

Article

Green and Controllable Crosslinked Gel Plugging Technology Based on Modified Natural Biofibers

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Abstract

To overcome the limited mechanical strength and poor stability of conventional gels in high-temperature, high-salinity oilfield environments, a novel nanocellulose-reinforced hydrogel (AM/AA/PCNF) was developed through a multistep chemical modification strategy. Nanocellulose served as a rigid backbone and was successively modified via epoxide ring-opening, methacryloyl esterification, and polydopamine functionalization, forming a three-dimensional network with multiple dynamic crosslinking interactions. The resulting composite hydrogel exhibited outstanding comprehensive properties when the PCNF content was 3 wt%: a tensile strength of 2.6 MPa, fracture energy of 8.95 MJ/m³, and compressive strength of 360 kPa—all markedly superior to those of conventional hydrogel systems. Under simulated downhole conditions (120 °C, 6 MPa, and 5 wt% salinity), the hydrogel demonstrated excellent plugging performance across sand beds of varying particle sizes (60–80 mesh to 20–40 mesh), maintaining cumulative fluid loss within 28.4–42.5 mL. Mechanistic investigations indicate that the enhanced performance stems from the synergistic combination of a rigid nanocellulose scaffold and multiple dynamic interactions, which facilitate a self-adaptive plugging mechanism. The study delivers both theoretical and practical foundations for designing advanced plugging systems.

Keywords: plugging technology; hydrogel; nanocellulose; polydopamine; compressive strength



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1. Introduction

Drilling through fractured, highly permeable, or unconsolidated formations often leads to wellbore leakage, constituting a major technical challenge in oil and gas operations [1,2]. Such leakage directly constrains operational safety, efficiency, and cost. With the global energy demand driving exploration targets toward ultra-deep reservoirs (depth > 4500 m) and unconventional formations, the downhole environment has become increasingly extreme and intense geostress. Under these harsh conditions, conventional plugging materials—such as rigid bridging particles (e.g., sawdust, walnut shells) and linear polymer gels (e.g., partially hydrolyzed polyacrylamide)—exhibit intrinsic performance limitations [3,4]. Exposure to high temperatures promotes increased mobility of polymer chains, leading to the collapse of physical network structures. Concurrently, thermal energy compromises hydrogen bonding and other non-covalent interactions, potentially inducing irreversible hydrolysis or degradation of the polymer backbone, thereby undermining the material's structural and mechanical integrity. Meanwhile, monovalent (Na⁺) and divalent (Ca²⁺, Mg²⁺) cations in formation fluids compress the diffuse double layer around the gel network via the Debye shielding effect, weakening its electrostatic stabilization. More

critically, as demonstrated by Fukuzumi et al., divalent calcium ions can bridge anionic functional groups (e.g., carboxylates), causing polymer aggregation and precipitation [5]. The synergistic thermo–mechanical–chemical degradation eventually results in substantial modulus loss, dehydration shrinkage, and even total network collapse, leading to rapid deterioration in plugging performance [6]. Therefore, developing next-generation intelligent plugging gels that combine robust network topology with exceptional environmental resilience is essential to overcoming the fundamental bottlenecks of deep-well drilling technology [7–9].

To address the limitations of traditional gels, the design paradigm of nanocomposite hydrogels has emerged. The key reinforcement mechanism lies in incorporating rigid nanomaterials as multifunctional crosslinking nodes and stress-bearing units within flexible polymer matrices [10,11]. Through strong interfacial interactions—encompassing hydrogen bonding, van der Waals forces, and covalent linkages—efficient stress transfer and energy dissipation can be achieved, thereby enhancing both stiffness and toughness simultaneously. Among various nanomaterials, cellulose nanofibrils (CNFs) derived from renewable resources exhibit distinctive theoretical value and application potential owing to their intrinsic superior properties [2,12]. First, CNFs possess outstanding mechanical performance: their highly crystalline, fibrillar morphology affords an axial elastic modulus approaching the theoretical limit (approximately 150 GPa), rendering them ideal rigid stress-transfer units. Second, CNFs feature a large specific surface area and hydroxyl-rich surface chemistry, providing abundant reactive sites for subsequent chemical modification and the construction of strong interfacial interactions. Finally, the unique one-dimensional morphology of CNF enables the formation of fiber-like reinforcing networks in three-dimensional space via physical entanglement, while microscale mechanisms such as fiber pull-out and interfacial slippage effectively dissipate externally applied mechanical energy [13,14]. Moreover, their one-dimensional morphology enables the formation of entangled fibrillar networks, which effectively dissipate external stress via fiber pull-out and interfacial sliding mechanisms. Empirical studies have validated their remarkable reinforcing potential: Yang et al. grafted polymer chains directly onto CNF surfaces to construct interface-strengthened hydrogels [15], while Wei et al. embedded covalently bonded CNFs into polyacrylamide networks to create rigid–flexible interpenetrating structures, achieving nearly an order-of-magnitude increase in compressive strength [16]. These findings confirm CNF as an ideal reinforcing component capable of fundamentally altering gel deformation and failure mechanisms.

The strong hydrophilicity and interfacial instability of CNF limit its performance, especially under the extreme temperature and salinity conditions encountered in oilfield environments [17–19]. The physicochemical origin of this limitation lies in the fact that elevated temperatures intensify water molecular motion, weakening the interfacial bonding between CNF and hydrophobic polymer segments; meanwhile, high ionic strength compresses the electrical double layer formed by surface carboxylate groups, leading to diminished electrostatic repulsion, fiber aggregation, and phase separation. Such environment-induced interfacial failure and microstructural instability ultimately degrade the CNF-reinforced gel network and impair its rheological and plugging performance. To overcome these challenges, researchers have focused on precise surface engineering of CNF to regulate interfacial chemistry and environmental stability. Representative modification strategies include: (i) the green sulfonation route developed by Sirviö et al., which introduces strongly hydrated sulfonic groups to enhance electrostatic stability and dispersion [20]; (ii) the acyl chloride functionalization method by Liu et al., where reactive carbon–carbon double bonds are grafted onto CNF via nucleophilic substitution, enabling CNF to act as an active macromolecular monomer in free-radical polymerization and thus construct covalently

crosslinked networks [5]; and (iii) other approaches such as maleic anhydride grafting or cationic etherification to introduce quaternary ammonium groups, thereby improving compatibility, reactivity, and chemical durability [21,22]. However, these modification strategies, which either prioritize improved dispersion or introduce a single covalent crosslinking functionality, still fail to systematically address the interfacial stability of CNF and the coordinated construction of multiscale energy-dissipation mechanisms under coupled thermo–mechanical–chemical fields. This directly constrains its long-term performance under harsh downhole conditions and represents the key challenge confronting current research.

