

Efficient Stabilization of Soil, Sand, and Clay by a Polymer Network of Biomass-Derived Chitosan and Carboxymethyl Cellulose

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Abstract

Biomass-derived polymers are being increasingly utilized as eco-friendly functional materials in fields ranging from medicine and food to agriculture and environmental engineering. In this report, we developed a novel efficient method for improvement of soil materials based on in situ gelation of a polyion complex formed by biomass-derived carboxymethyl cellulose (CMC) and chitosan (CS). Self-organized network of polymer films and microfibers assembled via electrostatic interactions between oppositely-charged polyions interconnects particles of soil material and imparts the resulted composite with a considerable mechanical strength. Treatment of soil even with a high water content (ca. 30%) by a mixture of CMC and CS at $m(\text{CMC} + \text{CS})/m(\text{soil})$ ratio of ca. 1% is sufficient to gain up to 150 kPa compression strength that further increases up to ca. 1 MPa after drying. Similar reinforcement effect by CMC-CS complex was observed for sand, and much higher yield strengths were measure for clay. Mechanical properties of soil materials strengthened

by CMC-CS complex depended on structure and stability of CMC-CS polyion network and controlled by the polymerization degrees of macromolecules and the charge ratio between them. Being composed entirely of biomass-derived polymers, the proposed soil treatment system is particularly attractive due to environmental friendliness and sustainability and it can be utilized not only for the soil improvement but also for the construction of functional platforms for soil pollution control and remediation.

Keywords

Soil stabilization, sand, clay, chitosan, carboxymethyl cellulose, interpolyelectrolyte complex (IPEC), hydrogel

1. Introduction

Improvement of soils is required in fields ranging from agriculture to civil engineering. Stabilization of soil in agriculture is performed to prevent soil degradation caused by wind and water erosion [1]. In civil engineering, such stabilization is often necessary to improve soil strength, bearing capacity, and other essential characteristics [2, 3]. In addition to conventional calcium-based additives, polymer materials have been actively tested as soil conditioners in the above fields [4-6]. Plastic fibers and strips as well as their composites with cementitious materials were used to improve mechanical strength and stiffness of soils [7, 8]. Reinforcement effects of various natural fibers of sisal, palm, bamboo, sugar cane and so on have been also explored [5, 7]. Treatment of soil with polymer solutions was shown to stabilize soil due to cohesion of polymers to soil particles and physical cross-linking in voids of soil materials [4, 9]. Earlier studies applied solutions of synthetic polymers such as polyacrylamides [4], styrene- and vinyl-acrylic copolymers [10], epoxy resins [11], and others for soils stabilization; however, negative environmental impacts related to the accumulation of synthetic polymers in nature and the release of toxic impurities they may contain during polymers' degradation raised serious concerns [12]. Therefore, solutions of

biomass-derived polymers such as guar gum, xanthan gum, chitosan, etc., have been increasingly considered for soil improvement thanks to their ecological safety [13-20].

Compared to single-component polymer formulations, two-component systems provide appreciable flexibility in design of polymer network for efficient soil structuring and reinforcement. In this regard, complexes of oppositely charged polyions, usually referred as polyion complexes (PIC) or inter-polyelectrolyte complexes (IPEC), have been actively explored as soil improvement formulations in the agricultural field during several past decades [21-23]. Stabilization of soil was performed by (i) successive treatment with aqueous solutions of polyanion and polycation taken at charge-stoichiometric ratios [22], (ii) treatment with an aqueous-salt solution of polyanion and polycation that form the IPEC in soil upon dilution with rain or irrigation water [22], and (iii) treatment by the non-stoichiometric IPEC [24]. More recent studies showed that utilization of a polyion microgels instead of linear polyions improved notably the strength and the wind erosion properties of treated sandy soils [25]. IPEC-based methods were applied to prevent wind erosion of soil contaminated with radionuclide during Chernobyl [22] and Fukushima [26] accidents and in the area of Semipalatinsk Nuclear Test Site (SNTS) [27]. Besides the mechanical improvement effect, IPEC bound to soil material was used as a barrier against environmental pollutants such as radioactive ions [28], heavy metal ions [24], and engineered nanomaterials [29].

Recent reports suggest that gel-based or *in situ* gelating formulations of polymers greatly enhance soil mechanical properties [19, 25]. In this regard, we [30] and others [31] demonstrated that mechanically strong polyion hydrogels were formed by acidification of chitosan (CS) dispersions in concentrated solutions of polyanions. Based on this approach, here we propose a conceptionally new efficient method of soil improvement based on *in situ* gelation of cationic CS and anionic carboxymethylcellulose (CMC). CS and CMC are the derivatives of the most abundant chitin and cellulose biomass polymers available at low cost. Chitosan is the product of chitin deacetylation, while carboxymethyl cellulose is obtained by cellulose carboxylation using chloroacetic acid. The commercial price of CMC is as low as \$1000/ton and the price of CS varies between \$1,000 and \$50,000 per ton depending on

purity. Low cost of CMC and CS makes them suitable for industrial scale applications and their use is in line with “the carbon neutral” and “the circular economy” principles. Therefore, to date, a vast number of “green” functional materials based on cellulose and its derivatives has been applied in fields of environment, construction, medicine, etc. [32-34] Similarly, CS was broadly used in materials for environmental remediation [35, 36], waste water treatment [37-39], and food storage [40] to mention a few.

The proposed in this study method of soil improvement by biomass-derived CMC and CS represents “green” and sustainable approach and, compared to earlier studies, it offers the possibility of a more flexible design of soil improvement systems. Utilization of such soil-polymer composites as functional geobiomaterials in fields of environmental engineering, civil engineering, and agriculture is anticipated.

2. Experimental part

2.1 Materials

Carboxymethyl cellulose sodium salt (90,000 g/mol and 700,000 g/mol), chitosan (50,000-190,000 g/mol, 75%-85% deacetylation degree), and D-(+)-glucono- δ -lactone (GDL) were purchased from Sigma-Aldrich (Japan). Ultrapure water was purified by Purelab Chorus 1 Life Science apparatus and used in all experiments.

Masado soil, silica sand No. 6, and kaolin (hereinafter soil, sand, and clay) with soil particle densities 2.72, 2.65 and 2.72 g/cm³, respectively, were used as soil materials. **Figure 1** shows particle size distributions of each soil material. The soil particle density test was carried out in accordance with JIS A 1202 and the particle size analysis was carried out in accordance with JIS A 1204. Elemental composition of studied soil materials determined by SEM-EDS is given in **Table S1 of Supporting Information**.

