Rheology and Adhesion of Poly(acrylic acid)/Laponite Nanocomposite Hydrogels as Biocompatible Adhesives

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ABSTRACT: Biocompatible nanocomposite hydrogels (NC gels) consisting of poly(acrylic acid) (PAA) and nanosized clay (Laponite) were successfully synthesized by in situ free-radical polymerization of acrylic acid (AA) in aqueous solutions of Laponite. The obtained NC gels were uniform and transparent. Their viscosity, storage modulus $G’$, and loss modulus $G''$ increased significantly upon increasing the content of Laponite and the dose of AA, while exhibiting a maximum with increasing the neutralization degree of AA. They showed tunable adhesion by changing the dose of Laponite and monomer as well as the neutralization degree of AA, as determined by 180° peel strength measurement. The maximal adhesion was shown when reaching a balance between cohesion and fluidity. A homemade Johnson–Kendall–Roberts (JKR) instrument was employed to study the surface adhesion behavior of the NC gels. The combination of peel strength, rheology, and JKR measurements offers the opportunity of insight into the mechanism of adhesion of hydrogels. The NC gels with tunable adhesion should be ideal candidates for dental adhesive, wound dressing, and tissue engineering.

1. INTRODUCTION

Polymeric hydrogels, composed of hydrophilic polymer networks, are soft materials that can absorb and retain large amounts of water. The cross-linked networks make the hydrophilic polymer chains swell in aqueous solution without dissolving.1 The tissue-like flexible polymers, with a high affinity for water, promote the biocompatibility of polymeric hydrogels.2 Hydrogels have been used for biomaterials for a long time.3 The three-dimensional network in hydrogel is formed physically or chemically by cross-linking polymer chains. The physical cross-linking can be driven by entanglement, van de Waals interactions, hydrogen bonding, or electrostatic interaction.4–6 Smart polymer hydrogels with stimuli (temperature, pH, ionic strength, light, solvent type, and electric and magnetic fields) sensitivity and response7–12 have many potential applications, including biological sensors,13 tissue engineering,14 drug delivery systems,15 bioadhesives,16 and wound dressings.17

In comparison to the conventional hydrogels prepared using a chemical cross-linker, N,N’-methylenebisacrylamide (BIS), a kind of novel nanocomposite hydrogel (NC gel) with extraordinary toughness, high transparency, and amazing elongation was first reported by Haraguchi et al.18–20,22 These hydrogels were composed of polymers of acrylamide or its derivative and Laponite, a nanosized synthetic silicate clay, which can be gradually cleaved into nanodisks in water. The clay platelets with negatively charged surfaces and positively charged edges tend to form a so-called house-of-cards structure above a critical concentration.21 However, most of the studies were focused on their mechanical properties,19,20,22 swelling properties,18 and stimulus sensitivity,18,19,23 while hardly any report on their adhesive properties can be found in the literature.

In fact, polymeric hydrogels can be used as biocompatible adhesives. Their adhesion is of great importance for biomedical application, such as denture adhesive24 and wound cover.17 To explore their surface adhesive behavior, an alternative adhesion measurement based on the theory of Johnson, Kendall, and Roberts (JKR),25 henceforth referred to as the JKR method, has become an important technique especially for elastomeric systems.26 Its high sensitivity and direct measurement on various surfaces make it widely applied in research.27

In this paper, we report the preparation of biocompatible NC hydrogels by in situ free-radical polymerization of acrylic acid (AA) in a Laponite aqueous solution. These NC gels show high transparency, tunable fluidity, and adhesion. To illustrate the interrelationship of interfacial and bulk contributions to the adhesion, we have prepared a series of nanocomposite poly(acrylic acid) hydrogels (PAA NC gels) with various doses of the monomer and cross-linker as well as neutralization degree of AA. The effect of carboxyl groups as well as cross-linking density on the adhesion of PAA NC gels is explored by rheological and peel strength measurements. The application of the JKR method is presented to study the surface adhesion and modulus of NC gels. It will provide insight into the mechanism of adhesion of NC gels for applications in bioadhesives.
2. EXPERIMENTAL SECTION

2.1. Materials. Synthetic hectorite “Laponite XLG” ([Mg_{5.34}Li_{0.66}Si_{8}O_{20}(OH)_{4}]Na_{0.66}; layer size, 20−30 nm × 1 nm; cation-exchange capacity, 104 mequiv/100 g) was obtained from Rockwood, Inc. and used as received. Potassium persulfate (KPS; 99% +), BIS, and AA (99%, distilled under vacuum prior to use) were purchased from Aldrich. The water used in all of the experiments was purified by osmosis and subsequent ion exchange (Millipore Mill-Q). During all experiments, oxygen was excluded from the system. An ultrasonic apparatus (SK7210LHC) was used to remove the bubbles from the solution before reaction.

