

Nanodiamond-Infused Microgels for pH-Tunable Rheology, Lubrication, and UV Protection

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Ultraviolet (UV) radiation exposure poses a potent threat to human health, with skin cancer cases still prevalent. While skin care formulations mitigate the situation, inherent problematic issues, including toxicity and unpredictable rheology, exist in many of these systems. In this study, the functional properties of carboxylated nanodiamond (cND) infused polyacrylic acid (PAA) hydrogels are explored as a potential alternative in terms of their UV protection, rheology control, and lubrication (skin-feel) properties. cNDs, carbon-based nanoparticles (≈ 200 nm), are used because of their innate biocompatible nature, UV filter capacity and tunable surface functional groups allowing for modulating interaction with the PAA matrix. In particular, it is demonstrated these properties can be controlled through varying pH and cND concentration. Dynamic rheology and confocal fluorescence microscopy reveal different degrees of microstructural reinforcement enabled by changing the nature of polymer-cND and interparticle interactions above (pH 5.5) and below the pKa (pH 4.1) of carboxyl groups. Tribological experiments in contrast, suggest that lubrication properties to be primarily governed by microgel particles at either pH. Most importantly, UV absorption and simulated irradiation studies show these systems to be photostable with broad-spectrum UV attenuation capacity rivalling that of commercial systems, while preserving gel microstructure after prolonged UV irradiation.

1. Introduction

Ultraviolet (UV) radiation-induced skin damage^[1,2] is the primary cause for skin cancer,^[3] the most prevalent form of cancer in the United States, accounting for ≈ 9500 new cases reported every day.^[4,5] While sunscreen formulations are typically used to mitigate the deleterious effects of UV radiation, there is growing health concerns with their usage. These include, but are not limited to, skin sensitization and carcinogenesis as well as aquatic toxicity of systems with organic UV absorbers,^[1,6] warranting the need to develop safer and sustainable formulations. New sunscreens also need to provide broad-spectrum UV attenuation in the UV-B (290–320 nm) and UV-A (320–400 nm) range while controlling formulation rheology and lubricity, which affect film formation and tactile perception of the sunscreen during application on the skin.^[7] Zinc oxide and titanium dioxide (TiO_2) nanoparticles, the most common broad-spectrum inorganic UV filters, have come under scrutiny due to their UV-activated photocatalytic nature that can generate reactive oxygen species (ROS) on the epidermis

and cause oxidative damage to skin cells.^[8,9] The high loadings of TiO_2 and UV exposure also unreliably alter formulation rheology due to particle sedimentation or flocculation, affecting stability.^[10,11] Nanodiamonds (NDs) entrapped in an appropriate microgel matrix offers a promising alternative with its inherently benign and biocompatible nature, photostable and UV attenuation abilities^[9,12–15] complemented by its antioxidant,^[9] rheology modulation,^[16–18] and lubrication^[19] characteristics.

NDs are carbon-based multifunctional nanomaterials that contain a sp^3 hybridized core, a graphitic outer shell and multiple surface functional groups that can be readily tuned.^[16,20,21] Antioxidant properties of NDs stem from the presence of these functional groups and C=C bonds that scavenge ROS and minimize oxidative skin damage, unlike TiO_2 nanoparticles.^[9] Poor skin permeation coupled with their biocompatibility and low cytotoxicity allow NDs to also function well as drug-reservoirs for topical drug delivery and skincare products.^[15,22] The high refractive index of NDs promotes light scattering while the

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DOI: 10.1002/adfm.202504604

functional groups and graphitic shell absorb UV photons, allowing broad-spectrum UV filtering. The UV attenuation efficiency is proportional to the concentration and size of ND particles.^[12] While individual particles are 3–5 nm in size, strong interparticle interactions cause the NDs to exist as self-assembled core (100–200 nm) aggregates.^[23–25] Additionally, external stimuli such as pH can play a significant role in controlling the nature and extent of interparticle interactions and consequently particle size and UV protection.^[15]

Other carboxyl group functionalized nanoparticles have been studied in the literature with varying core materials, including carbon-based, metal-based, metal oxide, ceramic, polymeric, and semiconductive nanoparticles. Among alternative nanoparticles that can be surface-functionalized with carboxyl groups, silica, gold and silver nanoparticles have been explored in UV protectant formulations in their non-carboxylated forms. Silica nanoparticles are widely used in topical formulations primarily to scatter UV radiation and improve the dispersion of organic UV absorbers; however, pure silica nanoparticles typically do not provide strong UV absorption and are most effective when combined with other UV-absorbing agents.^[26,27] Similarly, studies have shown that agglomerates of gold nanoparticles can enhance UV protection when used in conjunction with absorbing agents by providing a physical barrier to UV light.^[28,29] Another alternative, silver nanoparticles, have been identified as potential candidates capable of UV protection,^[30–32] however, the potential toxicity of silver nanoparticles is a subject of ongoing debate which may restrict their suitability in topical formulations.^[33,34] Our choice of cNDs is not only based on their surface chemistry, but also on their specific set of physicochemical properties that enhance several functionalities, including rheological tunability, lubrication, UV protection, biocompatibility and mechanical reinforcement, all combined into a single additive.

Although some of these functional attributes are known, interaction of NDs with formulation excipient hydrogels and the corresponding correlation with rheology, lubrication and UV attenuation critical to ensure formulation stability and consumer acceptance, remain largely unexplored. There is only limited work on NDs to modulate the microstructure and rheology in Pickering emulsions^[16,17] and low molar mass liquids.^[18] Candidate carriers for NDs include hydrogel excipients, which are popular in skincare due to their large water content, non-toxicity, and “non-greasy” tactile perception when applied. However, their weak mechanical properties and photodegradation under UV radiation limit their scope.^[10,35,36] We selected Carbopol, a high molecular weight polyacrylic acid (PAA) that forms a special class of lubricious microgel-based hydrogels, as our material of choice. Our rationale stems from its biodegradable nature, non-irritability, and non-toxicity to dermal application, FDA-approval for biomedical use, and ability to provide pH-mediated rheology tunability.^[37–39] At acidic pH values, the polymer chains collapse and exist as mostly non-interacting, dispersed microgel particles, whereas above the pK_a (5–6) of the carboxyl groups, electrostatic repulsions between the ionized PAA chains form a space-filling network of swollen, deformable microgel particles.^[40–42] While the pH-tunable behavior of PAA alone has been extensively investigated,^[41] studies on nanoparticles in conjunction with pH modulation are lacking.^[43,44] Attractive polymer-particle interactions have been leveraged previously to increase the stiffness of

hydrogels.^[35,43,45] Since both the microgel and NDs have significant pH sensitivity, understanding how pH can be used to tune the microgel-ND interactions that affect rheology and lubrication may facilitate precise control on sunscreen film formation post application that allows prolonged UV protection.^[2]

In this study, we demonstrate how carboxylated nanodiamonds (cNDs) impregnated in PAA microgels can be used to modulate the rheology, lubrication, and UV attenuation properties of these gel systems through pH and cND concentration control. Oscillatory shear rheology and confocal fluorescence microscopy reveal different degrees of microstructural reinforcement enabled by changing the nature of polymer-cND and interparticle interactions above (pH 5.5) and below the pK_a (pH 4.1) of carboxyl groups. Tribological experiments, in contrast, suggest that lubrication properties to be primarily governed by microgel particles at either pH. Most importantly, UV absorption and simulated irradiation studies show these systems to be photostable with broad-spectrum UV attenuation capacity. Beyond the favorable mechanical characteristics of cND microgels, cytocompatibility assays affirm that cND microgels are suitable for topical applications. Taken together, the unique aspects of our work lie in a) tunability of microgel rheology and lubrication through controlled modulation of pH and cND concentration, b) an understanding of the underlying interaction mechanism of pH-tunability for microstructural reinforcement, c) broad-spectrum, photostable UV protection by cNDs rivaling that of TiO_2 , and d) preservation of gel microstructure after prolonged UV irradiation, all of which leading to a promising material platform for protecting human skin from the deleterious effect of UV radiation.

