Scalable manufacturing of biomimetic moldable hydrogels for industrial applications

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Hydrogels are a class of soft material that is exploited in many, often completely disparate, industrial applications, on account of their unique and tunable properties. Advances in soft material design are yielding next-generation moldable hydrogels that address engineering criteria in several industrial settings such as complex viscosity modifiers, hydraulic or injection fluids, and sprayable carriers. Industrial implementation of these viscoelastic materials requires extreme volumes of material, upwards of several hundred million gallons per year. Here, we demonstrate a paradigm for the scalable fabrication of self-assembled moldable hydrogels using rationally engineered, biomimetic polymer–nanoparticle interactions. Cellulose derivatives are linked together by selective adsorption to silica nanoparticles via dynamic and multivalent interactions. We show that the self-assembly process for gel formation is easily scaled in a linear fashion from 0.5 mL to over 15 L without alteration of the mechanical properties of the resultant materials. The facile and scalable preparation of these materials leveraging self-assembly of inexpensive, renewable, and environmentally benign starting materials, coupled with the tunability of their properties, make them amenable to a range of industrial applications. In particular, we demonstrate their utility as injectable materials for pipeline maintenance and product recovery in industrial food manufacturing as well as their use as sprayable carriers for robust application of fire retardants in preventing wildland fires.

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Industrial settings present many unique and complicated engineering challenges. Inefficiencies arise in manufacturing because large volumes of material need to be pumped from one location to another and vast lengths of pipe of varying diameters must be cleaned frequently (1). Applications as diverse as hydraulic fracturing and cosmetics rely on processable fluids with complex viscoelastic properties. Moreover, many products and coatings are applied through spraying, which often requires uniform application and tunable retention of solvent and/or product. The advent of macromolecular chemistry has provided myriad polymeric materials that are used in diverse applications, including as food/cosmetic additives and viscosity modifiers. Several aqueous-based applications have exploited covalently cross-linked hydrogels, which comprise a class of soft materials that bind and retain large amounts of water and exhibit broadly tunable mechanical properties. However, the irreversibility of their cross-links is severely limiting and many applications would benefit enormously from new technologies allowing for stimuli-responsive aqueous viscosity modification and/or the ability to rearrange their shape in response to applied stress (2).

Recent advances in supramolecular chemistry and materials science are enabling unique solutions to many critical industrial challenges via the production of moldable polymer networks (2, 3). Moldable networks (or hydrogels in the case of an aqueous solvent) exploit specific and tunable noncovalent interactions and exhibit many of the properties of traditional chemically cross-linked hydrogels; however, they allow for precise tuning of flow properties of physically cross-linked hydrogels to meet the engineering requirements for diverse applications, from injection, pumping, or spraying. These hydrogels can exhibit viscous flow under shear stress (shear thinning) and rapid recovery when the applied stress is relaxed (self-healing). Although a variety of materials have been developed that demonstrate these beneficial properties (2, 3), there is a dearth of systems sufficiently simple and cost-effective to manufacture on large scales to enable their utility in a range of industrial settings. Indeed, many have exploited self-assembling peptide domains found widely in nature as cross-linking points between polymers or proteins for hydrogel formation (4–11). Moreover, systems have been reported leveraging synthetic host–guest motifs based on the macrocyclic oligomers cyclodextrin and cucurbit[n]uril that form inclusion complexes with a wide variety of guest molecules (12–24), or natural receptor–ligand pairs, such as (strep)avidin with biotin (25, 26). In each of these examples, self-assembly of functional materials via noncovalent, intermolecular interactions with dynamic and reversible macroscopic behavior allows for shear-responsive moldability of the formed materials; however, their applicability in many industrial applications is severely limited by challenging, costly, and poorly scalable synthesis of the macromolecular components, requiring resource-intensive protein engineering or complex, multistep functionalization chemistries.

Significance

Many industrial applications often require, or would benefit greatly from, "smart" materials with complex viscoelastic properties. Traditional materials often fail to adapt or respond to changing environmental conditions, limiting their use in many industrial applications that require flow, injection or spraying, or are prepared from starting materials that are too expensive, poorly scalable, or toxic to people or the environment. Here, we exploit biomimetic multivalent noncovalent interactions to build fully scalable hydrogel materials with complex viscoelastic properties from renewable and environmentally benign materials. These low-cost, safe materials have the potential to enable novel applications; here we use them for pipeline maintenance in food and beverage manufacturing and as carriers to enhance the utility of fire retardants in fighting wildland fires.

