25°C using a parallel plate geometry (20 mm in diameter). For the oscillatory shear experiments (dynamic rheology), gel samples were cut into discs of 20 mm diameter and 3-4 mm thickness. Through stress-sweep experiments, the linear viscoelastic region of samples was obtained, and strain (1%) within the region was used to run the frequency-sweep experiments.

**Drop-Weight Tests.** A HX711 module with an A/D converter chip was connected to a load cell (5 kg). The module and the load cell were purchased from amazon.com. A flat thin impact plate (1-mm thick) was attached on top of the load cell, which was subsequently drilled onto a base plate (5-cm thick). The thin impact plate is 3D printed using an Ender 3-D printer using a black colored plastic filling, whereas the base plate is made of wood.

The setup was then connected to a laptop through an Arduino USB cable, and the experiment was run using an open-source Arduino software. The load cell is first calibrated using known weights ranging from 1g to 500g. Next, the gels are placed on the impact plate and known weights are released from a height through a hollow tube for precise trajectory. Force vs. time curves are obtained as an output.

#### **3.3 Results and Discussion:**

The goal of our study was to examine whether flexible hydrogels could protect fragile objects. As models for fragile objects, we used (a) standard chicken eggs (long dimension  $\sim 3$  cm), which have a thin, brittle shell; (b) mini or 'grape' tomatoes ( $\sim 1-2$  cm); and (c) blueberries ( $\sim 1$  cm or less). The tomatoes and blueberries get crushed if a heavy weight ( $\sim 50$  g or higher) is dropped directly on them. The eggs crack if dropped in free fall from a height of  $\sim 30$  cm (1 foot) or higher. We were interested in exploring whether a flexible gel could be wrapped around the above objects and protect them from damage under the above conditions. First, we had to ascertain that the gel itself was both flexible and robust. That is, we wanted to ensure that the gel itself would not break or tear under the impact of a heavy weight, and moreover, that the gel would be robust enough to remain intact when wrapped around a fragile object with an arbitrary shape.

Туре	System	Property	
Physical gels	Gelatin	Flexible	
	Agarose	Brittle	
Chemical gels	AAm+BIS	Brittle	
	AAm+Laponite	Flexible	
Additives	System	Property	
Iron Oxide Carbon Black	Gelatin	Flexible	



Flexible gel



Brittle gel

**Figure 3.1.** Gels that were tested in this study. Some of the gels were brittle and these were not considered further.

We examined a number of gels with the above criteria in mind, including both physical gels (where the crosslinks are physical, i.e., non-covalent bonds, such as hydrogen bonds or ionic bonds) and chemical gels (where the crosslinks are covalent bonds). The tested gels are listed in Figure 3.1. Gels of the denatured protein, gelatin (typical concentration 10 wt%) were found to be flexible and robust, and these will be our main system of interest going forward. Conversely, gels of the polysaccharide agarose were not flexible or robust. Specifically, a 2% agarose gel would break if we tried to fold a rectangular strip. Thus, agarose gels are unsuitable for our purpose and were discarded.

Next, we prepared chemical gels of acrylamide (AAm) crosslinked with a multifunctional monomer, i.e., N,N'-methylene-bis(acrylamide) (BIS). We used the standard recipe from our previous studies, which is a gel of 10% AAm and 0.34% BIS. But, as we had observed before, this AAm-BIS gel is brittle and does not withstand bending

or twisting. Therefore, we used another recipe from our past studies, which is a gel of 10% AAm crosslinked by 2% laponite (LAP) particles. This is also a chemical gel, with the LAP particles acting as multifunctional crosslinkers for AAm chains. The AAm-LAP gel is flexible and robust: it can be stretched to more than 10 times its original length without breaking. Based on these studies, the AAm-LAP gels were suitable for our purpose, but not the AAm-BIS gels.