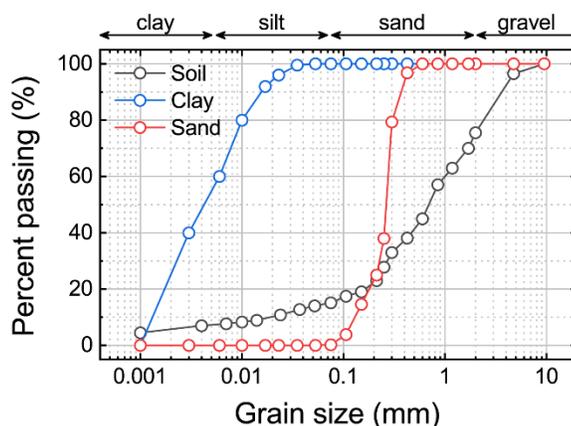


Figure 1. Grain size distributions of studied granular materials.

2.2 Methods

Optical microscopy. CMC-CS hydrogels and IPEC-treated soil and sand samples were pre-frozen at $-20\text{ }^{\circ}\text{C}$, freeze-dried overnight (FDU-1200, Eyela, Japan), and observed by VHX-6000 digital microscope (Keyence, Japan).

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). CMC-CS hydrogels and IPEC-treated soil, sand, and clay samples were pre-frozen at $-20\text{ }^{\circ}\text{C}$, freeze-dried overnight, coated with a thin carbon film, and observed by JSM-6610 microscope (JEOL, Japan) at an acceleration voltage 10-15 kV. EDS analysis of soil materials' composition was carried out at an acceleration voltage 15 kV.

Transmission electron microscopy (TEM). A small amount of freeze-dried IPEC-treated soil or clay composite was grinded with a pestle and mortar and mixed with $50\text{ }\mu\text{L}$ of Uranylless staining solution (Electron Microscopy Sciences, USA). Immediately after mixing, $20\text{ }\mu\text{L}$ of the resulted dispersion was placed on a piece of parafilm and covered with a carbon-coated copper grid (Alliance Biosystems, Japan) for 3 min. The droplet of the dispersion was removed by soaking out by a filter paper, and the surface of the grid was washed by placing the grid onto $20\text{ }\mu\text{L}$ water droplet for 30 sec. The solution remained on the grid was soaked out by a filter paper and the grid was dried in a dry box at relative humidity $< 10\%$ overnight.

TEM observations were performed on a JEM-2100 Plus microscope (JEOL, Japan) at 200 kV acceleration voltage at a room temperature. Samples of the CMC-CS hydrogel were prepared by a direct gridding of a small piece of freeze-dried CMC-CS hydrogel with 50 μ L of Uranylless solution and were next deposited on a carbon-coated grid as described above for soil samples and dried in a dry box prior observation.

Unconfined compression test. Unconfined compression test was carried out in accordance with JIS A 1216: 2009. First, the specimen of a height of 10 cm and an inner diameter of 5 cm was prepared by the method described hereafter, while its wet weight was measured. Then, the specimen was set in the unconfined compression test apparatus and vertically loaded at a speed of 1 mm/min. If no clear peak appeared in compressive stress and compressive strain diagram, the test was carried out up to an axial strain of 15% according to JIS standards. To measure the dry weight of the specimen after the test, the specimen was dried in a convection oven at 110 °C for 48 hours.

2.3 Sample preparations

Preparation of the CMC-CS hydrogel. CMC stock solution (1% w/v) was prepared by stirring sodium salt of CMC in ultrapure water overnight. To prepare small-scale samples for the microscopy analysis, CS powder of 30 mg was added to 3 mL of 1% CMC solution under vigorous 500 rpm stirring and, after 10 min, 70 mg of GDL was added to the CS dispersion. After additional 30 min, the stirring was stopped and the resulted CMC-CS hydrogel was kept overnight under ambient conditions. CMC-CS hydrogel was washed 2 times by placing for several hours in 500 mL ultrapure water and stored under ambient conditions in ultrapure water. CMC-CS aerogels were prepared using FDU-1200 freeze-drier (Eyela, Japan) and subjected to SEM and TEM analysis.

To prepare a CMC-CS hydrogel specimen for the compression test, a CS powder of 1 g and 2.33 g of GDL were successively added to 100 mL 1% CMC solution and vigorously mixed at 1000 rpm (Nanostar 7.5 digital, IKA, Germany) for 20-30 min. The resulted viscous CMC-CS hydrogel mixture was poured into mold of 5 cm in diameter and 10 cm in height,

wrapped with a plastic film to prevent water evaporation, and kept for 3 days before compression tests.

Soil, sand, and clay treatment with CMC-CS formulations. Unless otherwise mentioned, the CMC of molecular weight 700,000 g/mol was used in all the experiments. CMC stock solution (1-2% w/v) was prepared by stirring CMC in ultrapure water overnight. A CS powder of 1 – 3 g and 2.33 g of GDL were successively added to 100 mL of either 1% or 2% CMC solution under mixing at 1000 rpm. Stirring was stopped after 15-20 min and the resulted CMC-CS solution was thoroughly mixed with soil, sand, or clay. The mixed samples were put into molds of 5 cm in diameter and 10 cm in height and compacted several times with a rammer to prepare specimens. Loading and compaction of samples were carried out in a discrete manner through several consecutive steps. Specimens were wrapped with a plastic film to prevent water evaporation, and incubated for 3 days before compression tests. Dry specimens were prepared by 48 hours incubation in a convection oven at 110 °C.

Samples of IPEC-treated soil, sand, and clay for the microscopy analysis were prepared using smaller amounts (*ca.* 1/30) of chemicals and soil materials in the same manner as described above. The samples were freeze-dried using FDU-1200 (Eyela, Japan) and subjected to optical, SEM, and TEM observations.

3. Results

Interpolyelectrolyte complexes (IPEC) are formed between oppositely-charged polyions (polyelectrolytes, PE) driven by ionic binding and a release of counterions [21, 41, 42]. While the direct mixing of aqueous solutions of a polyanion and a polycation produces complex coacervates [43] having poorly defined structure, recently proposed approach based on acidification of CS powder dispersions in a solution of a polyanions such as xanthan [31], DNA [30], saponite (anionic clay) [44], etc. can be used to fabricate structurally homogenous, monolithic, and mechanically stable IPEC hydrogels of various polyanion/polycation compositions [30, 31].