Building upon these insights, this study proposes a synergistic strategy that integrates surface molecular design with hierarchical structural engineering. The core concept is to transform CNF from a passive physical filler into an active covalent crosslinking node capable of directing three-dimensional network construction. We designed a well-defined, synergistic three-step chemical modification strategy: first, hydrophobic functionalization via grafting long alkyl chains using epoxydodecane, aimed at enhancing high-temperature hydrophobic associations to improve the thermal stability of the hydrogel; second, active group grafting through the introduction of copolymerizable C=C double bonds using methacryloyl chloride, with the primary goal of transforming CNF from a physical filler into a “macromolecular crosslinker,” firmly anchoring it within the network via covalent bonds to strengthen interfacial adhesion; third, multifunctional coating by introducing dopamine, intended to leverage its abundant functional groups to provide numerous dynamic hydrogen bonds for toughening, while its biomimetic adhesive properties enhance the hydrogel’s plugging strength in formation environments. Our aim is to develop a novel nanocomposite hydrogel that integrates high mechanical strength, excellent environmental tolerance, and adaptive plugging capability, thereby addressing the technical bottleneck of failure of conventional lost-circulation materials under high-temperature and high-salinity conditions encountered in deep and ultra-deep oil and gas exploration. This work is intended to provide both a solid theoretical basis and a practical pathway for the development of next-generation intelligent plugging materials.

2. Materials and Methods

2.1. Materials

The nanocellulose (CNF) used in this study is a commercially available product (Aladdin Reagent, Riverside, CA, USA), prepared from wood pulp via high-pressure homogenization, and used directly without further purification. The main chemical reagents employed in this work were 1,2-epoxydodecane, methacryloyl chloride, acrylamide (AM), dopamine hydrochloride, acrylic acid (AA), and N,N'-methylenebisacrylamide (MBA), all of which were supplied by Aladdin Reagent Co., Ltd. Triethylamine (TEA), tris(hydroxymethyl)aminomethane (Tris), and anhydrous ethanol were purchased from Energy Chemical Co., Ltd. (Gunsan, Republic of Korea).

2.2. Sample Preparation

2.2.1. Preparation of Hydrophobically Modified CNF

A homogeneous dispersion of CNF was obtained by sonicating 0.50 g of dried CNF in 100 mL of anhydrous DMF at 200 W for 30 min. Subsequently, 1.50 g of 1,2-epoxydodecane (GE-10, three times the CNF mass) and 0.20 g of triethylamine were introduced into the dispersion. The system was maintained at 80 °C in an oil bath for 12 h to facilitate the ring-opening grafting of epoxide groups onto the CNF surface. Once the reaction finished, centrifugation at $8000 \times g$ rpm for 10 min was used to separate the solid product. The collected material was rinsed sequentially with ethanol and deionized water until the

supernatant became clear and odorless. Finally, the purified solid was dried under vacuum at 40 °C for 24 h, yielding the hydrophobically modified cellulose nanofibrils, referred to as CNF-C10.

2.2.2. Grafting of Methacryloyl Groups

CNF-C10 (0.30 g) was dispersed in 50 mL of anhydrous THF and sonicated for 20 min to obtain a uniform suspension. Under an ice-water bath, methacryloyl chloride (MACl, 0.50 mL) was added dropwise, followed by 0.60 mL of triethylamine to neutralize the HCl byproduct. Stirring at room temperature was maintained for 6 h to facilitate methacryloyl grafting on the CNF surface. Upon completion, the product was recovered by centrifugation and sequentially washed three times with THF and deionized water. The purified solid was then dried under vacuum to yield the methacryloyl-functionalized CNF, designated as CNF-MA.

2.2.3. Dopamine Modification and Polydopamine Coating

CNF-MA (0.20 g) was dispersed in 100 mL of 10 mmol/L Tris-HCl buffer (pH 8.5) and sonicated for 15 min to achieve a homogeneous suspension. Dopamine hydrochloride (DA·HCl, 0.40 g) was then introduced, and the mixture was stirred for 24 h to allow oxidative self-polymerization of dopamine and subsequent deposition of polydopamine onto the CNF surface. The product was isolated via centrifugation at $9000 \times g$ rpm for 10 min, rinsed three times with deionized water, and subsequently freeze-dried, yielding polydopamine-coated CNF (PCNF). A schematic of the modified CNF preparation is presented in Figure 1.

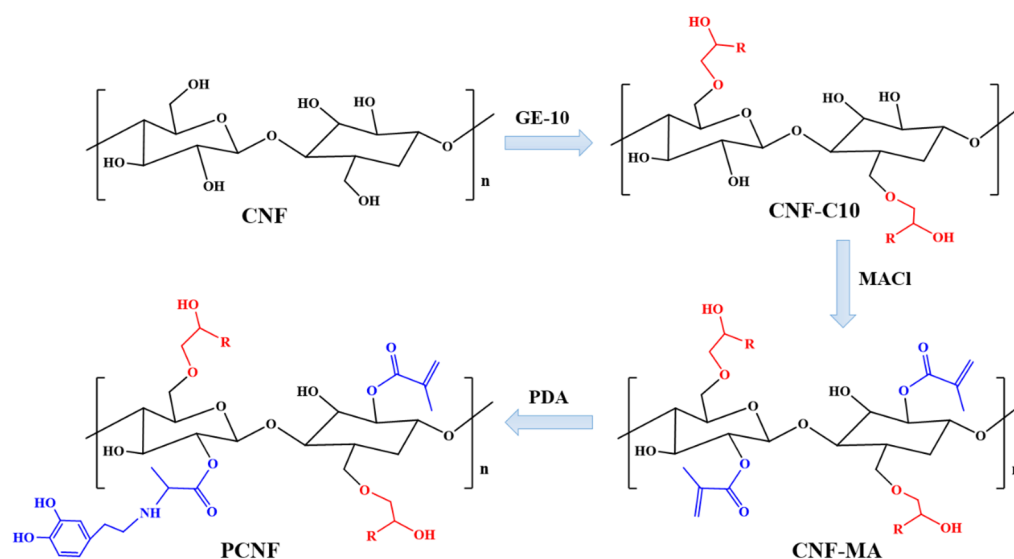


Figure 1. Schematic representation of the modified CNF preparation process.

