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Hybrid cross-linked poly(2-acrylamido-2-methyl-1-propanesulfonic acid) hydrogels with tunable viscoelastic, mechanical and self-healing properties

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ABSTRACT

Hydrogels derived from 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer are attractive materials for producing soft-biomimetic actuators, superabsorbents, and biomaterials. Here we present a simple synthetic strategy to prepare mechanically strong poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) hydrogels with self-healing ability. Initiator-free polymerization of AMPS in aqueous solution in the presence of Laponite nanoparticles and *N*,*N*′-methylenebis(acrylamide) (BAAm) cross-linker produces hybrid-cross-linked hydrogels with excellent mechanical properties. The hydrogels exhibit a high modulus (~700 kPa), compressive strength (45 MPa at ~90% strain), good resilience, and self-healing. The results reveal that the incorporation of Laponite and BAAm separately into the physical PAMPS network weakens hydrogen bonding interactions while their combination enhances these interactions and generate water-insoluble hydrogels with a high modulus. The superior properties of hybrid cross-linked hydrogels are attributed to strengthening of the interactions between chemically cross-linked PAMPS chains and nanoparticles. The hybrid approach presented here might enable preparation of mechanically strong nanocomposite hydrogels consisting of strongly or weakly charged polymer chains of different architecture.

1. Introduction

2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is an ionic monomer widely used for the synthesis of polyelectrolyte hydrogels possessing a large water sorption capacity [1–4]. AMPS has received attention due to its strongly ionizable sulfonate group (Scheme 1); it dissociates completely in the overall pH range [5–7], and therefore, chemically cross-linked hydrogels derived from AMPS exhibit pH independent swelling behavior and good electro-responsive property making them attractive material in a wide range of applications, such as in soft-biomimetic actuators, superabsorbents, biomaterials, bioengineering, water purification, agriculture, and food industry [3,8–11]. However, such hydrogels have a low strength and toughness due to the lack of an effective energy dissipation mechanism [12–15].

Xing et al. recently reported preparation of a self-healing hydrogel based on PAMPS using initiator-free polymerization of AMPS in aqueous solutions in the absence of a cross-linker [16]. Their results indicate that the polymerization ability of AMPS in the absence of an external initiator is due to the catalytic effect of H^+ counterions of the sulfonic acid groups, while its self-cross-linking ability arises due to the intermolecular hydrogen bonds acting as physical cross-links [16]. This simple, inexpensive, and one-pot synthetic procedure leads to the formation of PAMPS hydrogels with mechanical properties strongly dependent on their water contents. For instance, the hydrogels containing < 10% water exhibit a Young's modulus approaching to 400 MPa, while increasing water content above 15% produces mechanically weak hydrogels with a modulus of around 22 kPa [16]. Our preliminary experiments showed that PAMPS hydrogels prepared as described by Xing et al. completely dissolve in excess of water indicating that the inter-chain hydrogen bonds are too weak to resist the expansion of PAMPS chains in water due to the osmotic pressure of AMPS counterions.

In this study, we attempt to improve the mechanical performance of physical PAMPS hydrogels using three strategies, as schematically illustrated in Scheme 1. First, Laponite nanoparticles were incorporated into the physical network of PAMPS chains to increase the strength of intermolecular interactions. Laponite is a synthetic hectorite clay and, when suspended in water, it forms disk-like particles with a thickness of 1 nm, a diameter of about 25 nm, carrying strongly negative charge on the surface and weakly positive charge on the rim (Scheme 1) [17,18]. At a low concentration, Laponite forms a clear colloidal suspension in water due to the repulsive electrostatic interactions between particle surfaces. Increasing Laponite concentration leads to the formation of a clay hydrogel with so-called house-of-cards structure due to the

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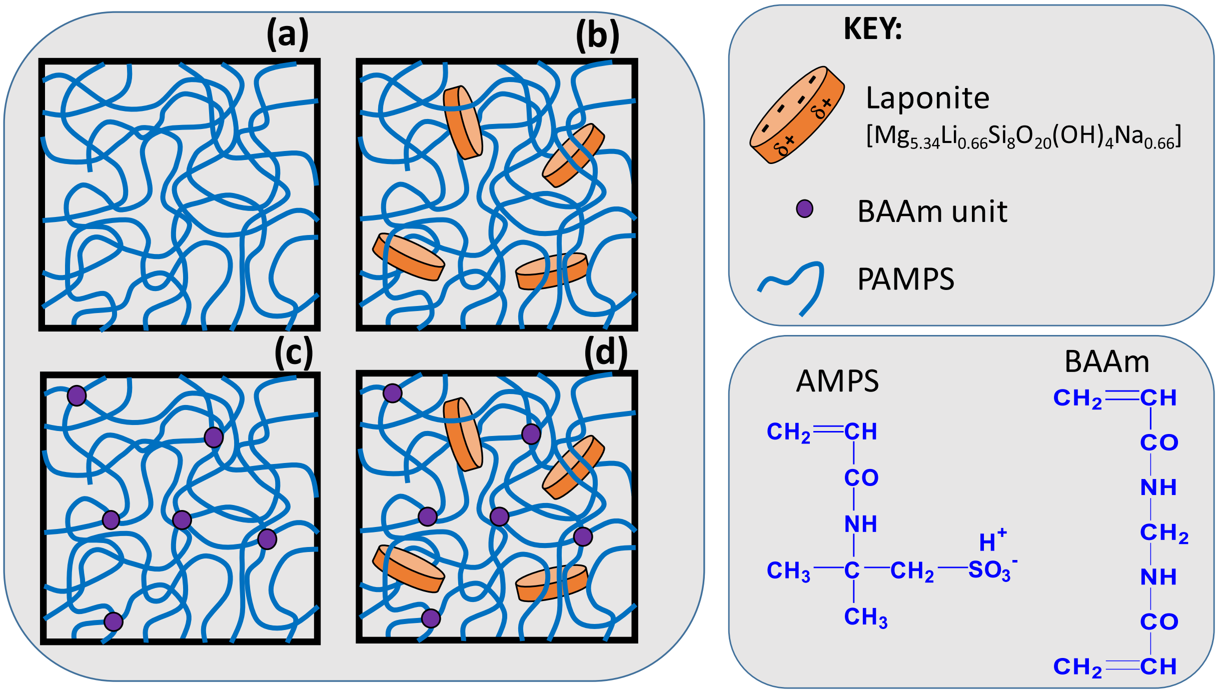

