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Poly(acrylamide)-MWNTs Hybrid Hydrogel with Extremely High Mechanical Strength

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Abstract: Poly(acrylamide)-multiwalled carbon nanotubes (PAAm-MWNTs) hybrid hydrogels were prepared through the radiation-induced polymerization and crosslinking of the aqueous solution of acrylamide and well-dispersed MWNTs for the first time. The PAAm gels obtained by the radiation-induced polymerization and crosslinking showed very high mechanical strengths, and the PAAm-MWNTs hybrid hydrogels had improved mechanical properties compared with the PAAm gels, and hence the PAAm-MWNTs hybrid hydrogels showed extremely high compressive and tensile strengths. The hybrid hydrogels with water contents more than 80 wt.% usually did not fracture even at compressive strengths close to or even more than 60 MPa and strains more than 97%. And the hybrid hydrogels had very high elongations (more than 2000% in some cases), especially when the water content was high. The tensile strengths were in sub-MPa. The hybrid PAAm-MWNTs hydrogel is one of the strongest hydrogel even made.

Keywords: hydrogels, CNTs, radiation, high-strength

Introduction

Hydrogels with high mechanical strength may find more practical applications, especially in biomedical and industrial areas. In recent years, significant achievements have been made in the fabrication of novel hydrogels with unique microstructures and high mechanical strength [1-6]. Topological (TP) gel [7], nanocomposite (NC) gel

[5] and double-network (DN) gel [4] are the first three types of strong hydrogel even made. There are also many outstanding bio-based hydrogels. We have also developed a novel macromolecular microsphere composite (MMC) hydrogel with high mechanical strength [6]. A common feature of these hydrogels is that they have energy dissipation mechanisms to slow crack propagation.

Carbon nanotubes (CNTs) have attracted enormous interest in recent years, due to their extraordinary mechanical, thermal, and electrical properties [8]. Many potential applications have been proposed for CNTs, including conductive and high-strength composites, energy storage and energy conversion devices, sensors, and some of them are realized in products [9]. The incorporation of CNTs into polymeric matrixes to develop functional polymer composites has become an important and active field [10-14]. A major problem herein is the poor solubility and low dispersity of CNTs in water or organic solvents. Modification of CNTs to improve their solubility and processability is commonly achieved by: (a) the covalent attachment of chemical groups through reactions onto the π -conjugated skeleton of CNTs, (b) the noncovalent adsorption or wrapping of various functional molecules [8]. Although chemical modification is programmable and may make CNTs more soluble, the latter way is more convenient. Moore et al reported that individual single-walled carbon nanotubes (SWNTs) have been suspended in aqueous media using various anionic, cationic, nonionic surfactants and polymers [15]. Islam *et al.* also reported a single process to disperse high weight fraction SWNTs in water by the nonspecific physical adsorption of sodium dodecylbenzene sulfonate [16].

Several hydrogels containing CNTs have been fabricated in recent years. The commonly used strategy for the synthesis of such hybrid hydrogels is physical mixing in aqueous polymer solution. The hydrophilic polymers used are gelatin [17-18], poly(vinyl alcohol) [19-20], chitosan [21-22] and alginate [23]. Both SWNTs and multi-walled carbon nanotubes (MWNTs) were used. Hybrids of SWNTs and β -cyclodextrins (β -CDs) were prepared by π - π interaction between pyrene modified β -CDs and SWNTs [24]. Chen *et al.* recently reported the

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preparation of supramolecular hydrogels hybridized with SWNTs by mixing an aqueous solution of α -cyclodextrin (α -CD) with an aqueous dispersion of SWNTs stabilized by pluronic copolymer which has dual roles in dispersing SWNTs and forming inclusion complexes with α -CD [25]. No reports on the synthesis of hybrid hydrogels by *in situ* polymerization of monomers in the presence of CNTs can be found yet. The hybrid hydrogels have potential applications as actuator [17, 19, 21] and sensor [22], as well as for tissue engineering [23]. The incorporation of CNTs into hydrogels, in most cases, could enhance their mechanical strengths to certain extents [20-21, 23]. It is also found that the strength declines with the increase of SWNTs [25].

Herein, we report a facile strategy to prepare hybrid hydrogels of polyacrylamide (PAAm) and MWNTs with extremely high mechanical strength through radiation-induced *in situ* polymerization and crosslinking of the aqueous solution of acrylamide (AAm) and well-dispersed MWNTs.

Experimental Part

Materials

Acrylamide (AAm, ultra pure, BioDev, Japan), surfactant p-octyl polyethylene glycol phenyl ether (Triton X-100), multi-walled carbon nanotubes (MWNTs, Shenzhen Nanotechnologies Co. Ltd., prepared by chemical vapor deposition method, 95 wt.% pure) were used without further purification.