2.2.4. Preparation of Composite Hydrogels

PCNF was sonicated in 20 mL of deionized water for 20 min to produce a stable suspension. Acrylamide (AM, 1.0 g) and acrylic acid (AA, 0.20 g) were then incorporated, and the solution pH was adjusted to 7.0. N,N'-Methylenebisacrylamide (MBA, 0.01 g) was added as a crosslinker, followed by ammonium persulfate (APS, 0.005 g) as the initiator. After thorough homogenization, the mixture was cast into cylindrical molds (10 mm diameter $\times$ 10 mm height) and polymerized in a water bath at 60 °C for 4 h, forming CNF-based composite hydrogels (denoted as PCNF) featuring multiple covalent crosslinks and dynamic supramolecular interactions, as illustrated in Figure 2. For comparison, hydrogels containing different amounts of modified CNF (0, 1, 3, and 5 wt%) were prepared under

identical conditions and designated as AM/AA, AM/AA/PCNF1, AM/AA/PCNF3, and AM/AA/PCNF5, respectively.

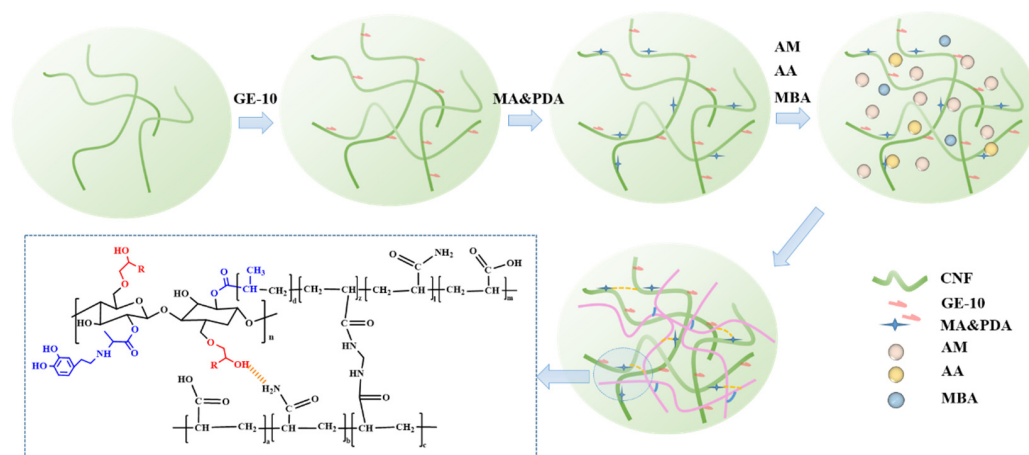


Figure 2. Schematic representation of the fabrication procedure of the modified CNF-based composite hydrogel.

2.3. Characterization

The samples were characterized for chemical structure, thermal stability, and morphology. FTIR spectra were collected on a Bruker Tensor II spectrometer (Billerica, MA, USA) using KBr pellets over 4000–400 cm^{-1} with 32 scans and background correction. Thermal behavior was evaluated by TGA (TG 209 F3, NETZSCH, Selb, Germany) under nitrogen from 50 to 600 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Hydrogel surfaces were observed via SEM (JEOL JSM-IT300LV, Tokyo, Japan) after freeze-drying and gold sputter-coating.

2.4. Rheological Measurements

Rheological behavior was characterized using an MCR302 rheometer (Anton Paar, Graz, Austria) equipped. Circular hydrogel disks were mounted between the plates, and dynamic frequency sweep tests were conducted at room temperature within the 0.1–100 Hz frequency range to determine the viscoelastic response.

2.5. Mechanical Properties

Mechanical properties were evaluated on an Instron 3366 universal tester (Norwood, MA, USA) under room-temperature conditions. For tension, hydrogels were machined into dumbbell specimens (1 mm thickness, 2 mm gauge width, 12 mm gauge length) and stretched uniaxially at 100 mm/min until rupture; the peak stress and strain at failure were read from the stress–strain response, and toughness was determined by integrating the curve area. For compression, cylindrical gels (10 mm diameter, 10 mm height) were compressed at 10 mm/min, and the stress value at 70% nominal strain was taken as the compressive strength.

2.6. Swelling Behavior

Swelling performance was assessed in a 5 wt% mixed salt solution at room temperature. Hydrogels were weighed at predetermined intervals after immersion, and the corresponding swelling ratio (SR) was computed using Equation (1).

$$\text{SR} = \frac{m_t - m_0}{m_0} \quad (1)$$

where m_t is the hydrogel mass at time t , and m_0 represents the initial dry mass.

2.7. Texture Analysis

After drying and grinding, 10 g of hydrogel particles were mixed with a 5 wt% salt solution and aged in a high-pressure reactor at 130 °C for 5 days. The gel strength was determined using a Brookfield CT3 texture analyzer (Middleboro, MA, USA) with a probe area of 4 cm². With a 70% compression ratio, the tests were performed at 0.5 mm·s^{−1} initially and 1 mm·s^{−1} subsequently.

2.8. Plugging Performance Evaluation

Plugging performance was evaluated using a simulated leakage apparatus. A base layer of 100 g quartz sand was established in the drilling mud cell to mimic a leakage pathway, after which 400 mL of the plugging slurry was introduced. The temperature was adjusted to the target value, and the valve pressure differential was incrementally raised to 6 MPa at a rate of 1 MPa per 2 min. The filtrate volume during this stage was recorded as V_1 . After depressurization to 1 MPa and a 6 h holding period, the process was repeated to obtain V_2 . The cumulative fluid loss was calculated as:

$$V = V_1 + V_2$$

This procedure allowed quantitative comparison of the sealing efficiency of hydrogels under simulated high-temperature, high-pressure, and saline conditions.

3. Results and Discussion

3.1. Structural Characterization

Before conducting chemical modification, the micro-morphology of the pristine CNF was characterized. As shown in Figure 3a, the transmission electron microscopy (TEM) images reveal that the pristine CNF exhibits a typical entangled nanofibrous network structure, with fiber diameters ranging from 10 to 30 nm and lengths extending up to several micrometers, resulting in a high aspect ratio. This confirms its excellent potential as a nano-reinforcing filler and provides a morphological basis for constructing a three-dimensional reinforced network in subsequent modifications.