Scheme 1. Scheme of pure PAMPS (a), nanocomposite- (b), chemically-cross-linked- (c), and hybrid-cross-linked PAMPS hydrogels (d).

Table 1

Synthesis conditions, gel fractions W_g, storage modulus G' and loss factor tan δ, both measured at 1 and 100 rad·s^{-1}, and water contents of equilibrium swollen hydrogels. Standard deviations in the water contents are < 1% while for G' and tan δ, they are < 5%.

Code	AMPS/g	H_2O/g	Laponite/g	BAAm/mg	AMPS wt%	Laponite wt%	BAAm mol%	W_g	H_2O wt%	G'/kPa		tan δ	
										1 rad·s^{-1}	100 rad·s^{-1}	1 rad·s^{-1}	100 rad·s^{-1}
PAMPS	5	5	0		50	0		0	–	8	18	0.38	0.25
NC-1	5	5	0.10		50	1		0	–	10	23	0.38	0.23
NC-5	5	5	0.53		50	5		0	–	9	21	0.44	0.23
NC-10	5	5	1.10		50	10		0	–	14	36	0.47	0.30
NC-15	5	5	1.765		50	15		0	–	13	43	0.62	0.35
BAAm-0.5	5	5		20	50		0.5	0	–	10	24	0.39	0.28
BAAm-1	5	5		39	50		1	0	–	9	21	0.39	0.28
BAAm-1.3	5	5		49	50		1.3	0	–	10	19	0.27	0.23
BAAm-2	5	5		78	50		2	1.0 ± 0.1	99.7	14	21	0.12	0.16
Hybrid-15/0.5	5	5	1.765	20	50	15	0.5	0.90 ± 0.01	93	37	55	0.077	0.37
Hybrid-15/1	5	5	1.765	39	50	15	1	0.90 ± 0.01	90	57	77	0.079	0.31
Hybrid-15/1.3	5	5	1.765	49	50	15	1.3	0.95 ± 0.01	87	70	117	0.095	0.49
Hybrid-15/2	5	5	1.765	78	50	15	2	0.96 ± 0.03	86	38	67	0.11	0.54

electrostatic bonds between the positively charged rim and the negatively charged surfaces. Laponite nanoparticles have been used in many studies along with in-situ produced hydrophilic non-ionic polymers to form nanocomposite hydrogels with improved mechanical properties [19–22]. The surface of the nanoparticles provides an interface on which polymer chains can physically absorb, thus acts as multifunctional cross-link zones of nanocomposite hydrogels. Hydrogen bonding, ionic, dipole interactions and polymer entanglements seem to be responsible for the formation of nanocomposite hydrogels. As a second strategy, we included the classical chemical cross-linker *N,N′*-methylenebis(acrylamide) (BAAm) into the gelation solution to improve the elastic properties of the hydrogels.

As will be seen below, incorporation of Laponite (1–15 wt%) or BAAm (0.5–1.3 mol%) into the gelation system leads to the formation of water-soluble gels, as the pure PAMPS hydrogel, due to the weak inter-chain hydrogen bonds. However, simultaneous incorporation of Laponite and BAAm into the network structure strengthens hydrogen bonding interactions and provides formation of water-insoluble, hybrid cross-linked PAMPS hydrogels with excellent mechanical properties. For instance, they exhibit a high modulus (~700 kPa), compressive strength (45 MPa at ~90% strain), good resilience, and self-healing. Because nanocomposite polyelectrolyte hydrogels are hard to prepare due to agglomeration of the particles, the hybrid-cross-linking approach presented here might enable preparation of a variety of mechanically strong nanocomposite hydrogels consisting of charged polymer chains of different architecture.

2. Materials and methods

2.1. Materials

The monomer 2-acrylamido-2-propane-1-sulfonic acid (AMPS,