2. Results and Discussion

2.1. Nanodiamond Characteristics

Figure 1a,b shows the fabrication process and visual images of the prepared microgels at pH 4.1 and pH 5.5. TEM image shows that cNDs form a 100–200 nm core aggregate (Figure 1c). The nanoaggregates are held together by robust cohesive forces, primarily arising from van der Waals forces and electrostatic interactions among individual particles measuring 4–5 nm in size.^[23,24] Consequently, the cND powder used in this study comprises this tightly bound core aggregate structure rather than individual nanoparticles. DLS measurements of dilute aqueous dispersions of cNDs revealed that both the size and the zeta potential of the cNDs were pH-dependent (Figure 1d). The pK_a of carboxylic acid falls within the range of 2–5,^[46] therefore, as the pH of the cND dispersion increases, deprotonation of the surface carboxyl groups results in a negatively charged cND surface with increased electrostatic repulsions that reduce both the particle size and zeta potential. At pH values of 4.1, 5.5, and 8.3, the Z-average diameter, which represents the intensity-weighted mean hydrodynamic size, was measured to be 202.0 ± 2.30 , 196.2 ± 0.51 , and 166.2 ± 1.42 nm, respectively, with the polydispersity index ranging from 0.25 to 0.35. Additionally, the cND samples displayed a unimodal size distribution (Figure S1, Supporting Information). Zeta potential became increasingly negative as pH increased, indicating good colloidal stability and enhanced

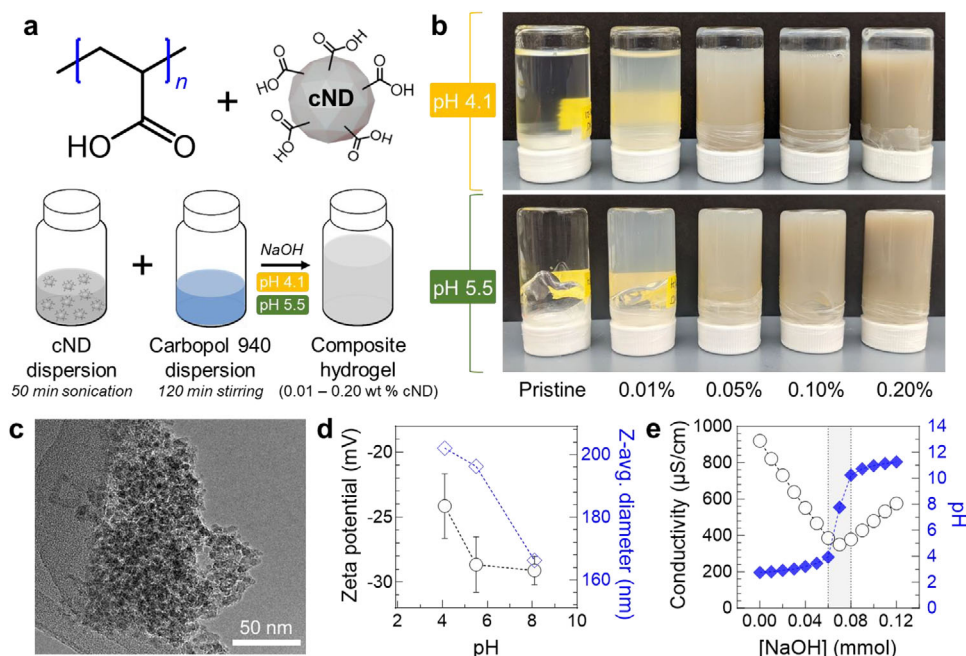


Figure 1. a) Preparation scheme of PAA-cND composite microgels. b) Optical images of the as prepared microgels with different cND concentrations at pH 4.1 and pH 5.5. c) TEM image of the cND powder showing 200 nm agglomerates. d) Zeta potential and the Z-avg. diameter of cND particles at different pHs. e) Conductometric titration curve of cND dispersion to estimate the concentration of surface carboxylic acid groups.

resistance to aggregation at higher pH levels as carboxyl groups fully ionize.^[15] Similar decreases in size and zeta potential of cNDs with pH have been observed, with the actual size and zeta potential dependent on the extent of carboxyl groups on the nanodiamond surface.^[15,47] Conductometric titration was used to identify the equivalence point, which appears as a minimum in conductivity corresponding to the neutralization and low concentration of H^+ and OH^- ions in the system (Figure 1e).^[48] While a higher concentration of cND particles would give different values in this figure, it would not change the resulting calculation of the surface carboxyl acid group concentration. Based on the mmol of NaOH required to reach the equivalence point, the surface carboxyl concentration was calculated to be 1.75 mmol g^{-1} .

2.2. pH-Dependent Rheology

Figure 2 shows the dynamic rheological behavior of pristine PAA and PAA-cND systems at two different pH, 4.1 and 5.5. Pristine PAA at pH 4.1 (Figure 2a) exhibits frequency-dependent moduli, with $G'' > G'$ at lower frequencies, followed by an overlap, and $G' > G''$ at higher frequencies, indicating viscoelastic behavior.^[49] In contrast, pristine PAA at pH 5.5 shows frequency-independent moduli with $G' > G''$, indicative of solid-like gel behavior (Figure 2c). This pH-dependent gelation is a typical phenomenon observed in various grades of PAA microgels (Carbopols 941, Ultrez 10, ETD 2050).^[41,43,50] Under slightly acidic conditions, the carboxyl groups of PAA are partially protonated, resulting in a lower degree of swelling of the microgel particles and a viscous sol-type behavior. Above the pKa (pH 5.5), the electrostatic repulsions between ionized carboxyl groups cause the polymer chains to uncoil, and the presence of sufficient mobile

counter ions creates a net outward osmotic pressure, resulting in a sample-spanning network of swollen, deformable microgel particles.^[41,51]

The addition of cNDs at pH 4.1 causes a transition from a viscous sol to a stiffer gel-like microstructure with increasing G' as cND concentration is increased, indicating strong reinforcement. Figure 2a shows that both moduli, for all cND concentrations barring 0.01%, exhibits weak to no frequency dependence with $G' > G''$. At 0.20% cND, the G' value was more than three orders of magnitude higher compared to the pristine PAA (Figure 2b). Decreasing $\tan \delta (= G''/G')$ values across the frequency range in Figure S2a (Supporting Information) with increasing cND concentration indicate that nanodiamonds contribute primarily to the elasticity of the gels without significantly altering the viscous component, an attribute previously observed in polymer-nanoparticle hydrogels.^[52] This increase in elasticity may stem from an increased number of attractive polymer-cND links in the system with increasing cND concentration.^[52,53]

Figure 2c,d shows that at pH 5.5, the reinforcement in gel elasticity (G') offered by cNDs is lower than at pH 4.1, with a non-monotonic behavior with increasing cND concentration. Both the pristine and cND-laden microgels showed stronger gel microstructure at pH 5.5 with G' and G'' values an order-of-magnitude higher than at pH 4.1, primarily due to the swollen, pristine PAA microgel network itself. At 0.05% cND, a maximum 2.7-fold increase in G' is observed compared to the pristine microgel followed by a reduction in reinforcement with comparable moduli between the 0.20% cND and the pristine microgels. Similar reduction in G' of PAA microgels has been observed previously with high loadings of stainless steel nanoparticles due to reduced polymer-polymer interactions in favor of weaker polymer-nanoparticle interactions.^[43] Consequently, at high

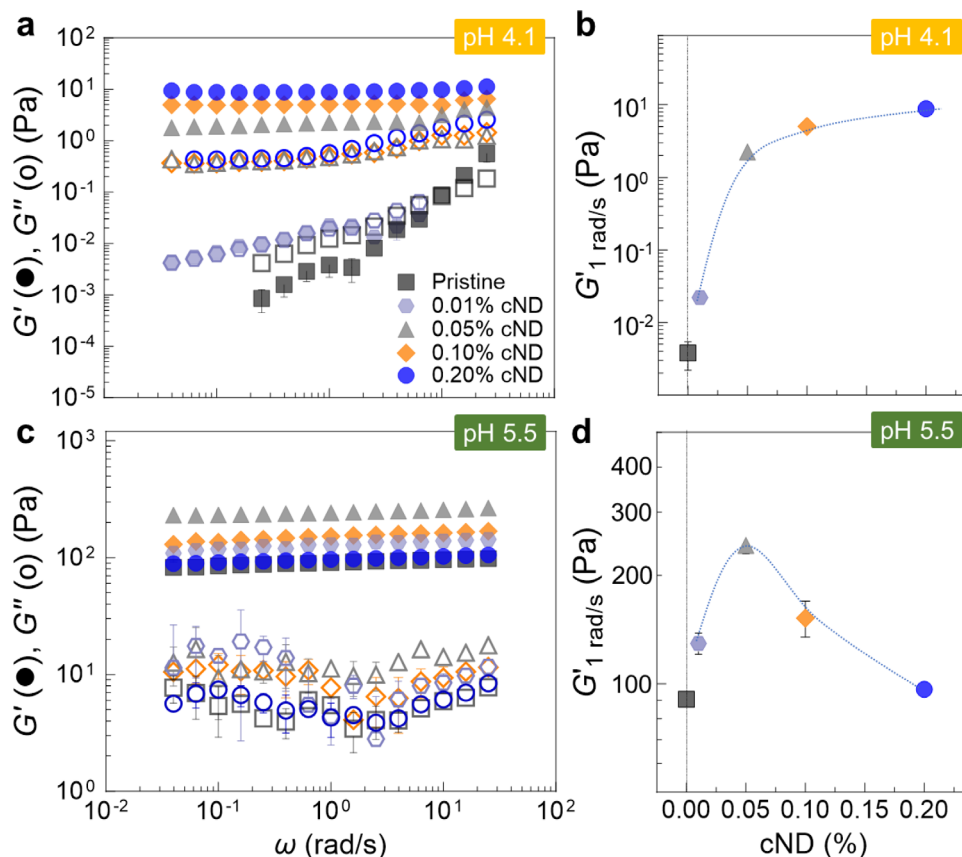


Figure 2. a,c) Oscillatory frequency sweeps at pH 4.1 and pH 5.5 with the elastic moduli (G' , closed symbols) and viscous moduli (G'' , open symbols) as a function of ω . b,d) G' in the linear viscoelastic domain at $\omega = 1 \text{ rad s}^{-1}$ as a function of the cND concentration at pH 4.1 and pH 5.5. Dotted lines are to guide the eyes. Error bars represent standard deviations across three independent measurements.

concentrations, cND particles may act as physical barriers that interfere with the swelling behavior of the microgels, thereby reducing reinforcement. The $\tan \delta$ (ratio of G''/G') frequency spectra remained close to 0.1, indicating analogous changes to both elastic and viscous dissipation (Figure S2b, Supporting Information), similar to other particle-reinforced physical gels,^[54] and unlike at pH 4.1, where cNDs primarily enhanced elasticity.