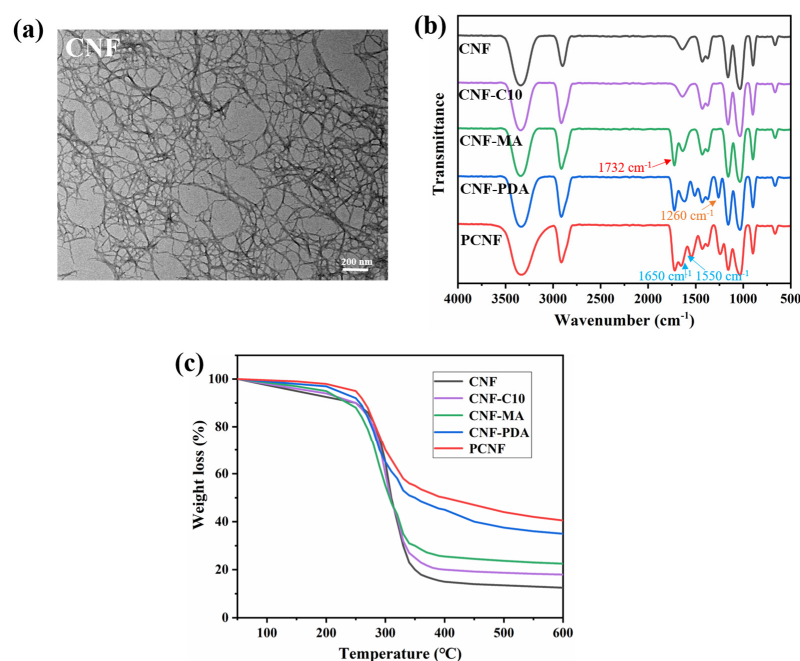


Figure 3. (a) Transmission electron microscope image of CNF; presents the FTIR spectra (b) and thermogravimetric profiles (c) of pristine, modified CNFs and the composite hydrogel.

FTIR analysis systematically illustrates the chemical evolution of CNF during sequential modification and hydrogel formation (Figure 3b). To better visualize the progressive chemical modifications, the key FTIR bands and their assignments are summarized in Table 1. Pristine CNF exhibits peaks at 3340, 2895, and 1058 cm^{-1} , assigned to OH stretching, C-H stretching, and C-O-C vibrations of glycosidic linkages, respectively. Following modification with epoxy decane (GE-10), new CH_2 stretching peaks emerge at 2920 and 2850 cm^{-1} , accompanied by a reduction in the hydroxyl band, suggesting successful grafting of long alkyl chains with partial hydroxyl substitution. Reaction with methacryloyl chloride (MACl) results in a carbonyl peak at 1732 cm^{-1} and a vinyl C=C band at 1635 cm^{-1} , indicating ester formation and successful grafting of polymerizable double bonds onto the CNF. Further dopamine modification results in aromatic ring vibrations (1505–1600 cm^{-1}), phenolic C-O stretching at 1260 cm^{-1} , and broadening of the 3200–3500 cm^{-1} region, indicating the successful deposition of polydopamine (PDA) onto the CNF surface. In the final PCNF hydrogel, amide I and II bands (1650 and 1550 cm^{-1}), along with carboxyl C=O (1715 cm^{-1}), confirm the effective copolymerization of AM, AA, and MBA, while the retention of PDA-related bands demonstrates that modified CNF is stably integrated into the 3D crosslinked network.

Table 1. FTIR characteristic bands, assignments, and corresponding chemical interpretations for CNF and its derivatives. Note: “new” denotes peaks that newly appear after modification, while “markedly decreased” indicates a significant reduction in intensity relative to the precursor.

Sample	Characteristic Bands (cm^{-1})	Assignment	Interpretation of Chemical Changes
CNF	3340, 1058	O–H stretching; C–O–C vibration	Native cellulose backbone
CNF-C10	2920, 2850 (new)	CH_2 asymmetric/symmetric stretching	Successful grafting of epoxide-decyl groups, introducing long alkyl chains
CNF-MA	1732, 1635 (new)	Ester C=O; C=C stretching	Methacryloylation with methacryloyl chloride, introducing polymerizable double bonds
CNF-PDA	1505–1600, 1260 (new)	Aromatic ring skeletal vibration; phenolic C–O	Successful dopamine/polydopamine coating
PCNF hydrogel	1635 (markedly decreased)	C=C stretching	Polymerizable double bonds consumed during copolymerization
	1650, 1550 (new)	Amide I and II bands	Successful polymerization of acrylamide monomers

TGA was performed to evaluate thermal stability (Figure 3c). Pristine CNF decomposes with $T_0 \approx 280$ °C and a char yield of 12.5 wt%. After epoxy decane grafting (CNF-C10), T_0 slightly decreases (~ 260 °C) due to the less stable alkyl chains, but the char yield rises to 18.0 wt%, suggesting enhanced carbon formation. Methacryloyl chloride modification (CNF-MA) further increases the char yield (22.5 wt%) while slightly lowering T_0 . Dopamine-functionalized CNF (PCNF) exhibits a two-step degradation with 35.0 wt% residual char, attributed to the aromatic polydopamine structure. Notably, the composite hydrogel achieved a superior char yield of 40.5 wt%, the highest among all prepared samples. This remarkable thermal resilience stems from a synergistic effect: First, the inherent chemical structure of polydopamine (PDA), which is abundant in aromatic moieties, imparts exceptional thermal stability and a high carbonization capacity, thus serving as the principal contributor to the enhanced char residue. Second, the modified CNF functioned as a polyfunctional crosslinking locus during polymerization, orchestrating the formation of a compact 3D covalent network with AM, AA, and MBA. This robust architecture physically hinders the escape of volatile fragments upon thermal decomposition, facilitating the development of an interconnected carbonaceous framework. Therefore, the achievement of a 40.5% char yield serves as compelling proof of the successful fabrication of a highly interconnected and thermally robust 3D network in the composite hydrogel.

SEM images (Figure 4) provide insight into the microstructural influence of PCNF on hydrogel morphology. The AM/AA hydrogel without PCNF (Figure 4a) displays a

loosely porous network with thin pore walls and evident structural defects (white arrows), leading to poor mechanical integrity. In contrast, the composite hydrogel containing 3 wt% PCNF (Figure 4b) exhibits uniform pore size, thicker walls (yellow arrows), and a dense, interconnected network. The incorporation of PCNF facilitates effective stress transfer and energy dissipation, thereby enhancing the macroscopic mechanical performance. Quantitative analysis of the SEM micrographs, conducted via ImageJ software (version 1.53k), demonstrates a clear distinction in pore morphology. The pristine hydrogel (Figure 4a) presented a broad pore size distribution spanning 5–20 μm , characterized by a large and heterogeneous average pore diameter. Conversely, the AM/AA/PCNF3 composite hydrogel (Figure 4b) exhibited a markedly narrower pore size range of 2–8 μm , indicating a more uniform and centralized distribution. The potential reason for the formation of this pore uniformity lies in the role of the modified PCNF nanofibers as heterogeneous nucleation sites within the polymerization system. The uniformly dispersed PCNF induces the surrounding polymer network to grow evenly, while their inherent rigidity and steric hindrance effect restrict the disordered expansion of the mesh pores. This, in turn, guides the formation of a three-dimensional network that is more uniform in size and denser in structure. At an addition of 3 wt%, this combined effect of nucleation and templating achieved an optimal balance.