Crucial requirements to the industrial translation of hydrogels of this type are energy-efficient synthesis, modular modification, and finely tunable control over mechanical properties, as well as facile and cost-effective manufacturing on a large scale. Here we develop a paradigm for the fabrication of self-assembled moldable hydrogels amenable to a range of industrial applications from renewable and environmentally benign starting materials. We then demonstrate the applicability of these materials for pipeline maintenance in the food and beverage industries and as carriers of fire retardants for more effective wildland fire management.

Results and Discussion

Polymer–Nanoparticle Hydrogel Production and Characterization. Within the field of self-assembly, polymer–nanoparticle (PNP) interactions have arisen as a simple route to assemble tunable and self-healing polymeric materials without the need for complex synthetic approaches or specialized small-molecule binding partners (27–29). The complementary affinity between polymers (molecular binders) and hard nanoparticles (clay nanosheets/silicates) emulates natural systems and has been used to fabricate biomimetic hydrogels of incredible strength (30, 31). The transient and reversible nature of polymer adsorption to the nanoparticles imparts these materials with shear-thinning and rapid self-healing properties. When the hydrogel is strained, chains adsorbed to the particles are under tension and detach from the particle surface to relax this tension, allowing the gel to flow with sufficient applied stress (shear thinning). Upon relaxation of the applied stress, the gel rapidly reforms (self-healing) as polymers adsorb to particles in a new configuration. Moreover, it has previously been reported that select cellulose derivatives can adsorb onto colloidal silica particles (32). Herein, we report the preparation and application of biomimetic PNP-based hydrogels driven by noncovalent interactions between renewable and environmentally benign polysaccharides and colloidal silica nanoparticles (CSPs) (Fig. 1). Polysaccharides provide an attractive starting material on account of their availability from renewable resources, aqueous solubility, high molecular weight, diverse chemical functionality, low cost, environmental degradability, biocompatibility, and large-scale production (33). Moreover, CSPs are also produced on a large scale and used across many applications ranging from personal care products to fining agents in industrial beer and wine production (34).
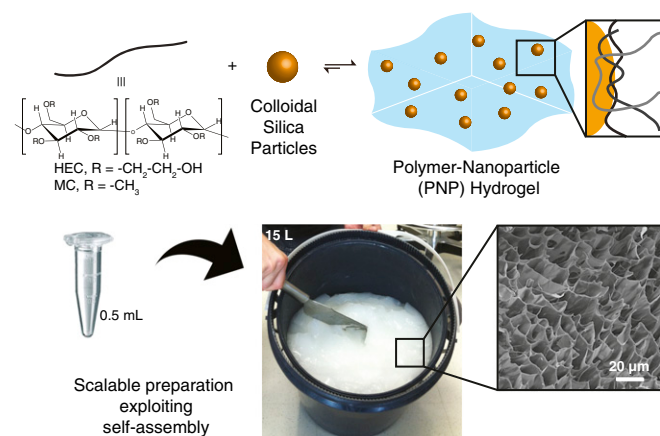

Fig. 1. Self-assembled moldable hydrogels from renewable and environmentally benign starting materials. PNP hydrogels can be prepared by exploiting strong yet dynamic multivalent and noncovalent interactions between CSPs and mixtures of biopolymers (as illustrated; polymer chains in grayscale and nanoparticles in orange), including HEC and MC. Hydrogel formation is driven simply by mixing of the component parts and thus allows for facile linear scaling of the formulation from 0.5 mL to over 15 L.
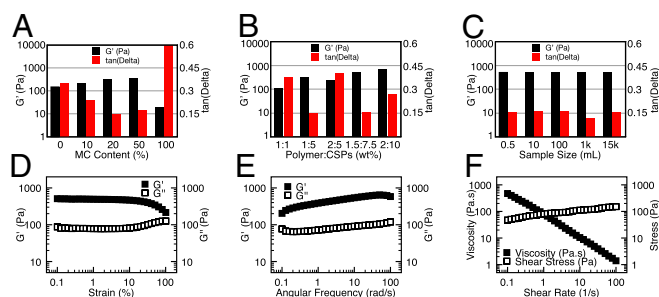