Figure 3a,c, derived from oscillatory amplitude sweeps (Figure S3, Supporting Information), show the elastic stress $G'\gamma$ as a function of strain, with the yield stress and strain determined from the curve maxima according to the elastic stress method.^[55] All microgels except the pristine samples and those prepared with 0.01% cND at pH 4.1 show a characteristic yield stress. The corresponding stress sweep from which the yield stress is derived (Figure S3, Supporting Information) shows a G' plateau at low stresses, followed by the overshoot of G'' during the onset of yielding at higher stresses (Payne effect).^[56] The yielding behavior of composite microgels is consistent with the frequency sweep measurements (Figure 2), with the yield stress increasing with cND concentration at pH 4.1 ($\sigma_y \approx [\text{cND}]^{1.6}$) while presenting a non-monotonic variation at pH 5.5 with a maximum 10-fold increase in σ_y at intermediate cND concentrations (Figure 3b,d). Yielding in swollen microgel systems originates from the critical stress and strain required to move microgel particles past one another and is strongly dependent on the microgel interface.^[50,57]

Considering this mechanism at play, addition of hard cNDs at the interface between fully swollen microgel particles likely contributes to the observed increase in yield stress and strain even at the highest cND concentration at pH 5.5 ($\sigma_y = 2.2 \pm 0.14 \text{ Pa}$, $\gamma_y = 6\%$ for pristine; $\sigma_y = 9.6 \pm 0.13 \text{ Pa}$, $\gamma_y = 18\%$ for 0.20% cND). At pH 4.1, although a higher stress is needed to deform the composite gel at higher cND concentrations, the strain necessary to surpass this energy barrier is unaffected, unlike at pH 5.5.^[50]

Figures 2 and 3 collectively demonstrate that cNDs can controllably tune the rheological properties of microgels through both concentration and pH modulation. Variations in the degree of reinforcement at pH 4.1 and 5.5 may arise due to the pH-dependent nature and extent of interactions between PAA and cNDs. At pH 4.1, the strong reinforcement may be due to attractive polymer-cND and cND-cND hydrogen bonding interactions between the partially protonated carboxyl groups on the PAA backbone and the cND surface. Consequently, hydrogen-bonded cND clusters may act as bridges between the dispersed microgel particles and form a space-filling network (Figure 4a, inset).^[45,58] Attractive nanofiller-hydrogel interactions can also cause a localized increase in gel density around the nanofillers that further adds to the reinforcement.^[35] Near the pK_a of carboxyl group at pH 5.5, deprotonation leads to repulsive polymer-cND and cND-cND electrostatic interactions.^[15,41] At low cND concentration, these repulsive interactions may cause the microgel particles to

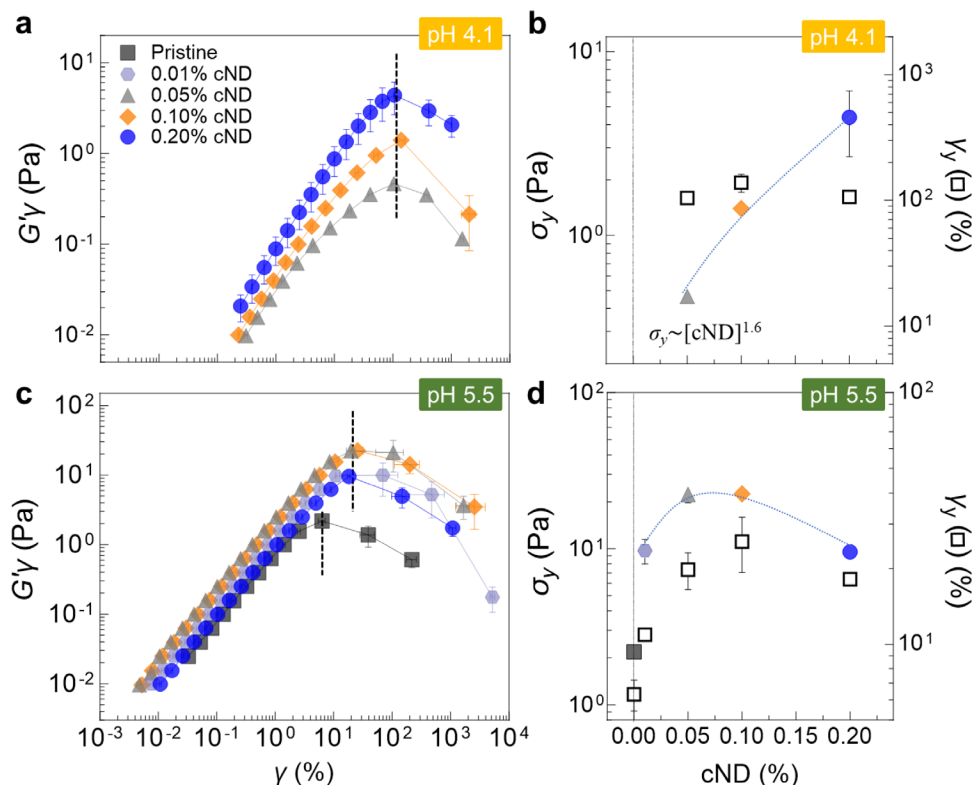


Figure 3. a,c) Elastic stress ($G'\gamma$) as a function of strain percent (γ %) at pH 4.1 and pH 5.5. The maxima correspond to the yield stresses, and the dotted lines represent the yield strains. b,d) Yield stress σ_y (closed, colored symbols) and yield strain γ_y (black, open symbols) as a function of the cND concentration. Dotted lines are to guide the eyes. Error bars represent standard deviations across three independent measurements.

further swell and strengthen the microstructure up to a critical cND concentration after which further addition may lead to a breakdown of polymer-polymer interactions, reducing the reinforcement. pH-modulated interactions of non-ionic surfactants^[58] and phospholipids^[45] with Carbopol microgels have shown similar trends with great reinforcement under acidic conditions. In polyacrylamide gels containing silica nanoparticles, increased gel stiffening occurred at lower pH due to attractive interparticle interactions and silica aggregation, while at higher pH, repulsive polymer-particle interactions resulted in well-dispersed silica that reduced reinforcement.^[59]

2.3. Microstructure and Role of Hydrogen Bonding

Figure 4 shows the confocal fluorescence microscopy images of the pristine and 0.20% cND microgels at pH 4.1 and pH 5.5. To visualize the microstructure, two separate dyes were used to stain the aqueous phase (Alexa Fluor 488, green) and the cND particles (Nile Red, red) (Experimental section). Since the Alexa Fluor 488 dye was mixed after sample preparation, it is unlikely to stain the microgel particles and stains only the aqueous solvent. Microgel particles thus appear black in the aqueous labelled images in Figure 4. The pristine PAA sol at pH 4.1 shows large pools of the solvent (water + NaOH), in green, in between the poly-dispersed^[41] partially swollen microgel particles without a space-filling network. Micron-scaled cND aggregates are seen in

red (cND label) when cNDs were added to the PAA sol at pH 4.1, confirming our hypothesis regarding cND clusters acting as bridges between microgel particles through attractive interactions that stiffen the microstructure (Figure 4a). Figure 4b shows that at pH 5.5, the pristine PAA microstructure consists of a dense network of microgel particles, unlike pH 4.1. cND particles are finely dispersed within the microstructure, likely due to interparticle repulsive interactions. Microstructure imaging thus reveals that the formation of cND clusters at pH 4.1 may play a dominant role in reinforcement of gel properties compared to the well-dispersed cND particles that provide only marginal reinforcement.