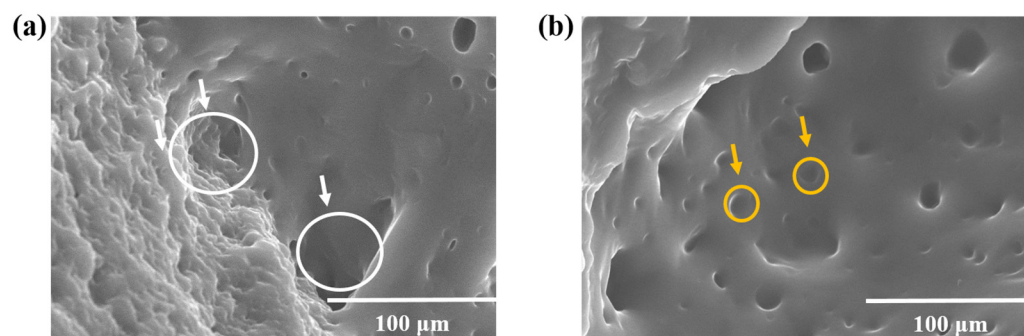


Figure 4. SEM images of (a) AM/AA hydrogel and (b) AM/AA/PCNF3 composite hydrogel.

3.2. Influence of PCNF on the Rheological Behavior of Composite Hydrogels

Rheological measurements were conducted to assess the influence of polydopamine-modified CNF (PCNF) on the viscoelastic behavior of composite hydrogels, with PCNF-0 and PCNF-3 selected as representative samples. The dependence of storage (G') and loss (G'') moduli on strain amplitude is presented in Figure 5a. Predominantly elastic behavior ($G' > G''$) is observed for both hydrogels within the linear viscoelastic region (LVR), indicating that the network structure remains largely intact under small deformations. Notably, the initial G' of PCNF-3 (~4250 Pa) is substantially higher than that of PCNF-0 (~1250 Pa), indicating that the incorporation of PCNF as a nanoscale reinforcing phase significantly enhances network rigidity and structural strength. This phenomenon can be ascribed to a synergistic mechanism. On one hand, the PCNF serves as a rigid nano-scaffold, providing physical reinforcement to the network. On the other hand, its surface functionalities establish multifaceted interactions—including hydrogen bonding, hydrophobic association, and coordination bonds—with the polymer matrix. This dual contribution significantly elevates the effective crosslink density of the network, thereby enhancing its rheological properties. Beyond the LVR, the decrease in G' results from the breaking of dynamic crosslinks, including hydrogen bonds and coordination interactions. However, the decline in PCNF-3 is more gradual, and its critical strain is higher, demonstrating superior structural stability and resistance to shear-induced network breakdown—an essential feature for maintaining integrity under high shear conditions during injection [23]. This finding confirms the presence of multiple dynamic and reversible bonds within the network, such

as dopamine-mediated hydrogen bonds. These dynamic linkages can break and re-form under shear deformation, effectively dissipating energy and thereby enabling the network structure to withstand larger strains before failure.

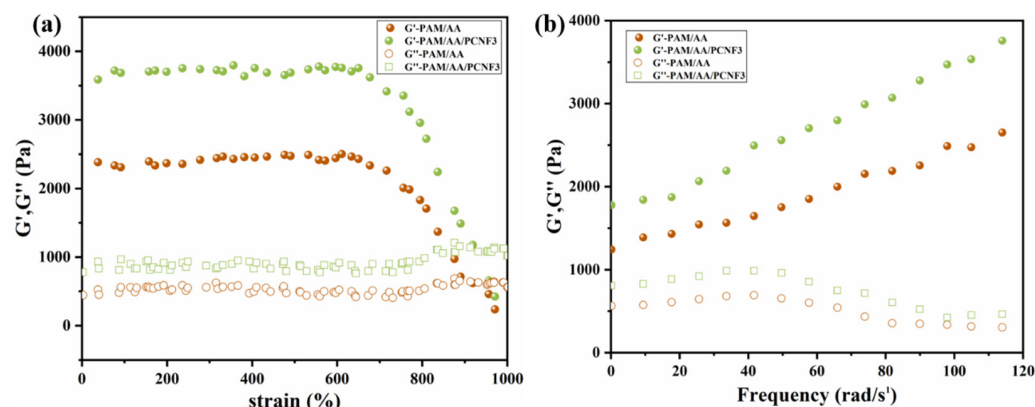


Figure 5. Rheological characterization of PAM/AA and PAM/AA/PCNF3 composite hydrogels: (a) Changes in storage (G') and loss (G'') moduli with increasing strain amplitude; (b) frequency dependence of moduli at a fixed strain.

Figure 5b presents the frequency dependence of the moduli at a fixed strain. Over the entire frequency range, G' exceeds G'' for both hydrogels, reflecting the stability of the gel network. PCNF-3 exhibits markedly higher G' values at all frequencies, reflecting a more robust network structure. Both hydrogels show modest frequency dependence, with G' gradually increasing at higher frequencies, indicative of the relaxation behavior of reversible dynamic bonds within the network. Importantly, the frequency dependence of PCNF-3 is weaker than that of PCNF-0, suggesting a more persistent and resilient network capable of maintaining long-term performance stability under operational conditions.

3.3. Mechanical Behavior of Composite Hydrogels with Varying PCNF Content

The mechanical performance of composite hydrogels with different loadings of polydopamine-modified CNF (PCNF) was systematically evaluated to elucidate the reinforcing mechanism of PCNF as a multifunctional nanoscale additive within the three-dimensional gel network. Tensile tests (Figure 6a) indicate that the incorporation of PCNF markedly enhances both tensile strength and toughness. The pristine hydrogel without PCNF exhibited a tensile strength of 0.65 MPa and a fracture energy of 5.20 MJ m³. Upon increasing PCNF content to 3 wt%, the tensile strength rises to 2.62 MPa and fracture energy to 8.95 MJ/m³, corresponding to enhancements of 118% and 72%, respectively. This synergistic reinforcement arises from the multifunctional interactions of the epoxy- and dopamine-modified PCNF within the hydrogel network. The long alkyl chains on PCNF surfaces contribute hydrophobic associations, dopamine moieties establish dynamic, reversible hydrogen bonds and π - π interactions with P(AA-co-AM) chains, while the rigid cellulose nanocrystals serve as physical crosslinking nodes that cooperate with MBA chemical crosslinks to construct an efficiently energy-dissipating network.

The substantial increase in toughness highlights the unique energy dissipation mechanism imparted by PCNF. During tensile deformation, dynamic interactions at the PCNF-polymer interface, including hydrogen bonding and π - π stacking, continuously break and reform, effectively dissipating external mechanical energy and significantly improving fracture energy [24,25]. Furthermore, well-dispersed PCNF hinders microcrack propagation, enhancing damage tolerance. Notably (Figure 6b), an excessive PCNF loading of 5 wt% results in a decrease in tensile strength to 1.15 MPa and fracture energy to

7.10 MJ/m³, suggesting that overloading induces aggregation, forming stress-concentration sites that diminish the reinforcing and toughening effect.