Fig. 2. Rheological characterization of PNP hydrogels. Oscillatory rheological properties of hydrogels from (A) polymer [1% (wt/wt)] and CSPs [5% (wt/wt)] at different loadings of MC in the polymer fraction, (B) HEC:MC [80:20% (wt/wt)] and CSPs at various loadings, and (C) HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSPs [7.5% (wt/wt)] prepared on various scales. All values collected at ω = 10 rad/s, ε = 2%, 25 °C. (D) Strain-dependent (ω = 10 rad/s, 25 °C) and (E) frequency-dependent (ε = 2%, 25 °C) oscillatory shear rheology of hydrogels from HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSPs [7.5% (wt/wt)]. (F) Steady shear rheology of hydrogels from HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSPs [7.5% (wt/wt)].

Initially, we screened a variety of commercially available polysaccharide compounds for their ability to form PNP hydrogels with CSPs (D_H ~15 nm) under ambient conditions. We set the concentration of the various polysaccharides to 1% (wt/wt) and screened various concentrations of CSPs [1–10% (wt/wt)]. We previously determined that efficient cross-linking in PNP hydrogels necessitates three criteria: (*i*) strong affinity between the nanoparticles and the polymer chains [i.e., the free energy gain (ε) resulting from adsorption of a polymer chain to the surface of a nanoparticle should be greater than or comparable to the thermal energy (k_BT)]; (*ii*) the nanoparticle diameter should be comparable to, or less than, the persistence length (l_P) of the polymer strands (required to favor polymer bridging of multiple nanoparticles over polymer wrapping around individual particles); and (*iii*) the number density of polymers and particles must allow for an average of at least two interactions per particle and polymer to comprise a cross-linked network (29). When these criteria are met, hydrogel formation is favored.

Through our qualitative screens we identified that hydroxyethylcellulose (HEC) and methylcellulose (MC) rapidly form robust PNP hydrogels when mixed with CSPs (Table S1). In each of these cases, hydrogel formation is exclusive to the presence of both CSPs and cellulose derivatives as solutions of CSPs [1–10% (wt/wt)] and cellulose derivatives [1% (wt/wt)] alone are each low-viscosity liquids. We then prepared a series of materials with various combinations of HEC and MC (Table S2) to optimize the formulation for initial mechanical properties, self-healing behavior, and stability over time. In these experiments the total concentration of polymer was maintained at 1% (wt/wt) whereas CSP concentration was altered between 1–5% (wt/wt). Although all of the formulations investigated demonstrated good or excellent mechanical properties and self-healing initially (Fig. 2A), many of them suffered from syneresis over time (Table S2). However, at HEC:MC ratios of 80:20, robust PNP hydrogels were formed and mechanical properties were maintained for at least 1 wk. These gels exhibited a shear storage modulus of G′ ~500 Pa (ω = 10 rad/s, ε = 2%) and comprised elastic gels, because the storage oscillatory shear modulus (G′) was much greater than the loss oscillatory shear modulus (G″). For these studies, we used G′ as a measure of hydrogel strength and the tanδ (tanδ = G″/G′) as a measure of hydrogel elasticity. Interestingly, if CSPs bearing different surface chemistry are used (Ludox TMA), the gels exhibit dramatically different mechanical properties (Fig. S1), whereby TMA-based materials, despite having only a slightly reduced G′ value, exhibit a much higher tanδ value, and consequently, a much higher degree of fluidity.

These data indicated that selective adsorption of the modified cellulose chains to CSPs enables cross-linking and gel formation, supporting our physical picture of gel assembly.

Using a formulation of HEC (0.8%):MC (0.2%):CSP [5% (wt/wt)], we then sought to examine the contribution of polymer molecular weight to the overall mechanical performance. We screened hydrogels comprising combinatorial mixtures of high- and low-molecular-weight HEC and MC polymers (Table S3). From these studies, it was apparent that HEC molecular weight was the primary determinant of hydrogel strength, whereby a decrease in molecular weight from M_v ~1,300 to M_v ~720 kDa resulted in a dramatic decrease in material properties. In contrast, lowering the MC molecular weight from M_v ~90 to M_v ~60 kDa exhibited no significant decrease in the initial material properties yet improved gel stability over time. Although only two different molecular weights were examined for each polymeric component, these results indicate that polymer molecular weight can be exploited to tune gel properties.