Although gelatin and AAm-LAP gels were flexible enough, initial studies showed that they did not provide sufficient protection to fragile objects. We varied the concentration of gelatin in the former and the concentrations of AAm (monomer) and LAP (crosslinker) in the latter, but these variables did not have a significant influence on the results. We then explored whether additives such as nanoparticles or microparticles could enhance the protective abilities of gels. Two kinds of particles were tested in a gelatin matrix, as indicated in Figure 3.1: iron-oxide (Fe<sub>2</sub>O<sub>3</sub>) and carbon black (CB). Gelatin gels with 2% Fe<sub>2</sub>O<sub>3</sub> or 5% CB remained flexible and stretchable – however, their protective abilities were unchanged.



**Figure 3.2** (A) Photo and schematic of (A) a gelatin gel; and (B) a gelatin-starch gel. The flexibility of the latter is shown by wrapping it around an egg in (C).

We then proceeded to test starch granules as an additive, and we found that they did enhance the protective properties of both gelatin and AAm gels. These results are described below in detail. Figure 3.2 depicts the gelatin-starch system. The matrix is 10% gelatin in water, which forms a clear gel (A). The protein chains form triple-helical crosslinks, as shown in the schematic. To make a gelatin-starch gel, we add 10% of starch granules (sizes of 10 to 30  $\mu$ m) to the hot solution of 10% gelatin and then cool the mixture to room temperature. The starch granules are dispersed in the gel matrix, but the composite gel remains strong, yet flexible (B). Note that the gel has a white color due to light-scattering from the starch granules. The photo in (C) shows that this gel can be easily wrapped around a fragile object such as an egg.

#### 3.3.1 Gelatin-Starch Gels: Load Cell Experiments



**Figure 3.3** A load-cell is used to quantify the impact-absorbing properties of gels. A schematic of the setup is shown in (A) and a photo is shown in (B).

We quantified the effect of starch on gelatin gels using a load cell, the setup of which is shown in Figure 3.3. A base plate (5-cm-thick block of wood) is attached to an impact plate (1-mm-thick plastic), which in turn is connected to a load sensor. A mass is dropped onto a gel sample (disc of 6-cm-diameter and varying thickness) placed on the impact plate, and the force detected by the sensor is recorded as a function of time. The hollow transparent plastic tube allows the weight to travel along a precise vertical trajectory before it contacts the sample. For the data shown in Figure 3.4, we used gels of 4-mm thickness and dropped a mass of 50 g onto the gels from a height of 20 cm.



**Figure 3.4** Force vs time plots when a mass of 50 g impacts various gels from a height of 20 cm. Data are shown for gels of 10% gelatin, 10% gelatin and 10% starch, and 10% gelatin and 20% starch.

The plots in Figure 3.4 are for the force recorded by the load sensor as a function of time following impact. Each curve shows a peak and then levels off at the same steadystate value of 0.5 N (corresponding to 50 g). In the case of a 10% gelatin gel, the force increases to 1.1 N at its peak. The mass then bounces off the gel, and thereby, the recorded force decreases beyond the peak. The mass then hits the gel a second time and this is manifested as a small second peak in the force. Thereafter, the mass stabilizes and settles down on the gel and thereafter the force is constant.

In the case of a gelatin gel with 10% starch, the shape of the curve is similar, but the peak force is lowered to 0.9 N. Lastly, in the case of the gel with 20% starch, the peak force is further lowered to 0.8 N (23% lower than for the bare gelatin). Such dissipation of the peak force signifies impact-absorption by the gel, and we can directly attribute this effect to the presence of starch. The impact-absorption is also reflected in another feature, which is that the second peak is nearly absent for the starch-bearing gels, indicating that the mass bounces less on these gels.



**Figure 3.5** Effects of different variables on the peak force recorded by the load cell in impact experiments: (A) 50 g dropped on gels of different thickness; (B) Higher weight of 100 g dropped on gels of different thickness; and (C) Weight of 50 g dropped on 4-mm-thick gels from different heights. Error bars represent standard deviations.