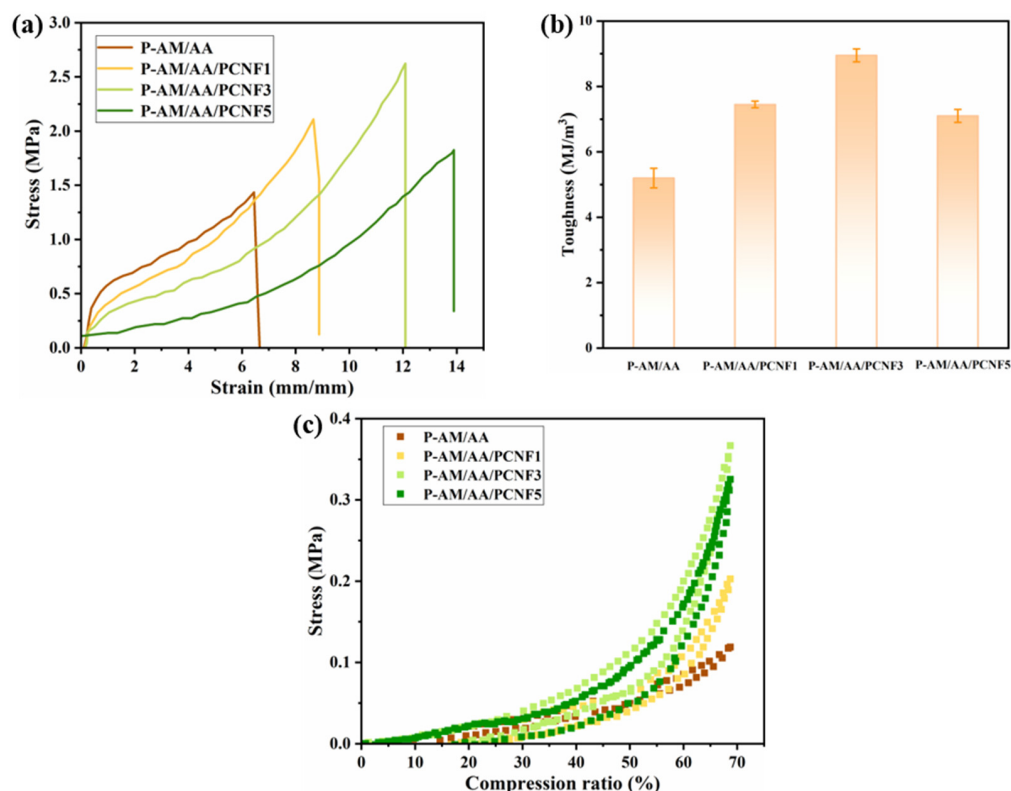


Figure 6. Mechanical characterization of composite hydrogels with varying PCNF contents: (a) Tensile curves; (b) toughness values; (c) Compressive curves.

Compression tests (Figure 6c) further confirm the reinforcement effect of PCNF. At 70% strain, compressive stresses of 145 kPa and 360 kPa were recorded for the pristine hydrogel and the hydrogel containing 3 wt% PCNF, respectively. This improvement is attributed to the uniform distribution of rigid PCNF nanofibers within the gel network, which effectively bear and transfer compressive loads. Dense interactions between PCNF and the polymer matrix further mitigate network collapse under high pressure. Performance evaluations revealed that when the PCNF content reached 3 wt%, the composite hydrogel exhibited significantly improved overall properties compared to the unmodified AM/AA system, which served as the conventional hydrogel control. Specifically, its tensile strength and compressive strength increased by 303% and 148%, respectively. The incorporation of PCNF facilitated the synergistic effect between multiple non-covalent interactions and covalent crosslinking, thereby achieving a simultaneous enhancement in both strength and toughness of the hydrogel [26,27]. At 3 wt%, PCNF achieves an optimal balance between the reinforcing effect and the agglomeration effect within the matrix. At lower concentrations, the reinforcing contribution is inadequate due to an insufficient number of filler units. Conversely, at higher concentrations, the propensity for nanofiber agglomeration prevails. These agglomerates act as stress concentrators, which detrimentally impair the overall strengthening and toughening performance.

3.4. Impact of PCNF Amount on Hydrogel Swelling Behavior

Composite hydrogels were tested for swelling in 5 wt% NaCl solution to assess their suitability for use as lost-circulation materials under high-salinity conditions. As illustrated in Figure 7a, all hydrogel samples exhibited an initially rapid swelling phase, followed by a gradual approach to equilibrium. The incorporation of PCNF notably

influenced the ultimate swelling capacity. The hydrogel without PCNF (0 wt%) displayed the highest equilibrium swelling ratio of 5.1 g/g, indicative of a relatively loose network. In contrast, the addition of PCNF markedly reduced the swelling ratio, with the 3 wt% PCNF hydrogel achieving the lowest equilibrium value of 2.2 g/g, reflecting the formation of a highly compact network (Figure 7b). According to the Flory–Rehner theory, the equilibrium swelling ratio is inversely proportional to the effective crosslinking density of the network. Therefore, the relatively low swelling ratio of PCNF-3 directly indicates its highest effective crosslinking density. This high degree of crosslinking arises from the synergistic contribution of the chemical crosslinker (MBA) and the multiple interactions introduced by PCNF acting as a “physical crosslinker,” including physical entanglement, hydrogen bonding, and hydrophobic association. Although the FTIR results reveal the presence of abundant hydrophilic groups ($-\text{COOH}$, $-\text{CONH}_2$) that provide sites for water absorption, the additional hydrogen-bonding sites introduced by PCNF enhance interchain interactions, effectively restricting polymer chain extension and water molecule penetration, thereby resulting in a controlled swelling capacity. Notably, the 3 wt% PCNF loading resulted in an optimally dense network. However, increasing the PCNF content to 5 wt% led to a slight rise in swelling, likely caused by localized aggregation and decreased network homogeneity.