Following the initial component screen, we sought to determine the impact of component loading and stoichiometry on the resulting hydrogel behavior (Fig. 2B). We observed that polymer: CSP stoichiometry of 1:5 (wt/wt) maximized hydrogel strength and elasticity, whereas deviation from this ratio (either with more polymer or more CSPs) led to lower G′ values and more fluid-like materials. Interestingly, increasing the overall loading of these components while maintaining this stoichiometry increases G′ while leaving tanδ unchanged, indicating a maintenance of the overall degree of elasticity.

With favorable formulations in hand, we investigated both the reproducibility and scalability of the preparation of these materials. PNP gels comprising HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSP [7.5% (wt/wt)] were prepared four times in parallel and the mechanical properties demonstrated excellent reproducibility (Fig. S2). We then scaled the production of these materials in a linear fashion from 0.5 mL to over 15 L (Fig. 2C). These observations demonstrated that self-assembly processes can be extremely powerful for hydrogel formation because manufacturing of these materials could be easily scaled in a linear fashion over 4.5 orders of magnitude in the laboratory without alteration of the mechanical properties of the resultant materials. The facile scalability of PNP hydrogels occurred because gel formation and mechanical properties are solely dependent on the selective adsorption between cellulose derivatives and CSPs, which, on the molecular size scale, is indifferent to total production volume.

Strain-dependent oscillatory rheology (Fig. 2D) of the HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSP [7.5% (wt/wt)] PNP hydrogels displayed an extremely broad linear viscoelastic regime and network failure only at high strains (>20%), indicating a wide processing range and shear-thinning behavior. The frequency dependence of the storage and loss oscillatory shear moduli in the linear viscoelastic regime confirmed hydrogel-like behavior because G′ was dominant across the whole range of frequencies observed (0.1–100 rad/s; Fig. 2E). Moreover, the observed shear-thinning behavior was corroborated with steady shear rheometrical measurements (Fig. 2F), which indicated that the materials exhibit a power-law decrease in viscosity with increasing shear rate.

New Materials Enable New Applications. New materials can enable new applications as well as provide unique solutions to existing challenges. Thus, with scalable PNP hydrogels prepared from environmentally benign and renewable starting materials and exhibiting useful and tunable flow behavior in hand, we sought to test their applicability in addressing several important industrial challenges. We focused on using these materials for pipeline maintenance in food and beverage manufacturing and as carriers for fire retardants for wildland fire prevention. A central feature of these two areas is the inapplicability of previously reported materials systems on account of a lack of scalability and/or required mechanical properties coupled with poor biocompatibility or

a lack of environmental degradability. In addition, water is grossly consumed in both of these applications, owing to inherent inefficiencies. However, water is an invaluable natural resource and total industrial self-supplied freshwater withdrawals in the United States reached an astonishing 15 billion gallons per day in 2010 (not including use for thermoelectric power or irrigation) (35). Recent water conservation efforts on account of long-standing droughts in California and elsewhere highlight the great need to develop novel materials to more efficiently address complicated engineering challenges.

PNP Hydrogels for Pipeline Pigging in Food and Beverage Manufacturing. Pipeline pigging refers to the practice of using devices to perform various maintenance operations (e.g., cleaning or inspecting) on a pipeline without stopping the flow of the product in the pipeline (the name "pigging" arises from the squealing and snorting sound traditional mechanical "pigs" produce while traveling through a pipe) (1, 36). These processes have been used for many years to clean large-diameter pipelines in the oil industry; however, the use of smaller-diameter pigging systems has seen recent growth in industries handling products as diverse as paints, chemicals, and cosmetics to avoid cross-contamination and to increase product yields and reduce waste. However, for all of its benefits, the process is limited by the availability of materials amenable to both the product and pipeline system at hand. For example, a pipeline cannot be "pigged" traditionally if it contains butterfly valves or reduced-bore ball valves, or comprises various sizes of piping (common in many older factories) (36). Moreover, many standard pigging systems cannot be used with food products. Currently, most operators of batch processes in food production ensure maximum product recovery from a line by flushing the line with water (in some cases, this can sometimes be done with the next product). During these processes it is often necessary to downgrade or dump the contaminated or diluted portion of the product. Further, because many food products lead to pipeline fouling, cleaning agents (e.g., hot caustic soda solutions) are often used, which must be subjected to effluent treatment or costly waste disposal (37–39). Many, if not all, of these problems could be eliminated with next-generation pigging systems, which would serve to both increase production and reduce the environmental impact of diverse batch operations.