2.2. Synthesis. The synthesis of PAA/Laponite NC gel is shown schematically in Figure 1a. The NC gels were prepared using different amounts of AA and Laponite. The resulting NC gels are named as NCX-Y, according to the amount of Laponite (X weight percent of water) and monomer AA (Y weight percent of water), respectively. For instance, to prepare the NC1-20 gels, 1 g of Laponite was added to 100 g of water in a three-neck flask and mixed to disperse utterly by a magnetic stirrer for nearly 4 h under nitrogen gas. Then, 0.2 g of KPS and 20 g of AA were dissolved in the above Laponite aqueous solution cooled by an ice bath. After thorough mixing, the mixture was poured into molds. Subsequently, sonication was used to remove the bubbles in the solution. Finally, free-radical polymerization was performed in an oil bath at the temperature of 70 °C for 5 h. For comparison, hydrogels were synthesized by partly replacing clay with BIS under the same conditions, which were named as NCX-BISZ-Y (Z molar percent of Laponite).

2.3. Scanning Electron Microscopy (SEM). The hydrogels were cut into disks with the diameter of 10 mm and thickness of 5 mm and then were quickly frozen in liquid nitrogen and freeze-dried to remove the water. The morphology of the cross-section was observed using JEOL JSM-6360LV SEM after coating freeze-dried white porous gels with a thin layer of gold.

2.4. Rheological Measurements. Both the steady and dynamic rheological measurements were performed on a Physica MCR501 (Anton Paar GmbH) stress-controlled rheometer equipped with a Peltier device for temperature control within ±0.1 °C. A parallel-plate made of stainless steel with a diameter of 25 mm was used. During all rheological measurements, the upper plate was set at a distance of 1 mm and a trap was used to minimize the solvent evaporation.

2.5. 180° Peel Measurement. The 180° peel test was following the ASTM D903-49 procedure. The measurement was performed using a SANS CMT-2000 tensile test machine by fastening cloth to a wood plate with the NC gels. A total of 1.5 g of NC gels was uniformly coated on the wood plate with a size of 30 mm in width and 100 mm in length. Peel strength measurements were performed at room temperature with a peel crosshead speed of 100 mm/min. The measurement was repeated at least 3 times.

2.6. JKR Measurements. The surface adhesion of PAA/Laponite NC gels was determined by employing a homemade JKR instrument based on the theory by Johnson, Kendall, and Roberts. In comparison to the traditional adhesion tests, the sensitivity of the JKR experiments is dramatically improved because the bulk losses are confined to the crack zone. As shown in Figure 2a, a rigid hemispherical metal indenter with radius R is pressed against a thin gel layer with thickness h, under a load P (Figure 2b). The contact area
with a radius of $a$ is viewed through the transparent glass slide and lens. A linear stepping motor is used to control the motion of the samples at a steady velocity. During the contact process, a load transducer monitors the normal force $P$ and a displacement sensor records the normal displacement $\delta$. ImagePro Plus software was used to observe the contact radius $a$ with a circle-fitting function, as shown in Figure 2c.

3. RESULTS AND DISCUSSION

3.1. Preparation of PAA/Laponite NC Hydrogels.

Uniform and transparent PAA/Laponite NC gels were prepared by in situ free-radical polymerization in solution with various concentrations of Laponite and AA. The NC gels display high transparency even at high monomer and enhanced Laponite concentrations (Figure 1b). The synthesized PAA/Laponite NC gels showed tunable mechanical properties and adhesion. The NC gel NC1-20 prepared with less amount of AA was semi-solid, ductile, and sticky. When the amount of AA increased to 40% and Laponite doubled (NC2-40), the NC gel becomes solid-like, tough, and sticky (Figure 1b).

To illustrate the effect of Laponite particles on the morphology of hydrogels, topological micrographs of the fractured cross-section of the freeze-dried chemically cross-linked PAA gel and PAA/Laponite NC gel were shown in panels c and d of Figure 1. Both of them exhibit porous structures, indicating the loss of the water during freeze-drying. The cross-section of chemically cross-linked PAA gel is smooth, while that of the NC gel seems quite coarse with plentiful sharp peaks because of the toughening effect of Laponite particles, which act as both cross-linker and filler to improve the bulk cohesion of the NC gel when using as an adhesive.