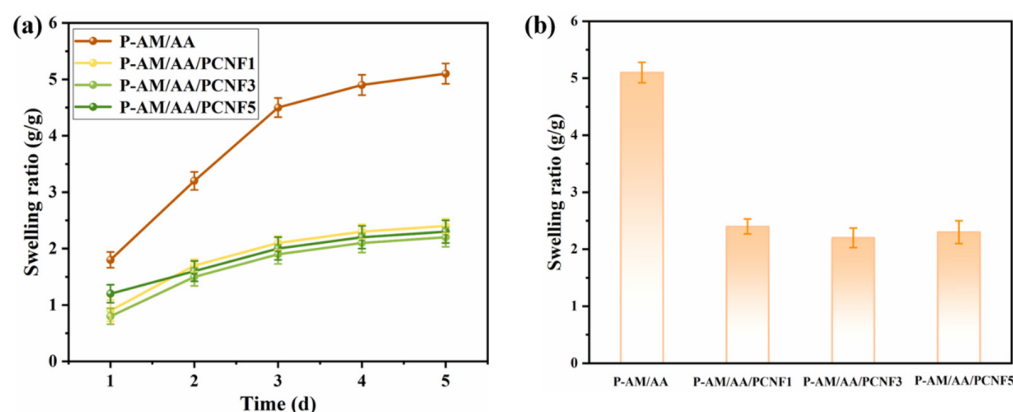


Figure 7. (a) Measured swelling kinetics of hydrogels in 5 wt% NaCl; (b) equilibrium swelling values.

From a practical perspective, these swelling characteristics are highly relevant for downhole applications. Moderate equilibrium swelling ensures dimensional stability, preventing excessive expansion that could damage surrounding formations. The dense network architecture also maintains mechanical integrity after swelling, allowing the hydrogel to withstand sustained fluid pressure. Furthermore, the rapid attainment of swelling equilibrium facilitates the swift formation of an effective seal upon injection, thereby enhancing operational efficiency and reliability [28].

3.5. Impact of PCNF Amount on Hydrogel Texture

Texture profile analysis further corroborates the significant enhancement of macroscopic mechanical properties imparted by the incorporation of functionalized cellulose nanofibers (PCNF) into the hydrogel network. Figure 8 illustrates that both gel strength and adhesion energy increase at low PCNF content but decline when the PCNF loading is further increased. Regarding gel strength (Figure 8), the hydrogel containing 3 wt% PCNF demonstrates the highest value of 2.35 N, which is 2.76 and 1.42 fold higher than those of PCNF-0 wt% and PCNF-1 wt% samples, respectively. The observed improvement is ascribed to a densely crosslinked network formed by PCNF. The rigid nanofiber scaffold provides effective stress support, while dynamic hydrogen bonding and coordination interactions between dopamine moieties on the fiber surface and the polymer chains contribute

to energy dissipation. Additionally, the hydrophobic interactions of grafted long-chain epoxy decyl groups further reinforce network stability. Notably, when PCNF content is increased to 5 wt%, gel strength decreases to 1.90 N, likely due to fiber aggregation inducing stress concentration points and disrupting network uniformity.

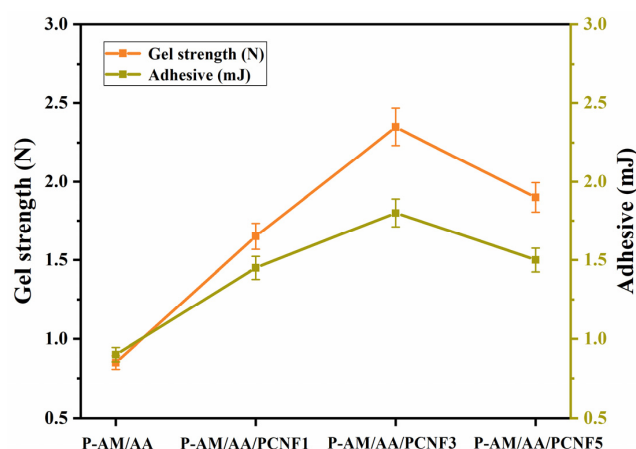


Figure 8. Textural profiles of hydrogels with varying PCNF content after aging at 130 °C in 5 wt% saline solution.

In terms of adhesion performance (Figure 8), the 3 wt% PCNF hydrogel again exhibits superior properties, with an adhesion energy of 1.80 mJ, significantly exceeding that of other samples. This improvement is mainly ascribed to the bioinspired dopamine functional groups, which endow the hydrogel with enhanced wet adhesion, facilitating stronger interfacial bonding with substrate rock surfaces. Such adhesion enhancement is crucial for maintaining long-term stability of plugging materials under downhole conditions. From a material design perspective, the 3 wt% PCNF formulation achieves an optimal balance between gel strength and adhesion energy, enabling the hydrogel to withstand complex stress conditions while preserving structural integrity. After 5 days of accelerated high-temperature aging, the gel strength and adhesion energy of the PCNF-3 sample remained above 85% of their initial values. This excellent retention of performance indicates the material's outstanding long-term service potential. Its intrinsic stability originates from a multi-level synergistic defense mechanism: first, the robust covalent crosslinked network provides the structural foundation; second, the rigid PCNF skeleton effectively suppresses thermal degradation of the polymer chains; and most critically, the abundant dynamic reversible bonds in the network (hydrogen bonds and hydrophobic associations) can dissipate energy and reorganize the structure under prolonged stress, endowing the material with resistance to fatigue and creep. Therefore, this unique network design offers a reliable microstructural basis for maintaining the hydrogel's plugging effectiveness over months or even longer in downhole environments.

3.6. Effect of PCNF on the Plugging Performance of Composite Hydrogels

Sandpack filtration tests were performed to investigate how varying PCNF content affects the sealing efficiency of composite hydrogels under simulated wellbore conditions (120 °C, 6 MPa). As shown in Figure 9, all PCNF-containing hydrogels demonstrated superior plugging performance compared to the unmodified hydrogel, with the efficiency strongly dependent on PCNF loading. In the 20–40 mesh sandpack, the 30-min cumulative fluid loss decreased from 98.2 mL (PCNF-0) to 42.5 mL (PCNF-3), representing a 56.7% improvement, while PCNF-5 showed a slight increase to 58.7 mL. A rigid nanofiber network coupled with dynamic reversible interactions primarily accounts for the observed enhancement. PCNF provides mechanical reinforcement within the gel, while dopamine-

mediated hydrogen bonds and coordination interactions enable self-healing and structural rearrangement, resulting in a stable three-dimensional sealing layer. The slight reduction in performance at 5 wt% PCNF is likely due to fiber aggregation, which diminishes dispersion uniformity and adaptive filling within fractures. Furthermore, plugging efficiency improved with decreasing sand particle size, indicating that finer porous media facilitate more effective hydrogel sealing [29]. These results demonstrate that moderate incorporation of PCNF can significantly enhance the mechanical integrity and sealing capability of hydrogels under harsh downhole conditions.