One promising approach reported recently is based on the use of a slurry of ice for pigging, which could be easily applied in the food and beverage industries (40–42). Because these ice slurries are pumpable, they can form a soft plug capable of adapting its shape to fill complex pipe architectures, enhancing produce recovery and pipeline cleaning. However, ice production, transportation, and storage are expensive, energy-intensive, and poorly scalable. Moreover, because ice melts rapidly when present in small particles, the distance over which an ice slurry may function as an effective pig is severely limited (43, 44). This is particularly problematic in industries where most product movement occurs during the summer months (e.g., wine production). We therefore sought to exploit our PNP hydrogel materials in engineering a cost-effective and scalable method for pipeline pigging amenable to use in the food industry.

We centered our efforts on large-scale wine manufacturing, which is highly dependent on product transfer through diverse pipeline systems during the many stages of production, including crushing of the fruit, fermentation, aging, and bottling (Fig. 3A). According to the Wine Institute, wine production in the United States is approaching 1 billion gallons/year and anecdotal evidence from within the industry indicates that up to 2% of product may be lost during production. Indeed, in large wineries, over 20 cases of wine may be lost per transfer. Beyond safety (both for use in food products and for the environment) a viable pigging system must be tasteless, scentless, and colorless to avoid any perturbation of the product. Because each of the components of our scalable hydrogel materials is highly pure, chemically
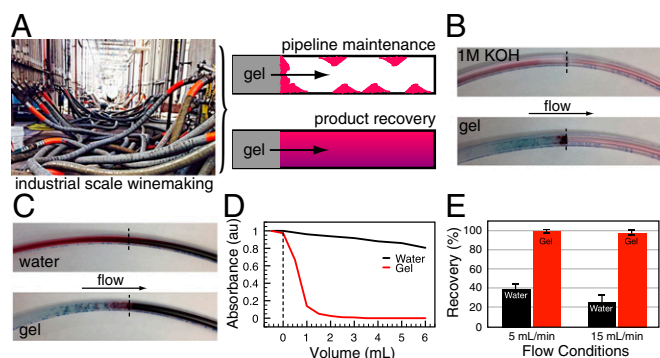
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Fig. 3. Pipeline pigging for enhanced product recovery and more efficient pipeline maintenance. (*A*) Industrial wine production requires frequent pipeline cleaning and maintenance to limit contamination between products. Transfer of product through pipelines at the various stages of production typically leads to losses of ~2% of the total product volume. (*B*) Investigation of either KOH (1 M; *Top*) or PNP hydrogel (*Bottom*) for the removal of grape residue from aqueous solutions of Purple 8000 grape concentrate [10% (vol/vol)] allowed to foul a test pipe (d = 1/2 inch, l = 24 inches) for 1 h. (*C*) Aqueous solutions of Purple 8000 grape concentrate [10% (vol/vol)] were propelled through a test pipe (d = 1/2 inch, l = 24 inches) with one pipe volume (~77mL) of either water (*Top*; consistent with industry standard practice) or PNP hydrogel (*Bottom*). (*D*) By monitoring the absorbance of the Purple 8000 (λ_{max} = 535 nm) in the eluent over time, it was possible to determine (*E*) the recovery of Purple 8000 from the pipeline (using a cutoff at dilution to 80%; error bars represent one SD with n = 3; P < 0.0001 for both groups).

simple, and widely used in food production, we hypothesized that the components would perform well in a blind taste test. For these experiments, one of three identical samples of wine was adulterated with PNP hydrogel [to a concentration of ~1% (wt/wt) hydrogel]. Three blinded professional wine makers were then asked to identify the adulterated sample. Collectively, the wine makers were incapable of detecting the adulteration with statistical significance. We therefore proceeded to investigate these materials for pipeline pigging both in the recovery of product and in pipeline cleaning.