3.2. Rheology. 3.2.1. Effect of the Laponite Content. The steady shear viscosities as a function of the shear rate for NC gels with various Laponite amounts are shown in Figure 3a. The viscosity of PAA/Laponite NC gels increased monotonically upon increasing the Laponite content. The AA polymerization was supposed to happen on the surface of the Laponite disk-like particle.29 The increase of viscosity is due to the enhancement of the cross-linking density. The oscillatory frequency sweep measurement was carried out at a constant strain of 1% (chosen in the linear viscoelastic range) to observe the dynamic rheological behavior of PAA/Laponite NC gel. As shown in Figure 3b, the storage modulus $G'$ and the loss modulus $G''$ evolution of the NC gels with different Laponite contents as a function of the frequency were compared. $G'$ and $G''$ increased monotonically by increasing the amount of Laponite. The curves of $G'$ and $G''$ as a function of the frequency crossed each other, and the intersection point ($G' = G''$) shifted to a lower frequency with an increasing Laponite content, which means that the relaxation time $\tau^*$ ($\tau^* = 1/f^*$) become longer, where $f^*$ is the crossover frequency at $G' = G''$.20 The $\tau^*$ gives information on the time scale of the mechanical relaxation process in the polymer network. A larger intersection time $\tau^*$ reflects a higher cross-linking density.24 The addition of Laponite improved the cohesion of PAA/Laponite NC gels.

3.2.2. Effect of the AA Dose. As shown in Figure 4a, the viscosity of PAA/Laponite NC gels with the identical Laponite

Figure 3. (a) Viscosity as a function of the shear rate. (b) Elastic modulus ($G'$) and viscous modulus ($G''$) as a function of the frequency at the oscillatory strain of 1%. The changing parameter is the Laponite content.

Figure 4. (a) Viscosity as a function of the shear rate. (b) Elastic modulus ($G'$) and viscous modulus ($G''$) as a function of the frequency at the oscillatory strain of 1%. The changing parameter is AA doses.
concentration increased monotonically upon increasing the dose of monomer AA. A higher monomer concentration leads to a higher molecular weight and longer polymer chains. The response of the materials in terms of the elastic modulus ($G'$) and the viscous modulus ($G''$) was measured by an oscillatory frequency sweep.

As shown in Figure 4b, more information on the structure of the NC gels network can be obtained. It revealed that the AA dose has a significant influence on both the elastic modulus and the viscous modulus ($G''$) in NC gels. For NC2-10 with a low AA dose, the loss modulus $G''$ was larger than the storage modulus $G'$ at high frequency, indicating that the viscous behavior is dominated and the sample displays liquid-like behavior. With an increase of the monomer dose, $G'$ exceeded $G''$ gradually and the intersection point moved to a lower frequency. The increased dose of AA resulted in the presence of entanglement of polymer chains in NC gels.22,31 These entangled polymer chains produce the additional cross-linking among Laponite sheets.

3.2.3. Effect of pH. The influence of pH on the rheological behavior of hydrogels is significant and non-monotonic. A series of NC1.5-20 hydrogels with different pH values were synthesized by neutralizing the AA monomer using sodium hydroxide solution with the concentration of 0.5 mol/L. As shown in Figure 5a, the viscosity of the NC gels increased upon increasing pH from 3.26, reached a maximum at pH 3.64, and then decreased until pH 4.68. The change of the storage modulus $G'$ and the loss modulus $G''$ as a function of the frequency was in accordance with the steady shear viscosity (Figure 5b).

It was found that the hydrogel tended to be a viscous fluid with $G'' > G'$ at a pH value of 4.68, where there was no intersection between $G''$ and $G'$ across the whole oscillatory frequency. The electrostatic effect between Laponite and PAA chains showed a strong impact on the rheological behavior of the hydrogel. The net charge of Laponite is negative, although there exists a positive charged edge.21 It is supposed that the PAA chains are grafted on the Laponite surface.32 Upon increasing the pH value, $-\text{COOH}$ groups in the AA chain begin to ionize. This may contribute to the binding between PAA and positive patches in Laponite at the beginning, but a further increase of the negative charge in PAA with higher pH will damage the binding between PAA and Laponite both with a negative charge.