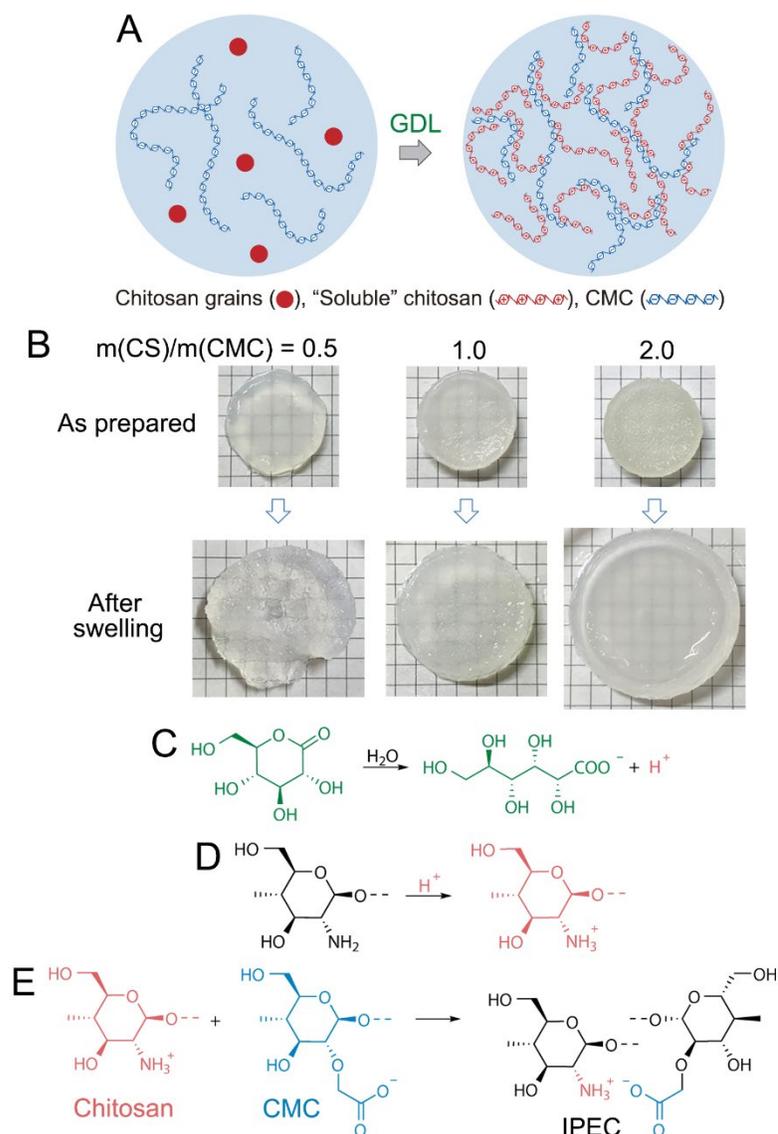


Figure 2. Formation of the CMC-CS hydrogel. **A.** Schematic representation of CMC-CS polymer network formation in an aqueous solution. **B.** Photographic images of CMC-CS hydrogels prepared at different m(CS)/m(CMC) ratios after gelation (top) and after swelling in excess of water (bottom). **C.** Reaction of GDL hydrolysis. **D.** Reaction of CS protonation. **E.** Formation of an ionic bond between charged groups of CMC and CS.

Acidification of CS powder dispersion in 1% solution of CMC results in the formation of the CMC-CS hydrogel (**Figure 2A, B**). Hydrolysis of an acidifying agent, glucono- δ -lactone (GDL), decreases the pH of the dispersion from neutral (pH 7.5) to slightly acidic (pH 4.5) (**Figure 2C**) that initiates progressive dissolution of CS caused by its amino groups'

protonation (**Figure 2D**). Gradually dissolving cationic CS interacts electrostatically with negatively charged CMC (**Figure 2E**) and forms CMC-CS polymer network (hydrogel) (**Figure 2A, B**). The ratio of $m(\text{CS})/m(\text{CMC})$ has a strong effect on properties of IPEC hydrogels. The stoichiometric hydrogels, i.e., the hydrogels with compensated negative and positive charges, demonstrate the lowest swelling ratios and best mechanical properties due to a large number of ionic bonds between polyions and low total charge of the polymer network [30]. The stoichiometric state of IPEC hydrogel can be determined by measuring swelling ratios of such hydrogels in water. For example, **Figure 2B** shows images of CMC-CS hydrogels prepared at $m(\text{CS})/m(\text{CMC}) = 0.5, 1, \text{ and } 2$ after swelling. The swelling degree of the hydrogel prepared at $m(\text{CS})/m(\text{CMC}) = 1$ is the lowest, indicating that this state is close to the stoichiometric.

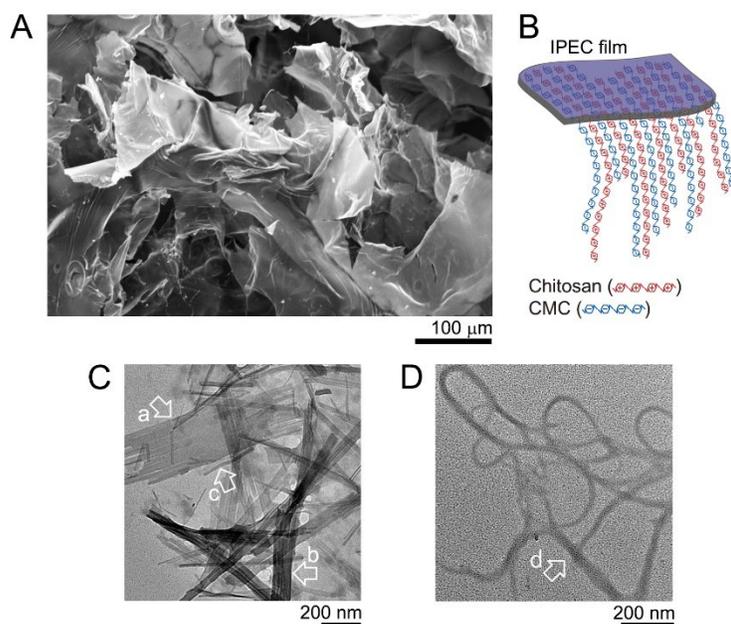


Figure 3. Micro- and nanostructure of the CMC-CS hydrogel. A. SEM image of CMC-CS hydrogel as prepared after freeze-drying. The weight ratio $m(\text{CS})/m(\text{CMC}) = 1$. **B.** Schematic representation of the proposed mechanism of IPEC films self-assembly from CMC and CS. **C-D.** Typical nanostructures in CMC-CS hydrogels observed by TEM: (a) films, (b) belts, (c) rigid fibers, and (d) flexible fibers.