Initially we investigated a selected PNP hydrogel formulation {HEC [1.2% (wt/wt)]:MC [0.3% (wt/wt)]:CSP [7.5% (wt/wt)]} for pipeline cleaning applications. This formulation was chosen on account of its material properties (maximizing G′ and minimizing tanδ) and low solids content (comprising 91% water). Laboratory-scale experiments were designed to emulate current approaches in batch processes in industrial-scale food and beverage manufacturing. A test pipe [diameter (d) = 1/2 inch and length (l) = 24 inches] was allowed to foul with Purple 8000 crushed-grape concentrate [10% (vol/vol)] for 1 h. Then, either KOH (1 M; industry standard) or PNP hydrogel was pumped through the pipe (at a rate of 15 mL/min) to remove the grape residue. As seen in Fig. 3B, PNP hydrogel provides greatly enhanced scouring of the piping over the industry standard, which often requires soaking for several hours before flushing through the pipe to effectively dislodge grape residue. Aqueous solutions of Purple 8000 grape concentrate [10% (vol/vol)] were then propelled through a test pipe (d = 1/2 inch and l = 24 inches) with one pipe volume (~77 mL) of either water (consistent with industry standard practice) or PNP hydrogel. By monitoring the absorbance of the Purple 8000 (λ_{max} = 535 nm) in the eluent over time, it was possible to determine the recovery of Purple 8000 from the pipeline (using a cutoff at dilution to 80%; Fig. 3 C–E). PNP hydrogel formulations clearly create a defined interface with the model product, allowing for greatly enhanced product recovery over the industry standard. Finally, we have demonstrated that these materials can be used with industry-standard pumps (e.g., progressive cavity pumps, peristaltic pumps, or diaphragm pumps). These materials exhibit the potential to serve as scalable, food-safe, environmentally benign and water-wise

options for pipeline pigging in industrial scale food and beverage manufacturing.

PNP Hydrogels as Carriers for Fire Retardants for Wildland Fire Prevention. According to the National Interagency Fire Center (NIFC), wildland fires in the United States destroy almost 10 million acres/y and the cost of fighting wildland fires in the United States is estimated to be roughly $2 billion annually. The NIFC is a federal organization coordinating the efforts of multiple federal agencies, including the Bureau of Land Management, Bureau of Indian Affairs, US Fire Service, US National Park Service, US Fish & Wildlife Service, and the US National Association of State Foresters. Fire retardants, typically comprising ammonium polyphosphates in aqueous formulation, constitute a primary tactical resource in fighting wildland fires, with over 30 million gallons pumped annually in the United States alone (45).* However, their tactical utility is severely limited by their current formulations, which must often be dropped from low altitudes on account of drift or rapid evaporation while falling, or they are incapable of retaining these retardants at the target site. Another class of highly effective retardants are aqueous film-forming foams, which comprise perfluorinated surfactants, the primary fire extinguishing chemical driving their performance (45). Wastewater from the use of these foams and its treatment have been the focus of rigorous investigative studies because fluorinated surfactants have been found to contaminate groundwater around the site of application (46) and thus have emerged as priority environmental contaminants on account of concerns regarding their environmental persistence, potential for bioaccumulation, and toxicity (46–50). The use of these foams is therefore highly restricted. Furthermore, "water-enhancing gels," which are aqueous dispersions of superabsorbent polymers similar to the materials used in disposable diapers, have demonstrated the capacity to extend water's effectiveness in preventing fires from starting and/or spreading (51–53). These water-enhancing gel materials, however, are nondegradable and petroleum-derived, posing significant environmental concerns and limiting their applicability.

Considering the major limitations of current technologies, an environmentally benign, aqueous-based material platform capable of imparting enhanced drop capabilities such as reduced drift, greater canopy penetration, and the potential to be dropped from greater altitudes, along with the ability to retain ammonium polyphosphates at the target site, would enable more effective and safe tactical approaches to fighting wildland fires. Moreover, enhanced retention of these retardants would enable application at sites of particularly high fire danger (e.g., roadsides or targets for lightning strikes), potentially preventing a vast number of wildland fires from starting in the first place.

Select PNP hydrogels {HEC [0.32% (wt/wt)]:MC [0.08% (wt/wt)]: CSP [2% (wt/wt)]} were formulated with Phos-Chek LC95A, an ammonium polyphosphate retardant that is typically dispersed in water. Phos-Chek LC95 is the most commonly used fire retardant in the United States, with ~15 million gallons pumped annually (45). We used the same component stoichiometry as above, but at a lower concentration so that these materials can be sprayed in a fashion similar to standard aqueous formulations of the retardant yet have the potential to provide better canopy penetration and dramatically enhanced persistence at the site of application. These properties are particularly intriguing for fire prevention in high-risk areas. Current fire retardant formulations include small amounts of thickening agents (e.g., Palygorskite clay); however, the efficacy of current formulations is completely negated by subsequent drops of water (limiting tactical approaches to directly