3.3. Peel Strength. An ideal adhesive should easily flow on the surface of the adherent to achieve good contact and adequate wetting. On the other hand, a failure may happen because of the cohesive failure of the adhesive itself. Thus, the balance between fluidity and cohesion of adhesives is essential for an overall good adhesion.24 From the rheological measurements, it is known that the viscosity, $G'$, and $G''$ of NC gels increased monotonically when the AA content increased from 10 to 40%. The increase in $G'$ reflects the enhancement of cohesive energy of the NC gels. The peel strength increased from 8.32 N/cm (NC2-10) to 11.98 N/cm (NC2-30) but decreased to 7.68 N/cm (NC2-40) upon increasing the dose of AA (Figure 6a). The adhesion of NC gels did not follow the tendency of viscosity because of the decreasing flowability with the increasing AA content. Indeed, the cohesion and flowability of hydrogels are contradictory. Therefore, a balance between...
the cross-linking and fluidity is required to obtain optimized adhesion.

As shown in Figure 6b, the peel strength also showed a maximum upon increasing the Laponite amount from 1 to 4% with the constant AA dose of 20. An increased Laponite content enhanced the cross-linking density and cohesion of the NC gels while leading to a decrease in flowability, which could lead to failure occurring at the interface between adhesives and the adherent during the peel process. As shown by inset photos in Figure 6b, the style of failure will change from cohesive rupture to adhesive failure with the increase of the cross-linking density. Appropriate rheology is an essential condition for adhesion but not a sufficient condition. This reinforces the belief that both appropriate rheology and sufficient cross-linking are required for proper adhesion.

According to the opinion of McLaren et al.,35 the cohesion between the adhesives and the adherent at the interface is one of the main contributions to surface adhesion forces. The peel strength can be significantly increased when the specimens are bonded at higher temperatures. Therefore, we compared the peel strengths of samples after treatment at different temperatures with the pressure of ca. 0.025 kg/cm² under seal for 2 h. From the results listed in Table 1, it was found that the peel strength increased significantly with the increase of the treatment temperature. The NC gels had good compatibility with the surface of the adherent because of the hydrophilicity of both PAA and wood fiber. When they came into contact, interdiffusion occurred at the interface because of intermolecular Brownian motion. This interdiffusion process was accelerated by increasing the temperature.

In addition, upon increasing the pH of the system from 3.26, 3.64, 4.23, to 4.68, the corresponded peel strength reached monotonically from 20.78, 17.92, 15.52, to 9.7 N/cm. According to the opinion of McLaren et al.,35 the cohesion force shows an exponential relationship with the concentration of the carboxyl group in the adhesives, which can form hydrogen bonding with the adherent fiber. The increased neutralization degree of AA at enhanced pH led to a decrease in carboxyl groups and, thus, the adhesion. The bonding efficiency of carboxyl groups was inhibited when parts of the carboxyl groups in the chains were neutralized.

3.4. JKR Measurement. The measurement was conducted using a homemade JKR instrument. The influence of the structure and binding chains on the adhesion of PAA hydrogels can be quantified by the fracture mechanics analysis based on measurement of load and displacement. The adhesive behaviors of PAA/Laponite NC gels with different Laponite contents and AA monomer doses as observed by JKR were shown in Figure 7. As a comparison, the adhesion of NC gels cross-linked by both Laponite and BIS was analyzed (Figure 8).

As shown by the JKR measurement, the unloading of NC gels could not finish completely within the allowable measurement range because of the high surface adhesion, high extensibility, and ductile flow of NC gels, while the unloading force increased with increasing the AA dose or Laponite content (Figure 7). It is believed that the enhanced amount of Laponite and AA dose increased the cross-linking degree, which promoted the moduli and cohesion of the NC gels. As shown in Figure 7a, a significant larger adhesion force was observed during the unloading for NC gels with an increased dose of AA. In comparison to Figure 7b, it seems that the increase in the AA dose is more effective to improve the surface adhesion for NC gels than the enhancement of the Laponite amount. It confirms that the hydrogen bonding between the $-\text{COOH}$ group does have the critical importance to adhering.

In Figure 8a, loading and unloading force ($P$) was plotted as a function of the displacement ($\delta$) for samples cross-linked by both BIS and Laponite. In our measurements, the crosshead velocity is 3 $\mu$m/s and the radius of curvature for the spherical indenter is 3 mm. All of the measurements were carried out at room temperature and repeated at least 3 times. As shown in Figure 8a, the maximum contact area was achieved at a displacement of 50 $\mu$m, where a similar compressive force of around 0.6 mN was reached during the loading stage. However, the individual pull-off force of three samples was quite different because of the various adhesions during the unloading stage.