Impact-dissipation by starch-bearing gels is observed consistently in all our experiments with the load-cell. The experimental details do influence the precise extent of dissipation in the peak-force, and this is seen in the plots in Figure 3.5. The y-axis in all these plots is the peak force. In (A) and (B), we compare gels of different thicknesses. As the gel thickness is increased from 0.5 to 8 mm, the peak force is reduced, and this is true for both bare gelatin gels as well as the same gels with 10% starch. Thus, a thicker gel, on its own, can dissipate impact. However, in all cases, the gels with starch show a lower peak force, indicating that they are more effective at dissipating impact. When the mass is increased from 50 to 100 g, the peak force is roughly doubled, indicating a larger impact. But with this higher mass also, the starch-containing gels are able to reduce the impact substantially. In (C), the same weight (50 g) is dropped from different heights on gels of 4-mm thickness. As the height increases, the peak force also increases, indicating that the impact is larger, but we again note a reduction of  $\sim 12$  to 15% in the peak force when the gel contains starch.

#### 3.3.2 Gelatin-Starch Gels: Coefficient of Restitution

Impact dissipation by gels can also be quantified by measuring the coefficient of restitution (COR). For these experiments, a 1-cm spherical glass marble is dropped from rest onto a surface (e.g., a gel) from a height *H*, and the height *h* to which the marble bounces is measured (see Figure 3.6A). The COR is defined as  $COR = \sqrt{h/H}$  and it is a measure of how elastic the collision is between the marble and the surface. If the marble is bounced on the hard tabletop, the COR is 0.86. We then tested the COR with various gels

of 4-mm thickness. In the case of a 10% gelatin gel, the COR of the marble is reduced to 0.60 (Figure 3.6B). For the same gel with 10% starch, the COR of the marble is 0.54 and with 20% starch, the COR is further reduced to 0.48. This reduction in COR with increasing starch in the gel is statistically significant (p < 0.007 in all cases). The COR reduction again reflects the ability of starch-bearing gels to dissipate the impact of a collision. Note that the greater the starch content, the more the impact is dissipated: this is observed both with the peak force in Figure 3.4 and the COR in Figure 3.6.



Figure 3.6 Coefficient of restitution (COR) for a marble dropped on a hard surface or various gels (4-mm thick). (Left) Schematic of the setup. (Right) Mean COR values for various gels. Results for p values from significance-testing of various data-pairs by the Student's t-test are also shown.

#### **3.3.3 Gelatin-Starch Gels: Rheology of the Gels**

Why does starch enhance the impact-absorbing ability of gelatin gels? To gain insight into this, we measured the dynamic rheology of a 10% gelatin gel without starch and with 10 or 20% starch. The data in Figure 3.7 are for the elastic modulus G2 and the viscous modulus G" as functions of frequency  $\omega$ . All samples show the expected rheology of gels, with G2 and G" being independent of frequency and G2 > G". Two trends are found in the data. First, the value of G2 (the gel modulus) is slightly higher in the presence of starch, indicating that the starch granules make the gel stiffer. Second, the loss tangent tan TM = G''/G2 increases from 0.02 for the bare gelatin gel to 0.05 when 10% starch is present to 0.09 when there is 20% starch. This implies that there is much more viscous dissipation from the gel in the presence of starch. However, the precise reason for the enhanced viscous dissipation is not clear.



**Figure 3.7** The elastic modulus G2 and the viscous modulus G3 are plotted as functions of the frequency 7for (A) a 10% gelatin gel; (B) a gel of 10% gelatin and 10% starch, and (C) a gel of 10% gelatin and 20% starch.

#### 3.3.4 AAm-Starch Gels

We also tested whether the addition of starch granules influences the properties of a chemical gel, specifically that of AAm-LAP. As noted in Figure 3.1, a gel of 10% AAm crosslinked by 2% LAP is flexible and robust, and we used this gel as the control. For comparison, we made the same gel with 10% starch granules. The two gels (each 4-mm thick) were tested using the load-cell, with a weight of 50 g dropped onto the gels from a height of 20 cm. The results (Figure 3.8) are similar to those for the gelatin gels: the peak force is reduced from 1.2 N for the AAm-LAP gel to 0.9 N for the same gel with starch. Thus, the effect of starch in dissipating impact is also seen in these chemical gels.