To understand the contribution of hydrogen bonding likely responsible for the attractive cND interparticle and PAA-cND interactions, we performed oscillatory shear rheology on the pristine and 0.20% cND microgels in the presence of urea. Urea is a known hydrogen bond disruptor since it competes for bonding sites and can break weaker hydrogen-bonded associations.^[60,61] In our case, we expect that the presence of urea could break the attractive interactions, especially at pH 4.1. To enable direct comparison of the microgel mechanical properties with and without urea, urea was first added to the formulations, and pH was subsequently adjusted to 4.1. Figure 5a shows the frequency dependence of G' for the pristine and composite microgel in the presence and absence of urea at pH 4.1. For the pristine PAA sol, addition of urea resulted in the formation of a gel network as seen by the frequency-independent

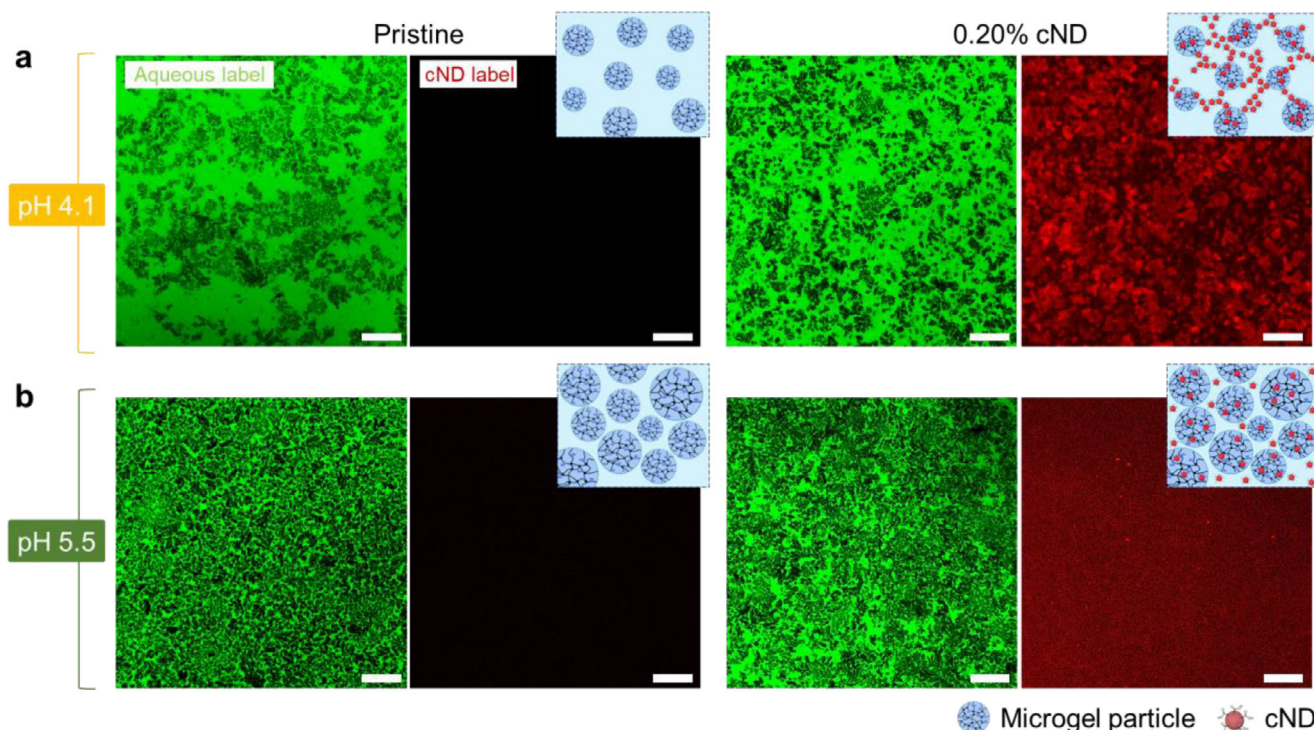


Figure 4. Confocal fluorescence microscopy images of the pristine (left) and the PAA-cND composite microgel with 0.2% cND (right) at a) pH 4.1 and b) pH 5.5. Aqueous label refers to the dyed aqueous phase (Alexa Fluor 488, green), and cND label refers to the separately dyed cND particles (Nile Red, red) within the microgel. (Insets) Schematic representation of the microstructure. Scale bars are 25 μm .

moduli with $G' > G''$ (Figure 5a; Figure S4a, Supporting Information). This may be due to the creation of strong hydrogen bonds between urea and the partially protonated PAA backbone. Addition of cND, however, led to a comparable G' value, implying that cNDs offer no reinforcement in the presence of urea (Figure 5a; Figure S4a, Supporting Information). This behavior contrasts with that seen in the absence of urea where the G' of the pristine sol increased by almost 2000-fold at 0.20% cND (Figure 5b). Below 4 M urea, increasing urea concentration increased the magnitude of storage modulus of the pristine PAA gel (Figure S5, Supporting Information). Presence of urea thus suppresses the attractive PAA-cND interactions (Figure 5c) and confirms that hydrogen bonding places a significant role in the reinforcement of gel properties at pH 4.1. This reinforcement can be visualized in confocal microscope images where the addition of urea creates a network structure (Figure S6, Supporting Information). At pH 5.5, since electrostatic repulsion is the primary driver of gelation and hydrogen bonding is minimal due to complete deprotonation of the carboxyl groups on both the PAA backbone and the cND surface, no reinforcement is observed with or without urea (Figure S4b,c, Supporting Information).

2.4. Lubrication

We investigated the lubrication properties of the microgels at different pHs using model bio-tribological soft PDMS tribopairs (Figure 6a) to mimic the low pressure (0.1 MPa) application of

topical products through rubbing action on skin.^[62,63] In this system, the microgel is entrapped between the rotating ball and three plates, as schematically shown in Figure 6a. Lubrication with a low friction coefficient, defined as the ratio of the friction force to the normal load ($\mu = F_F / F_N$), directly correlates with perceived tactile pleasantness.^[64,65] It is thus pertinent to ensure that the presence of cNDs does not alter the effective lubrication properties of the PAA microgels.^[66]

Figure 6b,c shows μ as a function of the sliding speed U , representative of the Stribeck curve^[67] that denotes three lubrication regimes: boundary regime at low U , mixed regime at intermediate U and elasto-hydrodynamic regime at high U . In the boundary regime, all microgels, pristine and containing cNDs, show lower μ values than water consistent with previous report for Carbopol systems.^[68] Boundary friction is characterized by a speed-invariant μ plateau and governed by contact asperities and adsorbed films of the lubricant without fluid entrapment.^[69] Since hydrophilic PAA is unlikely to adsorb on the hydrophobic PDMS surfaces, the observed friction reduction may arise from the confinement of swollen microgel particles within the interfacial film, which separate the contact asperities more effectively than water alone.^[68] The PDMS surfaces have a root-mean-squared roughness (S_q) of $0.09 \pm 0.02 \mu\text{m}$ for the plate and $0.61 \pm 0.08 \mu\text{m}$ for the ball (Figure S7, Supporting Information). The microgel particles, typically in the sub-micron to a few microns size,^[41] then, may act as micron-scaled “ball-bearings” to reduce friction, as proposed by Sarkar et al.^[70] At pH 4.1, since the microgels are only partially swollen, more particles can enter the confinement under shear as U increases and effectively reduce friction. This

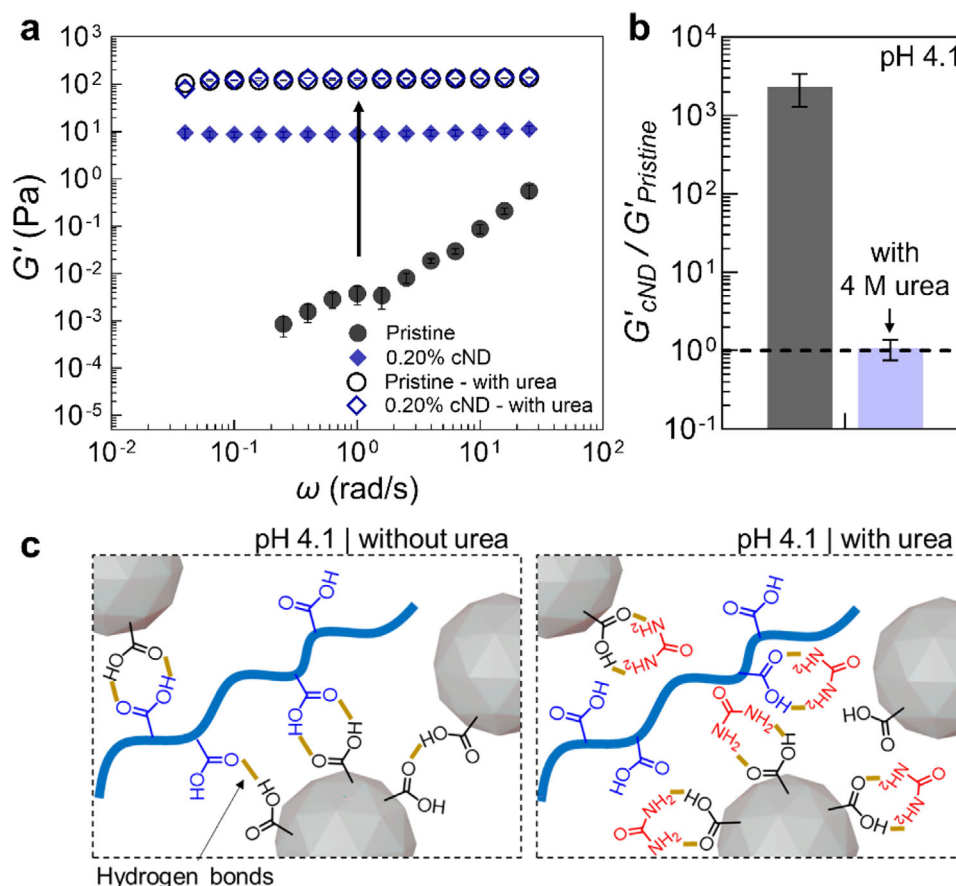


Figure 5. a) G' as a function of ω for the pristine and 0.20% cND composite microgels, with and without 4 mol L⁻¹ urea, at pH 4.1. b) Relative increase in G' at $\omega = 1$ rad s⁻¹ represented as the ratio of G' for the PAA-cND microgel to that of the pristine sample with and without urea at pH 4.1. c) Schematic of breakdown of hydrogen bonding between cND particles and PAA-cND in the presence of urea.

mechanism likely causes the shallow decline in the boundary μ values with increasing U at pH 4.1 compared to pH 5.5.