SEM images of freeze-dried CMC-CS hydrogels revealed a porous structure mainly composed of polymeric films (**Figure 3A**). The fragments of such films observed by TEM

appeared as nanofibers and nanobelts of different width (**Figure 3C**) as well as larger flat structures composed of nanofibers. Flexible fibers (**Figure 3D**) were also observed coexisted with rigid films and belts, and the difference in morphologies might be attributed to the difference in the hydration degree of IPEC complexes. TEM images suggest that CMC-CS films are formed by alternating lateral co-assembly of polyions: $CS^{m+} - CMC^{n-} - CS^{o+} - CMC^{p+}$ etc. (**Figure 3B**). The average length of typical nanofibers was on the order of the length of an extended CMC chain (a few μm for 700,000 g/mol polymer). The thinnest individual nanofibers were only a few nm that corresponds to the IPEC assembled by a few CMC and CS macromolecules.

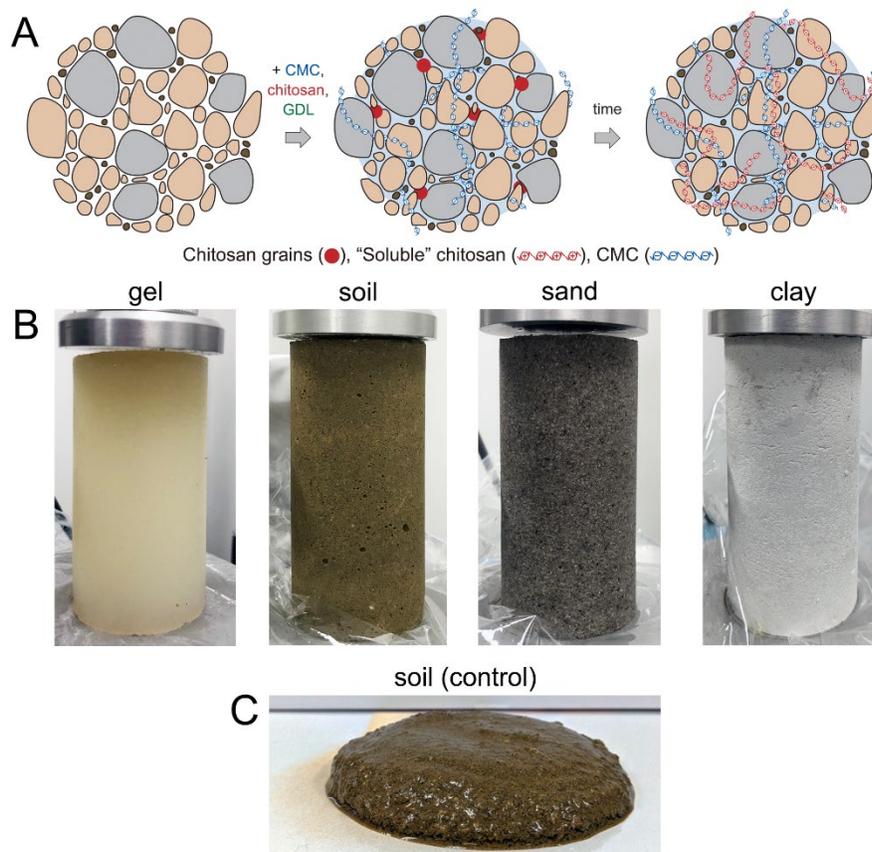


Figure 4. The treatment of soil, sand, and clay by IPEC. **A.** Schematic representation of CMC-CS polymer network formation in a soil matrix. **B.** Photographic images of specimens of IPEC hydrogel, IPEC-treated soil, sand, and clay ($h = 10\text{ cm}$, $d = 5\text{ cm}$) prepared for the compression tests under conditions shown in **Table 1**. **C.** Photographic image of soil of the same moisture content as in IPEC-treated soil specimen shown in B (soil).

Formation of the IPEC in solutions containing nano- and microparticles is accompanied by electrostatic or/and van der Waals interactions between polymers and colloids resulting in their co-aggregation or co-precipitation [45, 46]. Likewise, self-assembly of IPEC in voids of a granular material can stabilize the latter by co-aggregation and by establishing three-component network of polyanions, polycations, and soil particles (**Figure 4A**). To test the effect of *in situ* formation of CMC-CS polymeric network in a soil material on its structure and mechanical properties, treatment of soil was performed by mixing it with a dispersion of CS and GDL in a CMC solution (**Figure 4A**). For comparison, similar treatment of sand and clay was also performed. The total amount of polymers used in a typical treatment was *ca.* 1% (w/w) of the total weight of the treated soil material. Further details of specimens' composition and their physical characteristics are summarized in **Table 1**.

Table 1. Composition and physical properties of IPEC-treated soil, sand, and clay specimens at $m(\text{CS})/m(\text{CMC}) = 2$.

	Composition and physical characteristics	Soil	Sand	Clay
Specimen composition during treatment	Weight of solids (g)	300	300	300
	Volume of 1% CMC solution (mL)	100	100	100
	Weight of CMC in solution (g)	1.0	1.0	1.0
	Weight of CS (g)	2.0	2.0	2.0
	Weight of GDL (g)	2.4	2.4	2.4
Specimen characteristics	Polymer content (%) ^a	1.02	1.00	1.10
	Moisture content (%) ^b	32.6	31.4	32.6
	pH	6.30	4.84	3.90
	Wet density (g/cm ³)	1.91	1.84	1.69
	Dry density (g/cm ³)	1.44	1.40	1.27
	Specific volume	1.89	1.95	2.15

^a The difference in the polymer content among specimens is caused by different water content of the original soil material that was *ca.* 0% for sand, 2% for soil, and 10% for clay.
^b Moisture weight was calculated as the total weight of water, CMC, CS, and GDL in the specimens.