**Figure 3.8** Force vs time plots for a gel of 10% AAm + 2% LAP and for a gel with the same AAm and LAP and an additional 10% starch. The latter is then heated to  $70^{\circ}$ C to gelatinize the starch, cooled back to room temperature, and retested. In all cases, the data are recorded for a mass of 50 g dropped onto the gels from a height of 20 cm.

Starch granules when suspended in water make the fluid undergo shear-thickening, i.e., the viscosity of the suspension increases over a range of shear-rates (see Chapter 2). Is this property of shear-thickening connected to the impact-absorption? In this regard, we discussed in Chapter 2 that the shear-thickening will be eliminated if the starch granules get gelatinized. Our AAm-starch gels allow us to test the effects of gelatinizing the starch by heating the gels to 70°C (this could not be tested with gelatin-starch gels because those gels would be converted to sols upon heating). Following the heating regimen, we cool the AAm-starch gel to room temperature and repeat the load-cell experiment. The results in Figure 3.8 show that the peak force increases back to 1.2 N, similar to its value for the control AAm gel without starch. Thus, the impact-dissipating effect of starch is found only when the starch granules are intact. When the granules get gelatinized, the starch loses its shear-thickening property, and in turn, the composite gel also loses its impact-dissipating property. This can be seen in their COR values as well (Appendix I).

#### **3.3.5 Testing if Gels Can Protect Fragile Objects**

Finally, we put our gels to the test that we had originally mentioned: regarding their ability to protect fragile objects. First, experiments are done with eggs. As shown in Figure 3.9, a standard chicken egg is wrapped with a rectangular strip of gel (dimensions of 17 cm x 6 cm x 4 mm) and then dropped in free fall from a height of 15 in. (Note that, for consistency, the egg is always oriented with its pointy end parallel to the ground.) When a 10% gelatin gel is used (Figure 3.9A), the egg breaks upon impact. However, when a gel of 10% gelatin + 10% starch is used (Figure 3.9B), the egg survives the impact and remains

intact. This result was repeated from the same height with more than 10 eggs and the same above result was obtained in every case.



**Figure 3.9** (A) Egg wrapped in a 10% gelatin gel breaks when dropped from a height of 15 in. (B) Egg wrapped in a 10% gelatin + 10% starch gel remains intact when dropped from a height of 15 in.

Next, a different set of experiments were conducted with small, delicate objects, i.e., fruit like mini-tomatoes and blueberries. In this case, we wrap the fruit in a gel in a manner similar to ravioli, using two gel layers, each a disc of 6-cm diameter and 4-mm-thick (Figure 3.10). The fruit is placed on the first layer, then the second layer is placed on top and the ends are sealed by pressing both layers to form contact adhesion. A mass of 50 g is then dropped on the covered fruit from a height of 8 in (Figure 3.10A). Figure 3.10B shows results with blueberries using this 'ravioli' design. When the gel is 10% gelatin (control), the blueberry gets squished. However, when a gel of 10% gelatin + 10% starch

is used (Figure 3.9B), the blueberry is left intact. Thus, Figures 3.9 and 3.10 collectively show that gels with starch are able protect different kinds of fragile objects.



Blueberry

**Figure 3.10** (A) Fragile objects (blueberries) are encased in a gel sandwich ('ravioli' design). A weight of 50 g is then dropped onto the covered fruit from a height of 8 in. (B) Photos before impact, at the moment of impact, and after impact. The blueberry remains intact if covered by a gel of gelatin+starch.

#### **3.4 Conclusions:**

We have demonstrated the synthesis of a composite gel which has better impact protection and force dissipation compared to various control gels. The gel is proved to be flexible and robust and can be used to cover various fragile and brittle materials without any type of breakage. The key to achieving the result of decrease in peak forces is due to the addition of additive of starch granules in the hydrogel matrix. It has been proven to work in both cases of a physical gel system such as gelatin and in the case of chemical gel system such as AAm. The results have been concluded in four types of experiments split in both quantitative and qualitive manner. A load cell setup had been employed to find the peak forces of each sample when there is certain weight dropped on top of the sample. Force against time graphs indicated the decrease in the force values as starch composition is increased in the composite gel system indicating further, the role of starch. Other variables such as thickness of gel, the height from which the weight is dropped, and different weights were also varied to notice curves collaborating with the result of composite gel being better. Other techniques such as Coefficient of restitution were also measured and a decrease in the value was noticed as the starch content increase in the composite gels. Qualitatively, brittle material such as an egg was wrapped with control gel and the composite gel containing the starch and egg survived from any breakage from a free fall drop from the same height in the case of composite gel, which further helped proving the point that composite gels had better impact dissipating qualities. Further, fragile objects such as small squishy fruits were taken and wrapped from bottom and top using the same gels, also resulted in similar findings where the composite gel containing starch could protect the fruits from getting squished due to a weight dropped on them.