Hydrogel Preparation

Surfactant Triton X-100 and MWNTs were added into deionized water, the mixture was sonicated for 1h to obtain well-dispersed aqueous MWNTs dispersion. And then AAm aqueous solution was added and mixed thoroughly. The weight ratio of surfactant to MWNTs was 2, and the amount of MWNTs added was 0.05, 0.1 or 0.2 wt.% to the weight of the whole system for hydrogel synthesis. The samples were irradiated with ^{60}Co - γ rays for 2 h (dose rate: 10 kGy/h), resulted in PAAm-MWNTs hybrid hydrogels.

SEM Investigations

The hydrogel samples for SEM analyses were cut from the inner part of the hydrogels. To avoid the formation

of large ice crystals, the hydrogels were rapidly plunged into liquid nitrogen for about 5 min. The samples were subsequently freeze-dried until all water was removed. The dried samples were cracked to little pieces and the appropriate ones with fresh surfaces were analyzed with a Hitachi S-4800 scanning electron microscope (Tokyo, Japan).

Mechanical Tests

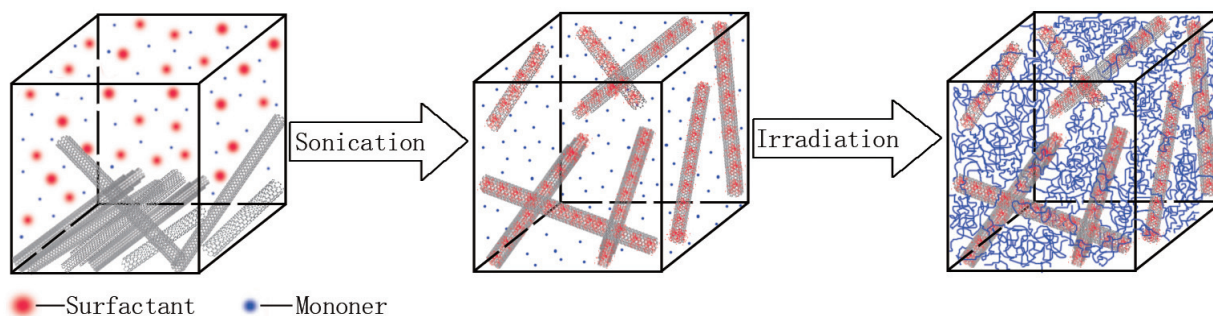
The compressive stress-strain measurements were described elsewhere [5]. The cylindrical gel samples were 19 mm in diameter and 10 mm in thickness. The stress σ_c is calculated as follows: $\sigma_c = \text{Load}/\pi r^2$ (r is the initial unloaded radius). The strain ε under compression is defined as the change in the thickness relative to the thickness of the freestanding specimen. Tensile mechanical measurements were performed using an Instron 3365 electronic universal testing machine (Instron Co., USA) at a cross-head speed of 200 mm/min. The cylindrical AA and AAm gels were 8.7 mm in diameter and the gauge lengths were 15-25 mm. The tensile stress σ_t is calculated as follows: $\sigma_t = F/\pi r^2$ (r is the initial unloaded radius and F is the loaded force). The elongation λ is defined as the change in the length relative to the gauge length of the freestanding specimen.

Results and Discussion

The Preparation of Hybrid Hydrogels

The proposed formation mechanism and the microstructure of the hybrid hydrogel are shown in Scheme 1.

Various surfactants can effectively disperse CNTs into aqueous solutions by sonication [15]. We finally chose p-octyl polyethylene glycol phenyl ether (Triton X-100) as the surfactant. Yu *et al.* reported that for effective dispersion the minimum weight ratio of surfactant to MWNTs is 1.5-1 and the maximum concentration of MWNTs that can be homogeneously dispersed in aqueous solution is ~1.4 wt. % [26]. To ensure the homogeneous dispersion of MWNTs, the weight ratio of surfactant to MWNTs in our work was 2 and the maximum concentration of MWNTs was 0.2 wt.%. Stable MWNTs aqueous dispersion could be obtained after being sonicated. It could be diluted further to form a steady and well-proportioned dispersion, which could last for at least 6 months without precipitation. On the contrary, the MWNTs could not be dispersed in water with or without sonication in the absence of a surfactant



Scheme 1: The fabrication process for the hybrid hydrogels.

(Figure S1). The addition of AAm aqueous solution into the dispersion did not induce the sedimentation of MWNTs. This process could also be achieved by a one-step method, i.e., MWNTs, monomer and surfactant are added into water together and then sonicated.

After the radiation-induced polymerization and crosslinking of AAm, the aqueous dispersion transformed into a PAAm-MWNTs hybrid hydrogel. The AAm aqueous solutions without any MWNTs in the presence or absence of Triton X-100 could also form hydrogels under γ irradiation. The optimized radiation time was 2 h, which was found to be sufficient for the full conversion of monomer into polymer. Excess irradiation led to the deterioration of mechanical properties, possibly induced by the degradation of polymers under gamma irradiation. The appearances of the AAm hydrogel and hybrid hydrogel are shown in Figure S2.