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*Yount B (2015) *Summary of National Retardant Use for 2015* (United States Department of Agriculture, Missoula, MT).
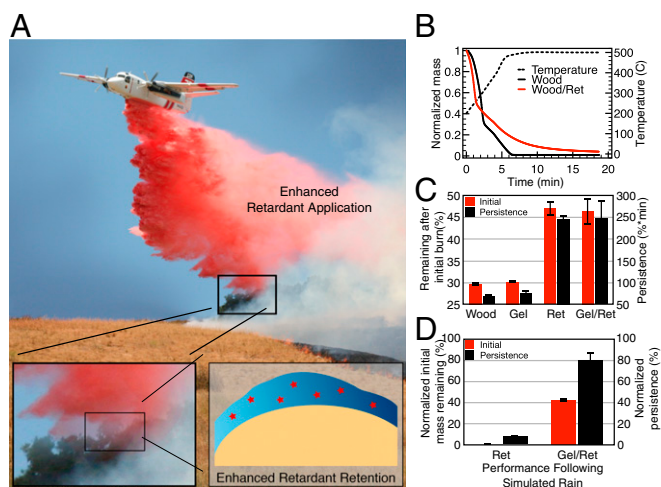
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Fig. 4. PNP hydrogels as carriers of fire retardants. (*A*) Select PNP hydrogels formulated with Phos-Chek LC95A fire retardant can be sprayed in a fashion similar to standard aqueous formulations of the retardant yet provide enhanced retention at the source of the fuel. (*B*) TGA of both treated and untreated model high-surface-area-to-volume fuel (e.g., pinewood flour). The fire retardant both decreases the dramatic initial mass loss and inhibits subsequent mass loss. (*C*) Quantification of the mass remaining after the initial burn and the persistence of mass over time for untreated wood, wood treated with hydrogel alone, wood treated with aqueous retardant formulation, and wood treated with retardant-containing hydrogel formulation (error bars represent one SD with $n = 3$; $P < 0.0001$ between samples treated with and without retardant). (*D*) TGA analysis of wood samples treated with standard aqueous retardant formulation and retardant-containing hydrogel formulation following simulated rainfall. Normalization was performed on the data, whereby 0% reflects the response of wood alone and 100% reflects the response of wood freshly treated with standard aqueous retardant formulation (error bars represent one SD with $n = 3$; $P < 0.0001$ between samples with treated with gel and those treated with standard aqueous formulations).

fighting fires) or even by minimal rainfall (precluding preemptive use). In these studies, a model high-surface-area-to-volume fuel, pinewood flour, was treated in various ways and thermal gravimetric analysis (TGA) was performed to characterize mass loss upon burning (Fig. 4*A*). TGA was performed on account of its prevalence in studies regarding material ignition and decomposition processes, as well as quantification of flame-retardant performance (54, 55). We quantified both the mass remaining after the initial burn and the persistence of mass over time for untreated wood, wood treated with hydrogel alone, wood treated with aqueous retardant, and wood treated with retardant-containing hydrogel (Fig. 4*B*). When comparing untreated wood and wood treated with standard aqueous retardant formulations, it is apparent the fire retardant both decreases the initial mass loss and inhibits subsequent mass loss. The addition of hydrogel in either case does not significantly alter the performance of the retardant. However, when wood samples treated with standard aqueous retardant formulation and retardant-containing hydrogel formulation are subjected to simulated rainfall their subsequent performance differs dramatically (Fig. 4*C*). To more easily identify the performance of the treatments following simulated rainfall, we normalized the TGA data to reflect the response of wood alone (yielding a performance rating of 0%) and wood freshly treated with standard aqueous retardant formulation (yielding a performance rating of 100%). This assay clearly indicates that hydrogel formulations retain the ammonium polyphosphate retardants on the fuel through simulated rainfall, whereas standard formulations are washed away, losing their performance. These data indicate the potential of these PNP hydrogel formulations to provide dramatically enhanced retardant persistence at the site of application while allowing for facile application through standard spray or drop approaches.