Overall, although many gels are flexible and robust, not all have any protective abilities or force dissipating abilities, compared to the composite gel we have synthesized. It is a novel method of synthesizing flexible, robust gels which could absorb impact and provide with protective abilities for fragile objects, and the key reason lies with the addition of starch granules which we hypothesize provides shear-thickening ability and a more viscoelastic nature to the hydrogel.

#### 4.1 Conclusions

In this thesis, we have demonstrated that a flexible composite hydrogel can be easily synthesized which can have better force dissipating qualities and better protective abilities compared to normal gels. We have engineered flexible, robust hydrogels which can be used to cover brittle and fragile objects such as an egg or small squishy fruits such as blueberry and tomatoes and can protect them from breakage when some weight or force is applied on them, which would generally result in their breakage. Our method to create such a composite gel is extremely simple, quick, and easy. It is also biocompatible and inexpensive compared to the options which are available in the market. Moreover, the gels also have a good mechanical integrity and are not easily breakable.

To demonstrate the force dissipating and impact absorbing abilities of the gel, we have provided multiple experiments and results through which it has been concluded that the composite gels have the said qualities. We have quantified the values of the peak forces under different variables such as the thickness, weights used and different heights, proving that there is a decreased peak force obtained between the composite gel containing starch and the control gel without the starch granules present. Also, COR was calculated which also showed a decreasing trend in the composite gels when starch was increased. To have a visual representation of the working of these gels, we covered egg with our gel and showed protection of the egg from breakage when dropped in free fall. Similar studies were also conducted with small fragile fruits such as blueberry and tomato to observe similar protective abilities. Our composite gel is a great example of novel protective hydrogels which can be used to cover and protect fragile objects from breakage under duress and stress. In closing, we note that our approach is simple and also versatile, this can be extended in many ways to create impact dissipating gels with unique properties.

#### **4.2 Future Directions**

Our approach can be extended to create different hydrogels with starch granules in the network and by varying the concentration of starch in the matrix of the hydrogel. Because our approach is simple and straightforward, it can be easily utilized in creating different gels containing even higher concentrations of starch granules or other shear thickening systems. Accordingly, it can be explored more in the future towards making a coating of the gels so that a thin layer would be enough to suffice having protective layer for different types of materials.

Another area of importance that is needed to be studied further is the drying of the gels, as hydrogels tend to dry out if left out in open, hence a thin layer of coating to protect drying of gels would be great to increase the longevity of the composite gels. Currently, there is very less studies done towards soft materials such as hydrogels being used as protective and impact dissipating systems. There is a lot of scope for future based on the work that we have presented.

## Abbreviations

AAm	Acrylamide
BIS	N,N'-methylenebisacrylamide
LAP	Laponite®
APS	Ammonium persulfate
DMAA	N,N2-dimethylacrylamide
СВ	Carbon Black
TEMED	N,N,N',N'-tetramethylethylenediamine
DI water	Deionized Water
COR	Coefficient of Restitution

### **APPENDIX I: SUPPLEMENTARY FIGURES**



Figure A.1 Mean values of the coefficient of restitution (COR) for a marble dropped on a hard surface (control) or 4-mm thick gels of (1) 10% AAm, (2) 10% AAm with 10% starch, and (3) Gel 2 after gelatinization (heating to 70°C). Error bars correspond to standard deviations from multiple measurements. Results for p values from significance-testing of various data-pairs by the Student's t-test are also shown.

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