After mixing of soil and CMC-CS solution, the pH of the soil material changed gradually from 6.3 to *ca.* 5.0 accompanied by a progressive hardening of the soil specimen during several hours apparently due to the formation of the hybrid soil-polymer composite. Importantly, despite of a high moisture content (32% w/w), molded specimens of soil, sand, and clay showed good structural stability (**Figure 4B**) in drastic contrast to the pristine soil and sand with the same moisture content that were structurally unstable and could not be used for the compression strength measurements (**Figure 4C**).

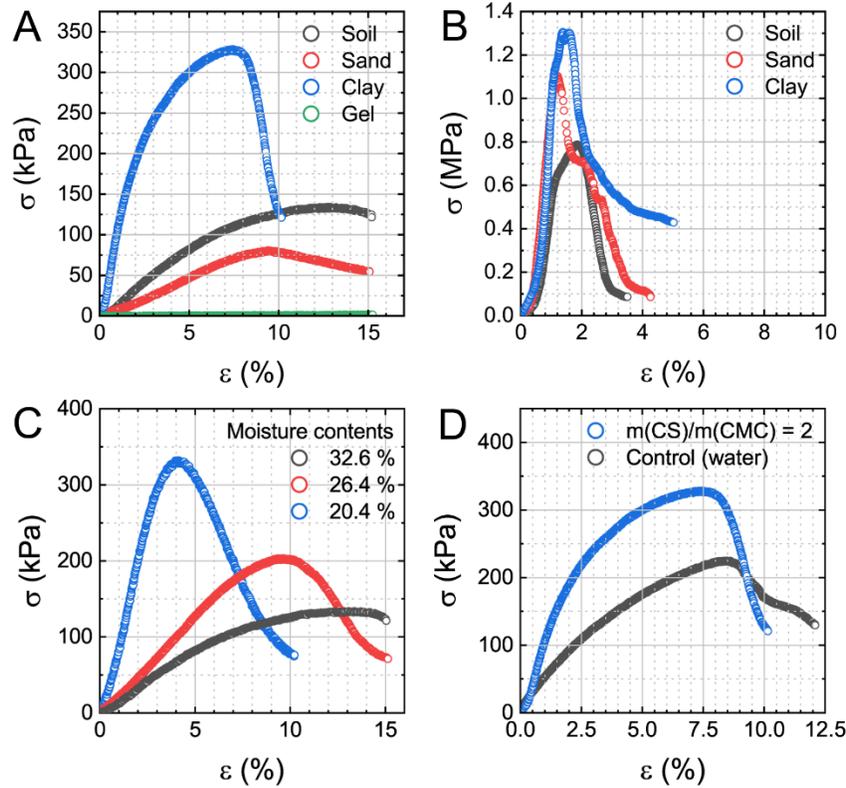


Figure 5. Mechanical behavior of IPEC-treated soil, sand, and clay. **A.** Compression behavior of soil, sand, and clay specimens after IPEC treatment at the final moisture content *ca.* 32% and $m(\text{CS})/m(\text{CMC}) = 2$. Measurements were performed 3 days after specimens' preparation. For comparison, compression curve for CMC-CS hydrogel at $m(\text{CS})/m(\text{CMC}) = 1$ is also shown. **B.** Compression behavior IPEC-treated soil, sand, and clay at

$m(\text{CS})/m(\text{CMC}) = 1$ after drying in oven for 48 hours at 110 °C. Drying of samples was performed 3 days after specimens' preparation. **C.** Compression behavior of soil specimens having different moisture content after IPEC treatment at $m(\text{CS})/m(\text{CMC}) = 2$. Soil specimens were prepared by mixing the soil and 1% CMC solution at the ratios 400 g / 100 g (moisture content 32.6%), 350 g / 90 g (26.4%), and 350 g / 70 g (20.4 %). Note that the density of soil specimens and the total amount of polymers are also different. **D.** Compression behavior of a specimen of clay (kaolin) mixed with water and after treatment with IPEC at $m(\text{CS})/m(\text{CMC}) = 2$. The moisture content of both specimens is 32.6%.

Mechanical properties of IPEC-treated soil materials were examined by unconfined compression tests (**Figure 5**). Test specimens were fabricated at the constant weight of treated soil material and the volume of treatment solution containing CMC, CS, and GDL (**Table 1**). Relationships of compressive stress (σ) and axial strain (ε) of IPEC-treated soil, sand, and clay specimens are shown in **Figure 5A**. Sand and soil mixed with a pure water at the same moisture content lacked the structural stability sufficient to fabricate test specimens (**Figure 4C**). IPEC-treated soil showed elastic behavior up to *ca.* 10% deformation observed as a linear correlation of the compressive stress (σ) and the axial strain (ε). The peak strength of *ca.* 150 kPa was measured at 13% strain. Compression strength of studied specimens increased in the order sand < soil << clay. For comparison, a specimen of CMC-CS hydrogel (**Figure 4B**) was also prepared in water and tested. As expected, the compression strength of CMC-CS hydrogel was negligibly low (several kPa). Results in **Figure 5** clearly show that despite a very low compression strength of the CMC-CS hydrogel itself, integration of CMC-CS polymer network into soil material results in its efficient reinforcement. Very high compression strength of IPEC-treated clay (*ca.* 350 kPa) is attributed to a large number of ionic bonds between IPEC and clay particles because of high surface area of clay particles. In contrast, small surface area of sand particles and the presence of large voids affect negatively the compression strength of the sand specimen. As it was mentioned earlier, mixing of soil or sand with the same volume of water resulted in the loss of structural integrity of soil materials. A specimen of clay mixed with water at *ca.* 32% water content could be prepared, yet its compressive strength was significantly lower compared to the sample treated by IPEC (**Figure 5D**).

Decrease of the moisture content in the IPEC-treated specimens after drying caused drastic increase in the compression strength of each studied specimen (**Figure 5B**). The highest compression strength was observed for IPEC-treated clay and sand (*ca.* 1.2 MPa) and somewhat lower for IPEC-treated soil (*ca.* 800 kPa) at 1-2% strain. Mechanical strength of IPEC-treated specimens was notably high considering their low dry density (1.3-1.4 g/cm³). Compression curves of soil specimens containing different amounts of soil and water (**Figure 5C**) show that a gradual decrease in the moisture content of IPEC-treated soil specimens and the increase of specimens' density results in progressive strengthening of soil material accompanied by a decrease of soils' ductility. Similar tendencies are also expected for sand and clay materials comparing **Figures 5A and 5B** or **Figures 6C and 6D**. Therefore, the proposed method can be successfully applied for soil treatment disregarding the final moisture content, while the mechanical characteristics of IPEC-treated soil can be adjusted by controlling the amount of water in IPEC-soil composites.