Conclusions

In summary, we have prepared self-assembled moldable hydrogels using dynamic and multivalent PNP interactions between commercially available cellulose derivatives and silica nanoparticles. The flexibility of the formulation provides a useful tool with which to tune the macroscopic properties of the resulting materials. Owing to the self-assembly process leading to hydrogel formation and the thermodynamic stability of the hydrogel state, fabrication of these materials is linearly scalable across many orders of magnitude, demonstrated herein between 0.5 mL and 15 L. This versatility is not only an asset for industrial development but also offers the opportunity to improve our understanding of challenging property–structure relationships and supramolecular material formation. Moreover, we investigated the use of these materials in two different industrial applications: pipeline maintenance in food and beverage manufacturing and as carriers to enhance the efficacy and safety of fire retardants in fighting wildland fires. Given the importance of pipeline maintenance across many industrial applications, our results suggest ways to develop more efficient techniques for pipeline maintenance by exploiting self-assembling hydrogels such as those described herein. Furthermore, the ability of these materials to be sprayed in a fashion similar to standard aqueous formulations of common fire retardants, yet impart dramatically enhanced retention of the retardants at the site of application, has the potentially to yield new and safer approaches to fire prevention in high-risk areas. Overall, this paper demonstrates a class of moldable hydrogels where the simplicity/scalability of their preparation, their availability from inexpensive renewable resources, and the tunability of their properties, when coupled with their exceptional functional performance, are highly distinguished for many important industrial applications.

Materials and Methods

PNP Gel Preparation. PNP gels were prepared by first dissolving HEC (M_v ∼1,300 or 720 kDa; Sigma) and/or MC (M_v ∼90 or 60 kDa; Sigma) in water (30 mg/mL) with stirring and mild heating. CSPs [Ludox TM-50; D_H ∼15 nm; 50% (wt/wt); Sigma] were diluted to 15% (wt/wt) solutions. HEC/MC polymer solution (150 μL) and CSP solution (300 μL) were then added together and mixed well by vortex (some samples were mildly centrifuged to remove bubbles arising from mixing). Large-volume preparation of PNP gels used the same ratios scaled linearly and mixing was performed with an impeller mixer.

PNP Gel Characterization. Rheological characterization was performed using a TA Instruments AR-G2 controlled-stress rheometer fitted with a Peltier stage. All measurements were performed using a 25-mm plate geometry and analyzed using TA Instruments TA Orchestrator software. SEM images where acquired using a FEI XL30 Sirion microscope using a beam voltage of 5 kV. Lyophilized samples were pressed onto carbon paint and sputter-coated with Au/Pd (60:40) before imaging.

Pipeline Pigging Experiments. Two experiments were designed to investigate the performance of the PNP hydrogels in pigging applications. For the first experiment, to simulate wine product movement, an aqueous solution of Purple 8000 grape concentrate [10% (vol/vol)] was pumped into a test pipe ($d = 1/2$ inch and $l = 24$ inches), followed immediately by either hydrogel (prepared as mentioned above) or water (control experiment consistent with industry practice). The absorbance ($\lambda_{max} = 535$ nm) of the eluent was monitored over time at varying flow rates. Analysis of the proportion of aqueous Purple 8000 recovered from the pipe was determined using a cutoff at 80% dilution. For the second experiment, to simulate pipeline cleaning, Purple 8000 solutions were pumped into the test pipe and allowed to settle for 1 h before draining. Following this, either hydrogel (prepared as mentioned above) or water was pumped through the pipe at varying flow rates for cleaning. Analysis of cleaning potential was determined by monitoring absorbance ($\lambda_{max} = 535$ nm) of the eluent over time. All experiments were performed in triplicate.

Fire Prevention Experiments. Two experiments were designed to investigate the performance of the PNP hydrogels in fire prevention applications. Initially, wood flour (System Three, Inc.) was dried at 120 °C under vacuum for 24 h. Dry wood flour (100 mg) was mixed with each treatment (20 mg),

including water (control), gel, retardant solution, and gel containing retardant. Each treatment group was dried at 120 °C under vacuum for 24 h before analysis. Using TGA, samples (~20 mg) were heated at a rate of 50 °C/min to 500 °C and then maintained at 500 °C for 15 min while monitoring weight loss. Subsequently, each treatment group was subjected to simulated rain, whereby samples were washed with water with vigorous shaking (1 mL for 10 s), isolated by filtration, and dried at 120 °C under vacuum for 24 h before TGA analysis. All experiments were performed in triplicate.

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