In the mixed regime, characterized by a steep decline in μ with increasing U , a partial fluid film starts forming as multilayers of microgel particles get entrained in the interfacial gap, and lubrication is dictated by both the surface and lubricant properties.^[62,70] Since the hydrophilic gels do not adsorb on the PDMS surface, friction in the mixed regime is governed mainly by the lubricant rheology. This is evident at pH 4.1 where the cND-laden microgel with greater stiffness (G') prompted an early transition to the mixed regime at a lower sliding speed ($U \approx 4.5$ mm s⁻¹) compared to the pristine PAA sol ($U \approx 12$ mm s⁻¹) since a viscous gel can more easily entrain than a liquid.^[62,71] At pH 5.5, since the rheology of both the pristine and 0.20% cND microgels are similar (Figure 2c,d), there is a negligible difference in their lubrication behavior in the mixed regime. To further explore the lubrication behavior under conditions representative of topical application the skin, additional experiments were conducted with porcine skins slabs of root mean square heights S_q of 13.24 ± 0.85 μ m (Figure S8, Supporting Information). Despite a significant increase in the S_q of the porcine skin slabs compared to PDMS, Stribeck curves with the porcine skin-PDMS tribopair show that the lubrication behavior with pristine and 0.20% cND-laden microgels remain comparable at both pH

4.1 and 5.5 (Figure S9, Supporting Information), highlighting cNDs not adversely affecting lubrication. Similarity in lubrication behavior between the formulations remain even when different normal forces were applied, $F_N = 2.1, 4.0$, and 10.0 N. These results collectively show that the addition of cNDs has no detrimental effect on friction. The PAA microgels sustain the effective boundary and mixed lubrication at either pH, indicating that the cNDs may be embedded inside the microgel matrix.^[62]

2.5. UV Protection and Photostability

Figures 7a,b and S10a,b (Supporting Information) show that cNDs significantly enhance UV absorbance of the PAA microgels in addition to tuning their rheology and lubrication properties. The UV absorbance increases with cND concentration at both pH 4.1 and 5.5 across the entire UV-B (290–320 nm) and UV-A (320–400 nm) regions with greater UV-B protection than UV-A.^[9] The pristine microgels show no absorbance in the entire UV range.^[10] The monotonic decrease in absorbance with wavelength for cND-laden microgels stems from a combination of scattering and absorption processes.^[9,12] sp^2 -hybridized carbon atoms on the nanodiamond surface absorb UV photons while their high refractive index of 2.4 provides extensive light scattering. cND-laden

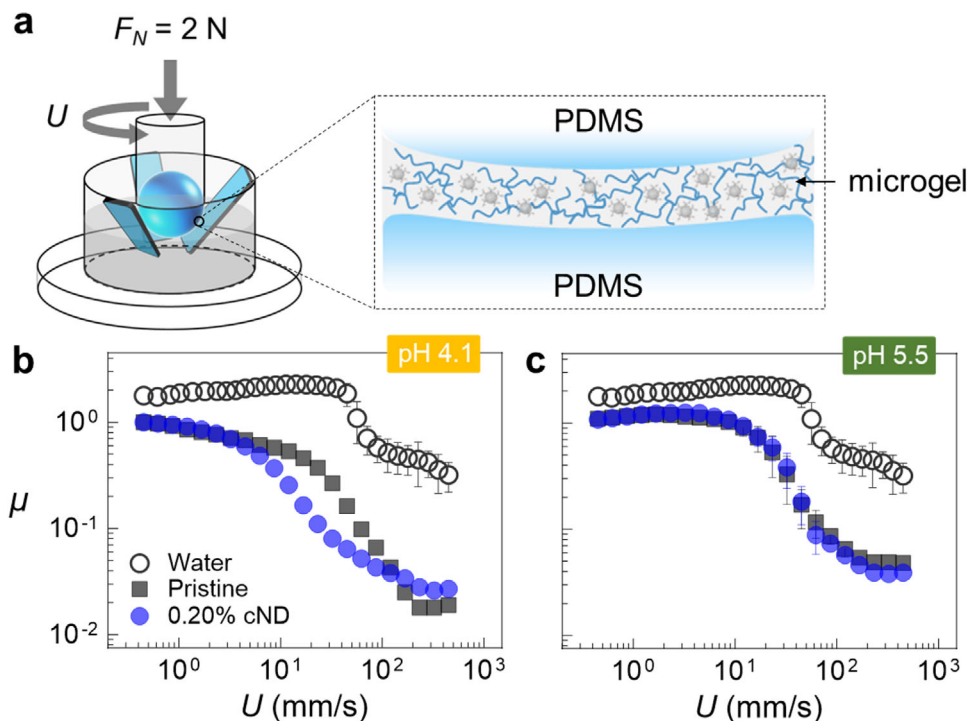


Figure 6. a) Experimental tribology setup with a soft PDMS-PDMS tribopair and microgel as the lubricant. Normal load kept at $F_N = 2$ N and sliding speed varied from $U = 0.1$ – 500 mm s^{-1} . Stribeck curves for the pristine and 0.20% cND-laden microgels at b) pH 4.1 and c) pH 5.5. Water was used as a reference lubricant without pH adjustment. Error bars represent standard deviations across three independent measurements.

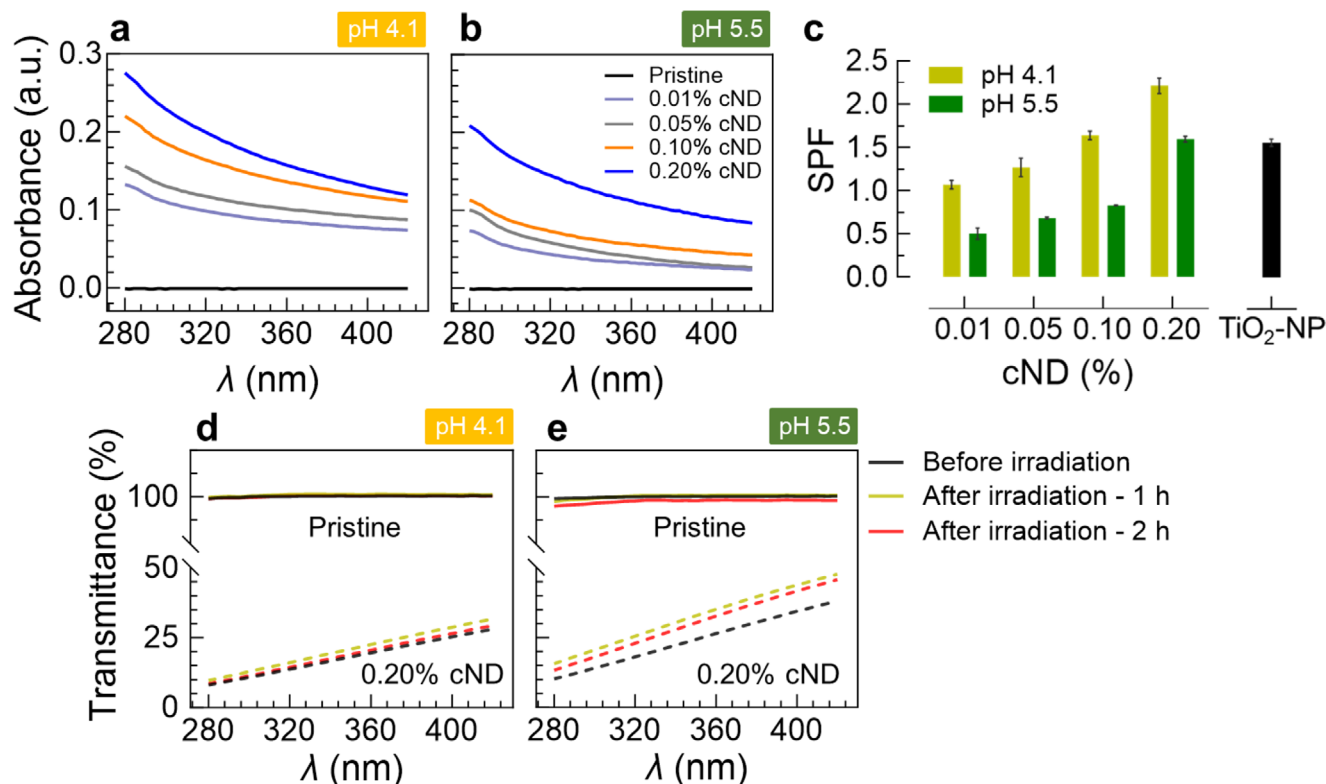


Figure 7. UV absorbance spectra of 2 mg mL^{-1} diluted samples of microgels with different cND concentrations at a) pH 4.1 and b) pH 5.5. c) SPF values calculated from the Mansur equation for diluted microgels at different cND concentrations and TiO_2 -NP dispersion. Transmittance spectra of 50 mg mL^{-1} diluted microgel samples before and after 1 and 2 h of UV irradiation for d) pH 4.1 and e) pH 5.5.

microgels at pH 4.1 shows stronger absorption than at pH 5.5 at each cND concentration. Since the UV absorbance efficiency of nanodiamonds is inversely proportional to their size,^[12] the stronger absorption at pH 4.1 likely originates from the larger size of the observed cND clusters compared to the dispersed cND particles at pH 5.5 (Figure 4).