Obviously, mechanical characteristics of IPEC-treated soil materials represent a complex function of factors related to chemical and physical characteristics of the IPEC and the soil material such as the weight fraction of applied polymers, their polymerization degree, the size and dispersity of particles in the soil material, the charge ratio between polymers and soil particles, etc.

The polymerization degree of IPEC polymers is of particular importance because it affects the degree and density of polyion cross-linking in tested specimens. Indeed, the compression strength of soil treated using CMC of 700,000 g/mol molecular weight (polymerization degree, $n \approx 2700$) was more than 5 times higher compared to CMC of 90,000 g/mol molecular weight ($n \approx 340$) (**Figure 6A**). On the other hand, soil treatment with more concentrated solutions of CMC and CS did not necessarily increase the compression strength of the soil material. For example, doubling of CMC and CS concentrations in the treatment formulation from 1% to 2% had no notable effect on the mechanical behavior of the treated soil (**Figure 6B**), but rather the ratio between CMC and CS was critical as follows from the 2-fold higher compression strength of the soil treated with 1% CMC and 2% CS solution. Such behavior is different from the case of soil material reinforcement with cement, where

larger amounts of applied cement progressively strengthen sand [47] or clay [48] materials. Results in **Figure 6B** can be interpreted as oversaturation of granular material with polymers that promotes electrostatic self-association of CMC and CS rather than electrostatic complexation with soil particles thus providing no significant gain in strength.

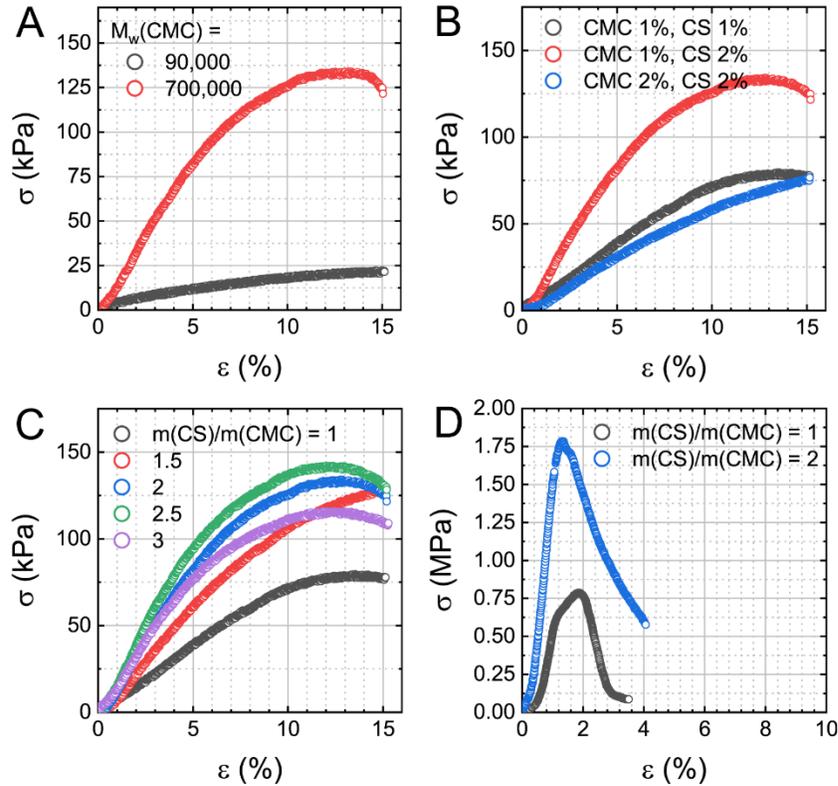


Figure 6. The influence of CMC-CS IPEC parameters on the compression behavior of treated soil material. A. The effect of CMC molecular weight (M_w) on the compression behavior of IPEC-treated soil at $m(\text{CS})/m(\text{CMC}) = 2$. **B.** The effect of CMC and CS concentrations. **C.** The effect of $m(\text{CS})/m(\text{CMC})$ ratio. **D.** The effect of $m(\text{CS})/m(\text{CMC})$ ratio on the compression behavior of IPEC-treated soil specimens after drying.

Earlier studies on IPECs noticed strong dependence of IPEC properties on the charge balance between anionic and cationic macromolecules [49]. Stoichiometric IPEC hydrogels, i.e. the hydrogels with compensated positive and negative charges, show lower swelling degrees and better mechanical characteristics [30]. Not surprisingly, we found that the charge balance between CMC and CS in treatment formulations affected the mechanical characteristics of the treated soil material. The effect of CMC-CS charge balance on soil

stabilization was studied by varying the amount of chitosan in 1% CMC solution between 0.5% and 3.5% (**Figure 6C**). At ratios $m(\text{CS})/m(\text{CMC}) < 1$, structural stability of treated soil was low and not sufficient to fabricate a specimen for the compression test. About 2-fold increase of the compression strength of IPEC-treated soil was observed upon increase of $m(\text{CS})/m(\text{CMC})$ ratio from 1 to 2.5. However, at $m(\text{CS})/m(\text{CMC}) > 2.5$ ratios the reverse effect was observed.

Interestingly, while the highest strength of IPEC-treated soil specimen was measured at $m(\text{CS})/m(\text{CMC}) = 2.5$ (**Figure 6C**), stoichiometric, and thus mechanically strongest, CMC-CS hydrogel was formed at $m(\text{CS})/m(\text{CMC}) = 1$ (**Figure 2B**). In other words, the maximum compressive strength of a free hydrogel and the soil-hydrogel composite is realized at different $m(\text{CS})/m(\text{CMC})$ ratios. This difference is apparently caused by the contribution from negatively-charged soil particles affecting the overall charge balance in the IPEC-soil system. In other words, an excess of cationic polymer (CS) is necessary to bind electrostatically to soil particles in order to obtain the most mechanically stable IPEC-soil composite. Thus, the optimal mass ratio $m(\text{CS})/m(\text{CMC}) = 2.5$ corresponds to the state of the maximum attraction interactions between CMC, CS, and soil particles. The influence of $m(\text{CS})/m(\text{CMC})$ ratio on the mechanical characteristics of dry soil specimens was more profound (**Figure 6D**). Compared to 1.5 times increase of wet soil strength with an increase of $m(\text{CS})/m(\text{CMC})$ ratio from 1 to 2 (**Figure 6C**), the maximum compression strength of the dry soil specimen had a remarkable 2.3 times improvement (**Figure 6D**) upon the same change. It should be finally mentioned that as far as the charge balance between polyions of IPEC and soil particles controls the mechanical properties of the final composite, an increase in the total anionic charge of soil material due to changes in its surface area or cation-exchange capacity (CEC) will generally require more cationic component of IPEC, i.e., chitosan, for the efficient stabilization. In particular, stabilization of clayey soils or clays having high CEC may require a significant excess of the chitosan to suppress the repulsion between negatively charged clay particles. In the present study, however, the clay (kaolin) has a low CEC and it could be stabilized using the same polymer formulation ($m(\text{CS})/m(\text{CMC}) = 2$) that was used for the stabilization of sand or soil. Beside the factors