The pull-off force during the unloading stage increased distinctly by increasing the content of Laponite or by decreasing the dose of BIS (Figure 8a). One potential explanation for this is that the Laponite, by uniformly dispersing in the system, acts as a cross-linking agent, with flexible polymer chains physically linking on the surface of the plate-like Laponite, which improves the fracture energy and the

Table 1. Adhesion of NC Gels after Treatment at Different Temperatures

<table>
<thead>
<tr>
<th>sample</th>
<th>untreated</th>
<th>treated at 20 °C</th>
<th>treated at 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC1-20</td>
<td>4.7 ± 0.2</td>
<td>10.8 ± 0.4</td>
<td>21.9 ± 0.9</td>
</tr>
<tr>
<td>NC2-20</td>
<td>3.6 ± 0.2</td>
<td>9.3 ± 0.6</td>
<td>19.1 ± 0.7</td>
</tr>
</tbody>
</table>

Figure 7. Load as a function of the displacement, for PAA/Laponite NC gels with various (a) AA doses and (b) Laponite contents.
cohesion of NC gels. On the other hand, decreasing the content of chemical cross-linker BIS could increase the flowability, which is beneficial to the surface adhesion. For viscoelastic materials, some energy will be dissipated at the fracture line because of the viscous losses. In almost all cases, a higher work of adhesion was obtained for an unloading stage compared to a loading stage. The area of triangle, which represents the work of adhesion, reached a maximum for NC2-BIS1-20. This result was compatible with the results of loss factor tan δ by a rheological test in Figure 8b, which represents the ratio of dissipated energy to stored energy during one deformation cycle.

To study the influence of contact surface and Young’s modulus on the contact between two bodies, the JKR equation is transformed to a linear form, as shown in eq 1.36 The Young’s modulus (E*) and the energy release rate (G) can be calculated after knowing the contact area (a) and tensile load (P), where the contact area (a) can be obtained visually, as shown in Figure 8d.

\[
\frac{4a^{3/2}}{3R} = \frac{1}{E^*} \left( \frac{P}{a^{3/2}} + \sqrt{\frac{8\pi G}{E^*}} \right)
\]

The E* could be found from the inverse slope of the linear fitting in Figure 8c.36 It was found that the sample NC2-BIS1-20 showed the smallest E* and the largest contact area among the three samples. It is believed that the contact area between the two materials and the force required to separate them are proportional to the balance between the work of adhesion and the stored elastic energy.37 As shown in Figure 8b, NC2-BIS1-20 possessed the highest tan δ, which means that it is much easier to flow and cover the indenter than the other two samples during the experiment. To separate bodies in intimate contact, the work needed during the unloading stage depended upon the contact area and the number of connected chains on the contact interface. Hence, a sample of NC2-BIS1-20 with the largest contact area required more energy to overcome the adhesive forces. Obviously, the JKR measurement can characterize the cohesion (E*) and surface adhesion of NC gels from a new viewing angle.

4. CONCLUSION

Biocompatible NC gels consisting of PAA and nanosized Laponite particles were synthesized by in situ free-radical polymerization of AA in the aqueous solution of Laponite. The obtained NC gels were transparent and uniform. Because of the presence of free carboxylic acid groups, the NC gels exhibited tunable adhesion and pH responsiveness. Rheological results showed that the cross-linking and entanglement density increased significantly with the increasing contents of Laponite and AA, respectively. Both peel and tip cracking methods have been applied to measure the adhesion of the NC gels. The peel strength showed a maximum with the increasing Laponite content and AA dose because of the balance between cohesion and fluidity. It may be concluded that the peel strength energy consists of two parts: the (reversible) work of adsorption and the (irreversible) work of deformation, which accounts for the balance between the storage modulus (G’) and the viscous modulus (G″) of the rheological properties. Furthermore, the adhesion of PAA/Laponite NC gels can also be tailored by regulating the neutralization degree of AA and treatment temperature. The JKR test showed that the surface adhesion of NC gels increased by increasing both the AA dose and Laponite content within our experimental range. In summary, the synthesized NC gels have an enhanced mechanistic understanding of the effect of the structure of gels and attachment chains on the interfacial adhesion. Because of the biocompati-
ibility and tunable adhesion, PAA/Laponite NC gels should be ideal candidates for bioadhesives.

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**Notes**

The authors declare no competing financial interest.

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