In vitro SPF, calculated using the absorbance values in the range of $\lambda = 290\text{--}320\text{ nm}$ from the Mansur equation^[72] (Equation (1)), is widely used to evaluate the effectiveness of sunscreen formulations against UV-B radiation. For 2 mg mL^{-1} dispersions with effective concentration of cNDs between 0.2 and $4\text{ }\mu\text{g mL}^{-1}$, the SPF values increase with increasing cND concentration and were higher at pH 4.1 than at pH 5.5 (Figure 7c), consistent with the absorbance spectra. We compare the SPF values of aqueous dispersions of titanium dioxide nanoparticles ($\text{TiO}_2\text{-NP}$) used as a UV blocker in commercial sunscreens to aqueous dispersions of cND-PAA gels at an effective cND concentration of $4\text{ }\mu\text{g mL}^{-1}$ (Figure 7c). The SPF values obtained for cND dispersions were 2.21 ± 0.09 at pH 4.1 and 1.60 ± 0.03 at pH 5.5, which are similar to those reported in the literature by Lin et al.^[9] while the TiO_2 dispersions at the same effective concentration had an SPF of 1.55 ± 0.04 (Figure S10c, Supporting Information). This suggests that cND microgels show similar or better effectiveness than traditional UV-B blockers, with the added potential of avoiding skin damage due to their antioxidant capacities, unlike $\text{TiO}_2\text{-NPs}$, which may result in photocatalytic skin damage under UV exposure. Broad spectrum UV protection of the cND microgels was measured by identifying the critical wavelength λ_c below which 90% of the area under the absorbance spectra falls (Equation (2), Table S2, Supporting Information). A “broad spectrum” sunscreen formulation has $\lambda_c > 370\text{ nm}$.^[73] All cND microgels at either pH have $\lambda_c = 384\text{--}388\text{ nm}$ and therefore provide broad-spectrum UV protection.

Sunscreens get exposed to prolonged UV radiation under sunlight when applied and hence the UV filters need to be photostable for effective protection until the next application. We verified the photostability of the cND microgels by exposing them to a UVA chamber for 1 and 2 h of simulated irradiation and assessed their transmittance spectra before and after exposure using a UV-vis spectrophotometer. The emission spectra of the UV lamp contained mostly light of the UV-A wavelengths (320–400 nm), where exposure durations of 1 and 2 h correspond to ≈ 119 and 238 days of equivalent natural sunlight exposure, respectively. This accelerated testing protocol follows established equivalency models commonly used in the sunscreen and photoprotection industry to simulate prolonged UV aging in a condensed timeframe.^[9] Figure 7d,e shows that cND microgels have excellent photostability with minimal changes to the transmittance spectra before and after different levels of UV exposure at either pH. The slight increase in transmittance at pH 5.5 may be due to removal of functional groups from the dispersed cND particles that are responsible for the UV absorption process. Interestingly, visual observations show that cND-laden gels (Figure S11b,d, Supporting Information) retain their solid-like microstructure even after irradiation. In contrast, the pristine PAA gel at pH 5.5 turns from a solid-like gel to a flowable viscous fluid (Figure S11a,c, Supporting Information), likely due to photodegradation of PAA chains^[36] while at pH 4.1, PAA is already a liquid prior to UV exposure (Video S1, Supporting In-

formation). The UV-blocking behavior and photostability of the microgel are maintained under conditions equivalent to greater than 6 months of outdoor UV exposure. Compared to a cND water dispersion, the microgel structure immobilizes the particles, preventing gravitational settling and enhancing UV attenuation (Figures S12 and S13, Supporting Information). These results collectively suggest cNDs provide effective photostable UV protection and preserve microgel rheology unlike TiO_2 suspensions that reduce viscosity under UV exposure,^[11] encouraging the adoption of nanodiamonds for emerging skincare products including sunscreens.

An interesting caveat to note for all sunscreens is that users often apply less or unevenly on their skin than the standard thickness used for SPF calibration (equivalent to 100–150 μm on the skin).^[74,75] The effective SPF could thus be 20 to 50% lower than the what the product label indicates.^[76,77] To account for these discrepancies, our cND-PAA microgel with its tunable viscoelasticity and shear-thinning capabilities could facilitate even spreadability while maintaining film continuity. We conducted preliminary visual experiments in this regard to assess the time-dependent behavior of the formulation on porcine skin surrogate and PDMS slab samples. Representative images of the gel at 0, 1, 4, 12, and 24 h are shown in Figure S14 and Video S2 (Supporting Information). While the gels on the PDMS surface shrink over time possibly due to water evaporation, those on porcine skin remain relatively intact and adhered to the surface. The cND particles seem to remain dispersed in the PAA matrix over time and thus could also be effective at deflecting and absorbing UV light over a wide angle of incidence due to their size, shape, and high refractive index ($n = 2.4$). While clearly exploratory, these indications of microgel stability on the skin surface motivate future work on investigating the cND microgel retention and adhesion under more dynamic and physiological conditions.

2.6. Cytocompatibility

To be suitable for use as a UV-protective skincare product, the cytocompatibility of the cND microgels formulation must be evaluated. Nanodiamonds have previously exhibited high biocompatibility, even in comparison to other carbon-based nanomaterials, making them an attractive option for topical formulations.^[9,78,79] To this end, in vitro LIVE/DEAD Viability/Cytotoxicity assays were performed using 0.2 wt.% cND microgels at pH 4.1 and pH 5.5. Human dermal fibroblasts from a neonatal source (HDFs) were treated with two volumes of microgel suspension, 50 and 100 μL , dispersed in 300 μL of cell culture medium, to assess the effect of pH and dosage on cell viability. Treatments were conducted for 24 and 48 h to evaluate the impact of exposure time. Cell viability was calculated as the percentage of live cells relative to the total cell count captured in fluorescent microscopy images. Figure 8a,b shows images of HDFs fluorescently stained for live/dead assay, where green fluorescence indicates live cells and red fluorescence indicates dead cells.

Figure 8c,d shows cell viability at different microgel treatments compared to pH-balanced collagen, used as a positive control, after 24 and 48 h of exposure, respectively. Across all treatment conditions, average cell viability remained greater than 94%. Within each pH formulation, Welch's *t*-test indicated no statistically