discussed above, the charge balance in IPEC and the mechanical behavior of IPEC-treated soil might also depend on the concentration of various ions and organic matter in soil. However, the strong electrostatic interactions between polyanions and polycations impart IPECs with a high stability that can be disrupted by ions only at very high concentrations that are typically orders of magnitude higher compared to environmental concentrations [50]. The presence of an organic matter might also have certain effect on IPEC stability in soil but only at very high concentrations [51] that are not relevant to actual environmental conditions.

The strength of IPEC-treated soil materials is apparently determined by structural organization of IPEC inside the granular matrix. To get insight into micro- and nanoscale morphology of IPEC in soil, sand, and clay, the corresponding specimens were examined by optical, SEM, and TEM microscopies (**Figures 7, 8**). Because of a large size of voids as well as small surface area of sand particles, self-assembly of CMC and CS in voids of sand underwent similarly to the CMC-CS gelation in water and morphological elements of the CMC-CS hydrogel, e.g., polymeric films and microfibrils, were found adsorbed on the surface of sand particles and interconnected them (**Figure 7A, B**). In samples of IPEC-treated soil and clay, CS-CMC films and microfibrils were also observed mainly in voids and in-between large agglomerates of particles (**Figure 7C-E**), but the number of films and microfibrils was smaller compared to the sand sample. It is assumed that more efficient electrostatic interaction of soil and clay anionic particles with cationic CS disrupted the process of CMC and CS self-assembly into films. Instead, more structurally homogenous complexes of CMC, CS, and soil or clay nanoparticles were formed. Such structural homogeneity determines better mechanical characteristics of soil and clay measured in compressions tests (**Figure 5A**).

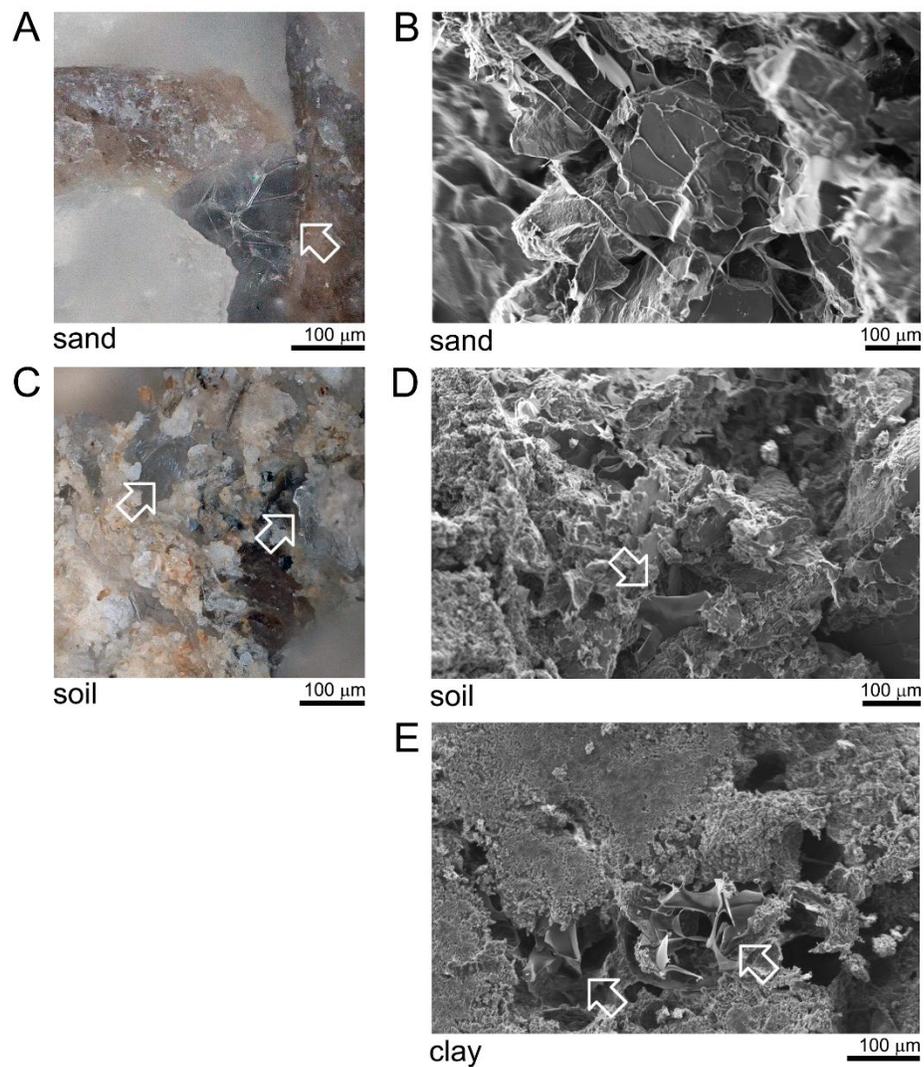


Figure 7. Microstructure of IPEC-treated soil, sand, and clay. A, C. Optical microscopy images of IPEC-treated sand (A) and soil (C) specimens after freeze-drying. B, D, E. SEM images of IPEC-treated sand (B), soil (D), and clay (E) specimens after freeze-drying. The weight ratio $m(\text{CS})/m(\text{CMC}) = 2$. Arrows indicate IPEC films.