SEM Investigations

The PAAm-MWNTs hybrid hydrogel has a more uniform porous microstructure than the PAAm hydrogel (Figure 1a and Figure S3a). The clusters of MWNTs could not be observed, indicating that MWNTs have been evenly dispersed in the hydrogel. When the hybrid hydrogel was in an equilibrium swelling state, some MWNTs could be observed. The MWNTs in the hydrogel are similar in size to those pristine ones (Figure S3 b, c), suggesting there were no observable polymer chains chemically attached to the MWNTs.

Mechanical Tests

Table 1 shows the synthesis conditions and the mechanical test results of the hydrogels. The PAAm gels obtained by the radiation-induced polymerization and crosslinking showed very high mechanical strengths, and the PAAm-

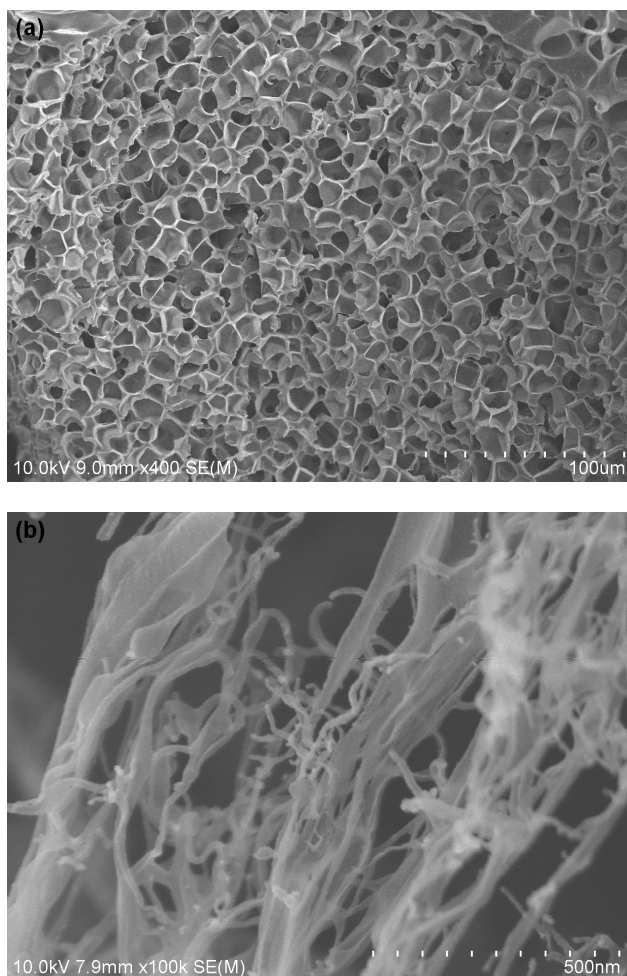


Figure 1: SEM micrographs of the PAAm-MWNTs hybrid hydrogel (0.2 wt.% MWNTs) with 82 wt.% water (a) and swelled to an equilibrium state (b).

MWNTs hybrid hydrogels had improved mechanical properties compared with the PAAm gels, and hence the hybrid hydrogels showed extremely high mechanical strengths.

The PAAm gels with different water contents were broken in the compressive tests, whereas the hybrid

Table 1: The composition of the raw materials, and the compressive and tensile properties of the hydrogels.

hydrogel	MWNTs	MWNTs/ Surfactant/ AAM/H ₂ O [wt.%]	Strain $\epsilon(\lambda)$ [%] [a]	Stress $\sigma_c(\sigma_t)$ [MPa]	Modulus $E_c(E_t)$ [kPa] [b]
Compressive tests					
PAAm	-	-/-/42/58	95.1	29.5	452
PAAm	-	-/-/30/70	96.2	39.1	260
PAAm	-	-/-/18/82	96.9	37.4	84
PAAm	-	-/0.2/42/58	94.1	23.8	367
PAAm	-	-/0.2/30/70	95.2	32.1	205
PAAm	-	-/0.2/18/82	94.1	17.8	55
PAAm-MWNTs	10-20	0.2/0.4/42/58	99.8	60.9[d]	508
PAAm-MWNTs	10-20	0.2/0.4/30/70	99.8	62.1[d]	305
PAAm-MWNTs	10-20	0.2/0.4/18/82	99.8	56.6[d]	122
PAAm-MWNTs	10-20	0.05/0.1/18/82	98.0	50.6[d]	54
PAAm-MWNTs	10-20	0.1/0.2/18/82	97.0	59.3[d]	90
PAAm-MWNTs	40-60	0.1/0.2/18/82	99.6	56.1[d]	57
PAAm-MWNTs	60-100	0.1/0.2/18/82	99.8	60.6[d]	188
Tensile tests					
PAAm	-	-/-/47/55	704	0.456	237
PAAm	-	-/-/25/75	1282	0.260	88
PAAm	-	-/-/15/85	1739	0.069	17
PAAm	-	-/0.2/47/55	658	0.402	239
PAAm	-	-/0.2/25/75	942	0.240	81
PAAm	-	-/0.2/15/85	1642	0.057	17
PAAm-MWNTs	10-20	0.1/0.2/45/55	658	0.338[d]	246
PAAm-MWNTs	10-20	0.1/0.2/25/75	1009	0.216[d]	96
PAAm-MWNTs	10-20	0.1/0.2/15/85	2087	0.081[d]	14
PAAm-MWNTs	10-20	0.2/0.4/45/55	433	0.355[d]	258
PAAm-MWNTs	10-20	0.2/0.4/25/75	700	0.229[d]	109
PAAm-MWNTs	10-20	0.2/0.4/15/85	2069	0.044[d]	18