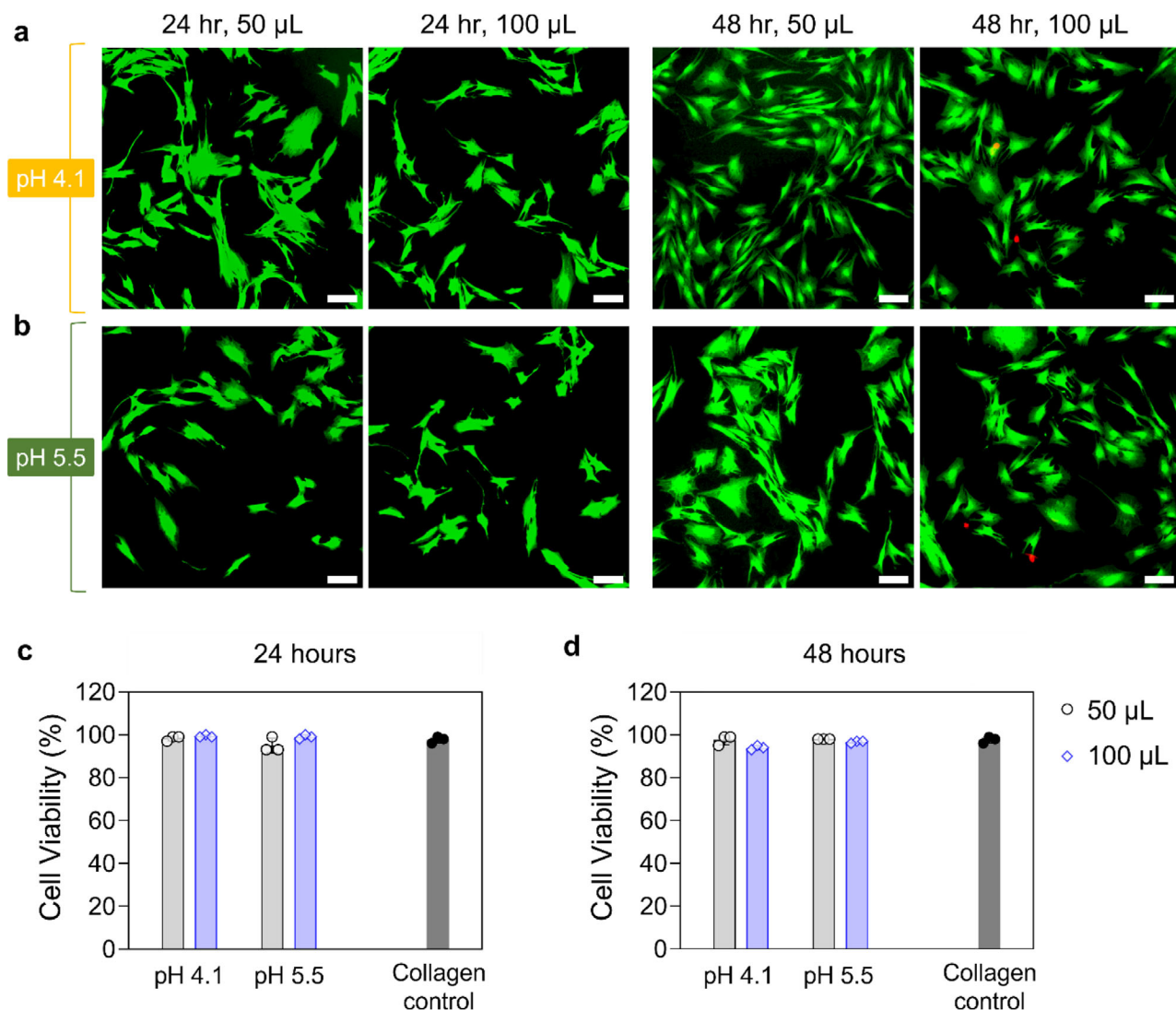


Figure 8. Fluorescent images from live/dead assays with HDFs are shown at a) pH 4.1 and b) pH 5.5. Green fluorescence indicates live cells, and red fluorescence indicates dead cells. Scale bars represent 100 μm . Cytocompatibility of 0.2 wt.% cND microgels at pH 4.1 and pH 5.5 with human dermal fibroblasts at two treatment concentrations, 50 and 100 μL per 300 μL of media, after a treatment of a) 24 h and b) 48 h. Experiments were completed in triplicate ($n = 3$). Statistical significance was determined at $p < 0.05$.

significant difference ($p > 0.05$) between any pairs of concentration and exposure time treatment conditions. To determine differences in cell viability between treatment conditions and the positive collagen control, one-way ANOVA followed by Dunnett's post-hoc test was conducted. This analysis revealed no statistically significant ($p > 0.05$) reduction in viability between the pH 4.1 and pH 5.5 formulations compared to the positive control. These results demonstrate that cND microgels at pH 4.1 and pH 5.5 retain high cytocompatibility and are suitable for topical applications.

3. Conclusion

Our study shows that multifunctional carboxylated nanodiamonds can be used to tailor the rheology, lubrication, and UV pro-

tection of PAA microgels through pH-tunable interactions. Below the pK_a of carboxyl groups at pH 4.1, cNDs turned the viscous PAA solution to a solid-like gel with increasing stiffness and yield stress with cND concentration. Enhanced reinforcement originates through formation of cND clusters and attractive polymer-cND interactions via hydrogen bonding between the partially protonated carboxyl groups. Above the pK_a at pH 5.5, deprotonation of the carboxyl groups results in electrostatically repulsive interactions and a microstructure with fully swollen microgel and finely dispersed cND particles. Consequently, cND addition results in a less pronounced reinforcement. Soft lubrication is primarily driven by microgel particles and cNDs sustain the effective boundary and mixed lubrication at either pH without adsorbing at the sliding interface. UV absorption and irradiation studies underscore the potential of cNDs as photostable UV filters, offering

broad-spectrum protection with minimal photodegradation and preservation of gel microstructure after prolonged UV exposure, crucial attributes for safer sunscreen formulations. Live/dead assays confirm that cND microgels do not have a statistically significant effect on cell viability, demonstrating the biocompatibility necessary for topical applications. The pH-tunable behavior of polymer-nanodiamond interactions can thus be exploited to design nanocomposite microgels that combine mechanical robustness with enhanced functional versatility for a range of applications, from skincare products to advanced biomaterials, leveraging the unique properties of nanodiamonds.

4. Experimental Section

Materials: Crosslinked polyacrylic acid under the trade name Carbopol 940 (Lubrizol) was used as received. Detonation ND powder functionalized with surface carboxylic acid groups (0.6 wt.% ash content, Adamas Nanotechnologies, RTP NC) was used without further purification. Sodium hydroxide (NaOH) and hydrochloric acid (37% HCl), purchased from Fisher Scientific, were used to adjust the pH values of the dispersions. Titanium dioxide nanoparticles (Aeroxide TiO₂ P25, Fisher Scientific) with a nominal particle diameter of 21 nm, as provided by the manufacturer, were used as received for UV absorbance analysis.

Nanodiamond Characterization—Transmission Electron Microscopy (TEM): cNDs were visualized using a Talos F200X scanning transmission electron microscope (Thermo Fisher Scientific) operated at 200 kV. Samples were prepared by dipping TEM grids (Ted Pella) in 0.001 wt.% cND dispersion for 30 min and dried overnight.

Nanodiamond Characterization—Dynamic Light Scattering (DLS): Particle size and zeta potential of cNDs were obtained using a Zetasizer Nano ZSP instrument (Malvern Instruments). Dispersions were adjusted to three pH values (8.2, 5.5, and 4.1) using small additions of HCl. pH 8.2 corresponds to the native pH of the dispersion, while pH 5.5 and 4.1 represent values above and below the pK_a of cNDs, respectively. These pH values also correspond to conditions for the rheological and tribological experiments. DLS measurements were conducted on a dilute 0.1 mg mL⁻¹ cND dispersion. It was standard practice to perform these measurements at concentrations low enough to ensure that the zeta potential was independent of concentration, thereby avoiding measurement artifacts.^[80,81] Reported values are an average of five independent measurements.

Nanodiamond Characterization—Conductometric Titration: The surface carboxylic acid group concentration on cNDs was determined using conductometric titration as described by Farias et al.^[16] Briefly, 40 mg of cNDs were dispersed in 55 mL of deionized water and 5 mL of 0.01 M NaCl under magnetic stirring. pH of the dispersion was then adjusted to 2.5–3.0 with 0.1 N HCl. The cND dispersion was titrated with 0.04 N NaOH at 0.25 mL increments up to pH 11. Conductivity and pH were recorded at each increment. The concentration of NaOH at the equivalence point was then used to determine the concentration of surface carboxylic groups in mmol g⁻¹ of cND.

Microgel Preparation: 0.2 wt.% pristine microgels were prepared by first dispersing 40 mg PAA powder gradually into 20 g deionized water under continuous stirring at 600 rpm, and left overnight to allow complete dispersion. The pH value of the dispersion was raised from 3.3 to below the pK_a of PAA (pH = 4.1 ± 0.2) and subsequently to near the pK_a (pH = 5.5 ± 0.2) using 0.1 N NaOH solution and monitored using a digital pH meter (Thermo Scientific). The PAA microgels are naturally soft and hydrated, containing more than 90% water by weight, making it difficult to determine reliably the actual size in their swollen state. They also adapt to the shape of the surface they are applied to and are comparatively flexible.^[82] Techniques such as DLS fail, as do SEM, since they require dehydration and conductive coatings, which would collapse the gels and distort the shape. Nevertheless, confocal images were taken of the pristine and 0.2% cND-PAA gels, which gave a representation of the 2D shape, as described in later sections. For PAA-cND composite microgels,

40 mg PAA powder was dispersed in 10 g of deionized water, and cNDs were dispersed separately in the remaining 10 g of deionized water. cND dispersions were sonicated for 50 min in a bath sonicator and then added to the overnight PAA dispersions, followed by an additional 2 h of stirring. The pH value of the PAA-cND dispersion was then adjusted to 4.1 and 5.5. Composite microgels were prepared at four different cND concentrations: 0.01, 0.05, 0.10, and 0.20 wt.%.

Rheology: Dynamic oscillatory shear rheology experiments on pristine and PAA-cND composite systems at pH 4.1 and pH 5.5 were performed on a stress-controlled rheometer (DHR-3, TA Instruments) at 25 °C. A 40 mm sandblasted parallel plate geometry was used to avoid wall slip, and the gap was maintained at 500 μm. A solvent trap was also employed to minimize evaporation losses. Prior to each measurement, the samples were pre-sheared at 10 1/s for 30 s followed by 120 s of equilibration time to minimize variations in the microstructure. Oscillatory frequency (ω) sweeps were applied between $\omega = 0.01$ and 100 rad s⁻¹ at a constant stress amplitude $\sigma = 0.1$ Pa, which was within the linear viscoelastic regime of all microgels, to obtain the dependence of the elastic (G') and viscous (G'') moduli as a function of ω . Oscillatory amplitude sweeps were performed between $\sigma = 0.01$ and 100 Pa at $\omega = 0.2$ rad s⁻¹ to obtain the yield stress (σ_y) and strain (γ_y).^[55] All experiments were performed in triplicate.