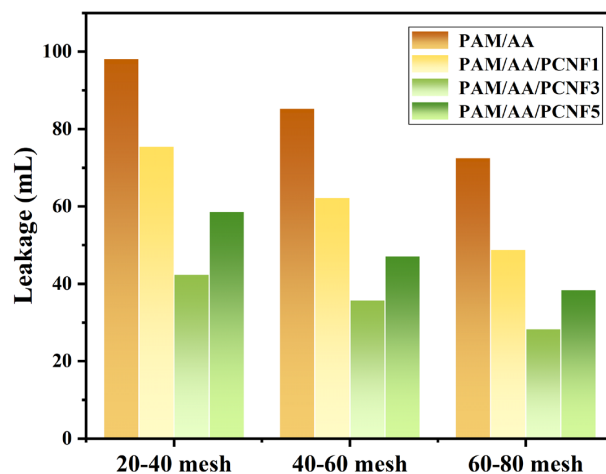


Figure 9. Plugging efficiency of hydrogels with varying PCNF content in sandpacks of different particle sizes.

3.7. Plugging Mechanism of PCNF-Reinforced Composite Hydrogels

Based on the unique mechanical properties and dynamic reversible characteristics of the PCNF-reinforced hydrogel, we have developed a conceptual model to illustrate its multi-stage, self-adaptive plugging mechanism in formation fractures, as shown in Figure 10. The hydrogel network is constructed from a rigid nanocellulose skeleton, dynamic hydrogen bonds, hydrophobic associations, and dopamine-mediated coordination interactions, endowing it with exceptional deformability and re-crosslinking capability [30,31].

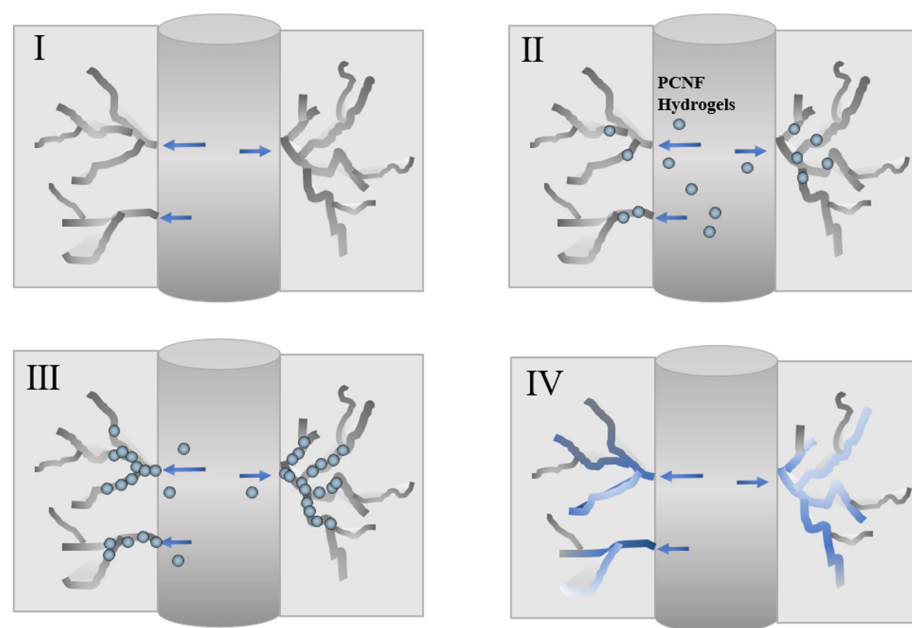


Figure 10. Schematic illustration of the multi-stage plugging process and gelation-based sealing mechanism of PCNF hydrogels.

During the plugging process, dry PCNF gel particles are transported into the lost circulation channels by the drilling fluid and undergo rapid water absorption, transitioning from rigid particles to an elastic, viscous gel state (Stage I $\rightarrow$ II). This transition allows the particles to conform to irregular fracture geometries. Under the influence of the pressure differential, the deformable gel particles migrate further into the fractures and, upon continued swelling, interact and interlock to form a preliminary mechanical sealing layer (Stage III). The rigid nanocellulose fibers act as a “micro-skeleton,” embedding within the soft polymer matrix to enhance the structural integrity of the sealing layer and prevent disintegration under fluid shear.

As the sealing process proceeds (Stage IV), the elevated formation temperature activates dynamic interactions at the gel interfaces. Dopamine-mediated hydrogen bonds and coordination interactions reorganize, while hydrophobic associations among alkyl chains further stabilize the network. These reversible non-covalent interactions continually break and reform at the contact interfaces between adjacent gel units, promoting the fusion of initially discrete particles into a continuous, dense three-dimensional network. This results in a robust and persistent blockage of the entire lost circulation channel. The proposed mechanism highlights the synergistic contribution of rigid reinforcement and dynamic reconfiguration: nanocellulose fibers provide sustained structural support, while multiple reversible interactions impart self-healing and adaptive restructuring capabilities [29,32,33]. Together, they enable the hydrogel to withstand complex downhole stress conditions and maintain long-term plugging stability.

4. Conclusions

A nanocellulose-reinforced composite hydrogel (PCNF) with a multi-dynamic crosslinked network was successfully developed via stepwise functionalization. Nanocellulose served as a rigid scaffold and was sequentially modified with epoxidized decane, methacryloyl chloride, and dopamine, followed by copolymerization with acrylamide (AM) and acrylic acid (AA). This strategy enabled synergistic reinforcement through rigid support, hydrophobic association, and dynamic reversible interactions. Characterization confirmed the efficient incorporation of functional groups and enhanced thermal stability, with a 600 °C residual carbon content of 35.0%. Microstructural analysis indicated that PCNF-3 formed a uniform and dense network. Rheological testing revealed high viscoelasticity and excellent structural recovery (>92%). Mechanical evaluation showed that PCNF-3 exhibited superior performance: tensile strength of 2.6 MPa, fracture energy of 8.95 MJ/m³, compressive strength of 360 kPa, gel strength of 2.35 N, and adhesion work of 1.80 mJ, outperforming unmodified hydrogels. Under simulated downhole conditions, cumulative fluid loss in sand packs (28.4–42.5 mL) was substantially reduced compared to conventional plugging materials. Although this study has achieved promising results, it is important to acknowledge its limitations and outline directions for future work. First, the material's performance was validated under simulated conditions of 120 °C, and its long-term stability at higher temperatures (>150 °C) remains to be further investigated. Second, the current laboratory-scale preparation involves relatively high costs, necessitating future optimization of the synthesis process and identification of more economical raw materials to enhance its feasibility for commercialization. Regarding application scenarios, the material is particularly suitable for mitigating microfractures and porous fluid loss in high-temperature, high-salinity formations; however, for severe loss conditions such as large caverns, it may need to be combined with other bridging and plugging agents. Future research will focus on: (1) evaluating long-term performance under more stringent conditions; (2) optimizing formulations and scaling up production; and (3) conducting

large-scale physical simulation experiments, ultimately progressing toward pilot field tests to facilitate the translation of this technology from the laboratory to oilfield applications.

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