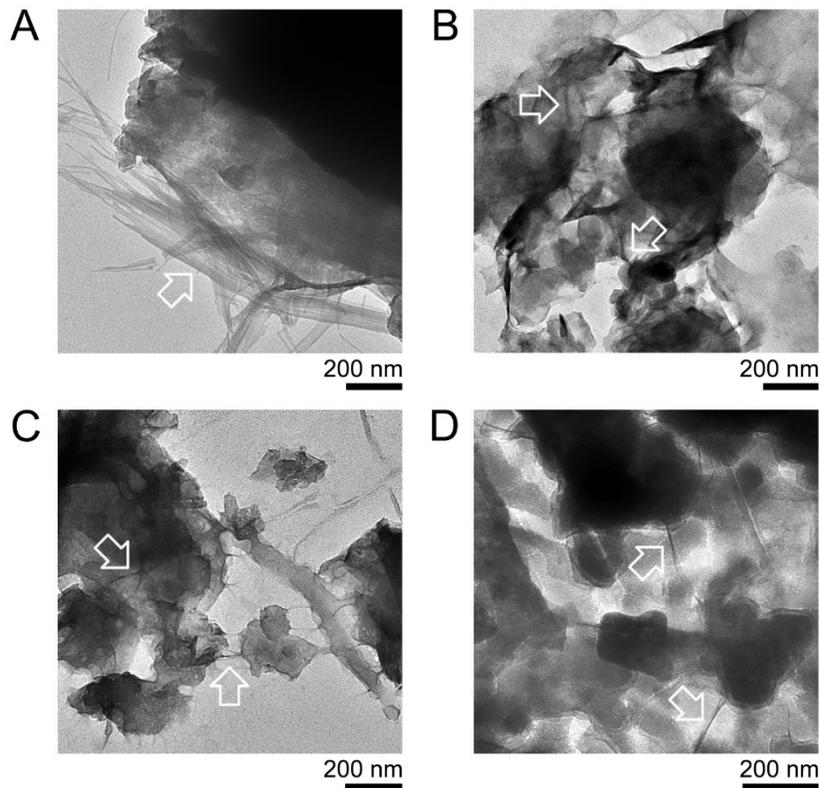


Figure 8. Nanostructure of IPEC-treated soil. Typical TEM images of IPEC-treated soil specimens at $m(\text{CS})/m(\text{CMC}) = 2$. Arrows indicate IPEC fibers.

TEM micrographs of IPEC-treated soil specimens provided further details on the interaction of the IPEC with soil particles. A part of IPEC in the treated soil matrix was observed as CMC-CS bundles or belts composed of nanofibers (**Figure 8A**) similarly to micrographs of the original CMC-CS hydrogel (**Figure 3C**). Most of these structures, presumably formed by disintegration of IPEC films observed by optical microscopy and SEM (**Figure 7C, D**), were found free standing or attached to soil particles (**Figure 8A**). Another part of IPEC was observed as numerous nanofibers interconnecting soil particles (**Figure 8B, C**). Fibers of IPEC were also found penetrated the soil granular matrix and bound to soil grains (**Figure 8D**). Morphological features of IPEC-treated soil material observed in **Figures 7 and 8** suggest a combined effect of long-range reinforcement by scaffolds of rigid IPEC microfibers and films embedded into the soil matrix and a short-range reinforcement by electrostatic network between individual polyions, IPEC nanofibers and soil particles.

4. Discussion

The proposed soil treatment method based on gelating of IPECs represents a sustainable approach for soil improvement. Its sustainable character is ensured by utilization of biomass-derived CMC and CS that are totally renewable owing to overwhelming abundance of cellulose and chitin in nature. Approximate soil treatment cost, calculated based on the cheapest available CMC and CS (\$1000/ton for each) and the use of 25 L of the formulation per square meter that is sufficient to stabilize 10-20 cm of the top soil, is estimated as several thousand dollars per hectare of treated area.

The proposed soil improvement method has field-specific merits as well as challenges. In agriculture, the method can efficiently prevent soil and wind erosion. Compared to previously reported treatment methods based on IPECs [22], the reported method is more facile as it is salt-free and the single-pot. Results in **Figure 5** suggest suitability of the method for treatment of both sandy and clayey soils. Beside soil stabilization, the hydrogel formed in soil matrix can help retaining water during droughts. In case of degradation of the biomass-derived IPEC, released carbohydrate molecules can be consumed by plants and soil organisms, yet recurrent treatment could be necessary.

In civil engineering applications, geomaterials with a high compression strength and durability are required. Although mechanical properties of soil materials having low densities and high moisture content investigated in this study are not sufficiently high, they can be greatly improved by suitable adjustment of water contents and an increase of soil material density by compaction. Noteworthy, typical chemical additives used for soil improvement including cementitious materials adversely affect its ductile behavior. In contrast, IPEC-treated soil material demonstrates good ductility and no failure at large deformations. Durability of the IPEC-treated soil might be affected by the biodegradability of biomass polymers and this should be addressed in further studies. Nevertheless, low toxicity and environmental friendliness of the proposed method offers an attractive “green” alternative to more traditional methods based on lime and cement [6, 52], that cause significant alkalization of soil [53].

Finally, in environmental applications, IPEC bound to soil material can be used as a “barrier” for adsorption and retention of pollutants to prevent the contaminants from spreading to the clean soil and the ground water. In this regard, recently reported IPEC hydrogel constructed from chitosan and DNA showed high adsorption capacities toward toxic heavy metal ions such as mercury, lead, cadmium, etc., as well as some of pharmaceuticals found in polluted waters [54]. Functionality of such IPEC “barrier” can be further improved by immobilizing chemical or biochemical reaction centres using suitable material design.

5. Conclusions

We showed that treatment of soil, sand, and clay with a gelating biomass-derived polyion complex (IPEC) provides the efficient stabilization of soil material by polymeric scaffolds of films and nanofibers. The hydrogel-like polymer network is equally suitable for the mechanical improvement of the soil containing a large amount of water as well as a dry soil material. The compression strength of the IPEC-treated soil material can be controlled by adjusting the polymerization degree of polyions, the polycation/polyanion charge ratio, and other parameters of treatment solution. Strong dependence of mechanical properties of IPEC-treated soil materials on the above parameters offers a possibility of further enhancement of IPEC-treated soil stability by controlling the manner of soil-IPEC composite assembly and the interaction between its components. Besides providing the mechanical improvement of the soil material, functionality of the IPEC in soil matrix can be extended to chemical adsorption of soil pollutants and soil remediation.

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