Confocal Fluorescence Microscopy: PAA-cND microgels were imaged using an inverted confocal laser scanning microscope (Leica TCS SP8) equipped with a 63x oil immersion objective. Fluorescent cND particles were synthesized by incorporating hydrophobic 0.1 mg mL⁻¹ Nile Red into the particles suspended in isopropanol. The Nile Red-labeled cND particles were used to prepare a 0.20 wt.% PAA-cND composite microgel. A hydrophilic dye, Alexa Fluor 488, was mixed with the microgel to label the aqueous phase. Nile Red was excited with a 552 nm laser, while Alexa Fluor 488 was excited at 496 nm. Pristine and 0.20 wt.% PAA-cND microgels at pH 4.1 and pH 5.5 were then placed into glass vials and loaded onto the microscope. Microstructure images with a total resolution of 1024 px x 1024 px were obtained at a minimum of 10 μm above the coverslip to avoid wall effects.

Tribology: The lubrication properties of the microgels were investigated using a ball-on-three plates tribology geometry on a stress-controlled rheometer (DHR-3, TA Instruments) at 25 °C. The geometry consists of a 0.5"-diameter ball attached at the top and three rectangular plates inserted at 45° to the horizontal plane. Polydimethylsiloxane elastomer (PDMS) (Sylgard 184, 10:1 base to curing agent ratio, Dow Chemicals) was used as both the ball and plate substrates. During each experiment, the PDMS ball was lowered to contact the three PDMS plates, in the presence of the microgel sample, at a constant normal load of $F_N = 2.1$ N, and the relative sliding velocity was varied from 0.1 to 100 rad s⁻¹. Steady-state sensing was employed to reach tolerances < 10% at each velocity. Pristine and PAA-cND composite microgels were assessed at both pH 4.1 and pH 5.5. For reference, measurements were also performed with deionized water as the lubricant without pH adjustment. All tribology tests were performed in triplicate.

UV Absorbance and SPF Determination: The sun protection factor (SPF) of microgels was estimated in vitro using the UV absorbance spectrum based on the method developed by Mansur et al.^[72] While SPF, defined as the ratio of UV energy required to produce a minimal erythema dose on protected skin to that for unprotected skin, was more accurately determined by in vivo studies, the in vitro technique used here is useful for screening the UV shielding properties. The pristine and PAA-cND composite microgels at pH 4.1 and pH 5.5 were diluted to a concentration of 2 mg mL⁻¹ with deionized water. The UV absorbance spectra of the dilute dispersions were captured from wavelengths $\lambda = 190$ –420 nm at an interval of 2 nm using a quartz cuvette with a UV-vis spectrophotometer (Genesys 10S, Thermo Scientific). All measurements were performed in triplicate. SPF was calculated using the Mansur Equation (1):

$$SPF = CF \sum_{290}^{320} EE_{\lambda} I_{\lambda} Abs_{\lambda} \quad (1)$$

here, EE_{λ} is the erythemal effect spectrum, I_{λ} is the solar intensity spectrum, Abs_{λ} is the measured absorbance, and $CF = 10$ is the correction factor. The values of $EE_{\lambda} \times I_{\lambda}$ are constants and determined by Sayre et al. as shown in Table S1 (Supporting Information).^[83]

To capture the effectiveness of cNDs in both UV-B and UV-A regions ($\lambda = 290\text{--}400\text{ nm}$), the critical wavelength (λ_C) was estimated using Equation (2). λ_C represents the wavelength below which 90% of the total area under the UV absorbance spectrum between 290 and 400 nm falls.^[73] The trapezoidal rule for area under the curve was used to determine the λ_C for the different samples.

$$\int_{290}^{\lambda_C} Abs_{\lambda} d\lambda = 0.9 \int_{290}^{400} Abs_{\lambda} d\lambda \quad (2)$$

UV Irradiation: The photostability of pristine and PAA-cND composite microgels was evaluated using a UV flood lamp chamber (Sunray 400 SM, Uvitron International). Emission spectra of the UV lamp consisted mostly of light in the UV-A wavelengths (320–400 nm). In UV attenuation measurements, a gel layer thickness was maintained at $1.0 \pm 0.5\text{ cm}$, which was akin to the optical path length (13.4 mm) used in the quartz cuvette applied for UV-vis spectroscopy measurements. The samples were placed 5" away from the light source, where the irradiance was between 360 and 430 W m^{-2} . For comparison, the average solar irradiance, which accounts for emissions in the visible, UV-A, and UV-B regions, was on average 4410 Wh m^{-2} in a single day in North Carolina, United States. The UV component of the solar irradiance that causes sunburns, however, was only 3.32 Wh m^{-2} .^[84] Hence, 1 h of radiation inside the UV chamber exposed the samples to ≈ 119 days of UV irradiance under natural sunlight. To prevent overheating the samples inside the chamber, a water bath was used to regulate temperature.

Cytocompatibility—Cell Culture: Human dermal fibroblasts (106-05N; Sigma-Aldrich, St. Louis, MO, USA) were cultured in Dulbecco's Modified Eagle Medium (DMEM), high glucose, with GlutaMAX (Gibco, Cat. No. 10-566-024; Thermo Fisher Scientific, Waltham, MA, USA), supplemented with 10% fetal bovine serum (GenClone, Cat. No. 25-550H; Genesee Scientific, San Diego, CA, USA) and 1% penicillin-streptomycin (Gibco, Cat. No. 15070063; Thermo Fisher Scientific, Waltham, MA, USA). Cells were maintained in T182 flasks at 37 °C in a humidified incubator with 5% CO_2 . Medium was replaced every 3 days.

Cells were passaged at $\approx 80\%$ confluence using 0.25% trypsin-EDTA with phenol red (Gibco, Cat. No. 25-200-072; Thermo Fisher Scientific, Waltham, MA, USA) diluted to 0.05%. Trypsinization was performed for 5 min at 37 °C in the incubator and neutralized with an equal volume of complete medium. Cells were collected by centrifugation at $300 \times g$ for 5 min, resuspended in fresh medium, and counted using an automated cell counter (Countess, Thermo Fisher Scientific, Waltham, MA, USA).

For experiments, cells were seeded at a density of 10 000 cells cm^{-2} in 48-well plates (0.84 cm^2 /well; Corning, Corning, NY, USA), corresponding to ≈ 8400 cells per well. After plating, cells were allowed to adhere and stabilize for 24 h before initiating treatment. Cells were then exposed to treatment conditions for 48 h. All experiments were conducted using cells plated at passage 5.

Cytocompatibility—Treatment: PAA-cND microgels were prepared at pH 4.1 and pH 5.5. Prior to adding to the well plate, the microgel was sterilized by UV light for 1 h. 50 or 100 μL of each sterilized gel solution was mixed into 300 μL of the prepared cell culture media to create an evenly distributed gel-fragment solution, which was then plated on the cells.

Cytocompatibility—Live/Dead Fluorescence Imaging: Live/dead fluorescent cell imaging was conducted to quantify cell viability after being in contact with PAA-cND microgels. After the contact time had elapsed, the media was aspirated and washed with 1X PBS. Following treatment, cell viability was assessed using the Invitrogen LIVE/DEAD Cell Imaging Kit (488/570) (Cat. No. R37601; Thermo Fisher Scientific, Waltham, MA, USA), following the manufacturer's instructions. Briefly, the Live Green component (Component A) was mixed into the Dead Red component (Component B) to prepare a 2x working solution. This solution was added

at a 1:1 ratio to cell culture medium, and cells were incubated for 15 min at room temperature (20–25 °C), protected from light.

After staining, cells were washed with PBS and imaged immediately. Live cells exhibited green fluorescence (excitation/emission $\approx 488/515\text{ nm}$), while dead cells emitted red fluorescence (excitation/emission $\approx 570/602\text{ nm}$). Imaging was performed using a Leica fluorescence microscope equipped with FITC and Texas Red filter sets and captured using a K3M camera. Three images per well in consistent locations were taken. The images were processed using ImageJ image processing software. Fluorescence images were analyzed using ImageJ (Fiji distribution, NIH) via a custom macro to quantify live and dead cells. Images were first scaled to fit the display and converted to an 8-bit grayscale. A Gaussian blur ($\sigma = 2$) was applied to reduce noise, and an automatic threshold was applied using the Default (dark) method. Users were prompted to manually adjust the threshold, if necessary, before conversion to a binary mask. Post-thresholding, binary masks were processed through the following morphological operations to optimize segmentation: fill holes, dilate, erode, and watershed. Cell objects were identified using the Analyze Particles function with a size filter of 100–10 000 pixels², and results were displayed with overlay masks and summary tables. Quantitative data, including total particle count and area, were extracted from the ImageJ summary output and used for further statistical analysis. Triplicates were conducted of each sample and the positive control of pH-balanced collagen.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

P.K.J., S.A.N., and K.J.E. are co-first authors of this article. The authors thank Farrah Haeri for her initial contributions to the project. The authors acknowledge Orin Velev for access to the Zetasizer and the UV flood lamp chamber. This work was performed in part at the North Carolina State University Analytical Instrumentation Facility (AIF), which was supported by the State of North Carolina and the National Science Foundation (ECCS-2025064). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI). The authors would also like to thank the Kenan Institute for Engineering, Technology and Science (KIETS) at NC State for partial support of this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

colloidal hydrogels, nanodiamond, SPF measurements, tribology, UV radiation

Received: February 19, 2025

Revised: July 25, 2025

Published online: September 2, 2025

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