[a] The strain ϵ is for compressive tests, and the strain for tensile tests is the elongation (λ). [b] The E_c was calculated from compressive stress (σ_c) and ϵ ($\epsilon=10-40\%$), and the E_t was calculated from tensile stress (σ_t) and λ ($\lambda=10-50\%$). [c] x-y denote the diameter range (in nanometer) of the CNTs, the CNTs are 5-15 μ m long. [d] The hydrogels did not break at these strains, and the stresses are not the fracture stresses. The hybrid hydrogels for tensile tests did not break but slipped from the clamping apparatus.

hydrogels did not break even when the strains were close to 100%. The typical compressive stress-strain (σ_c - ϵ) curves of a PAAm gel and a PAAm-MWNTs hybrid hydrogel are shown in Figure 2a. The PAAm hydrogel (70 wt.% water) had a yield point in the σ_c - ϵ curve, and the fracture σ_c was 39.1 MPa and the ϵ was 96.2%. The strain-stress curve of the

PAAm hydrogel till 99.9% strain rather than only to the yield point (96.2% strain) is shown, since the PAAm hydrogel broke slightly rather than into many pieces as those normal hydrogels, it could still sustain very high strength. The hybrid hydrogel (0.2 wt.% MWNTs, 70 wt.% water) could endure a 62.1 MPa stress and a 99.8% strain without any breakage and it quickly recovered its original shape after the release of load (See Figure S4). The stresses of the hybrid hydrogels in Table 1 are marked with a letter [d] to indicate that the samples did not fracture and the stresses listed are not the fracture stresses. When the strains were lower than 77.4%, the σ_c of the PAAm-MWNTs hydrogel was higher than those of PAAm hydrogel at the same strain. However, before the breakage of PAAm hydrogel ($\epsilon=77.4-96.2\%$), the σ_c s of PAAm hydrogel were higher than those of the hybrid hydrogel, due to the stress concentration in the PAAm hydrogel. The elastic moduli (E_c) of the hybrid hydrogels were usually higher than those of the corresponding PAAm hydrogels with similar water contents. And the E_c decreased with increasing water content for both PAAm hydrogels and PAAm-MWNTs hydrogels.

All kinds of MWNTs with different diameters could enhance the compressive strength of the hydrogels. Their σ_c s at the highest strains tested were typically 50-60 MPa. And the E_c of the hybrid hydrogel varied with the type of MWNTs used. The content of MWNTs in the tested range had little effect on the final σ_c s of the hybrid hydrogels, 0.05 wt.% MWNTs could effectively increase the compressive strength of the hybrid gel. The E_c of the hybrid hydrogel increased with MWNTs content.

The PAAm hydrogels and PAAm-MWNTs hybrid hydrogels also show very high tensile strengths. The PAAm hydrogels broke during the tensile tests, though they had relatively high elongations. The hybrid hydrogels for tensile tests did not break but slipped from the clamping apparatus. The PAAm-MWNTs hybrid hydrogel with 85 wt.% water could be stretched to about 22 times of its original length without breakage (Figure S5). The maximum elongation (λ) of the hybrid hydrogel is similar to or even higher than those of NC gel [5, 27-30] and DN gel [31]. Figure 2b shows the stress-strain (σ_t - λ) curves of the hybrid hydrogels with different water contents. The σ_t and elastic modulus (E_t) increased dramatically with decreasing water content. The E_t s of the PAAm hydrogels were usually a little lower than the hybrid hydrogels with the same water content. And the E_t s of the hybrid hydrogels increased slightly with MWNTs content. For the same sample, the E_c and E_t obtained from compressive test and tensile test are in the same order.

The Triton X-100 contained PAAm hydrogels without MWNTs were also synthesized and tested. As shown in

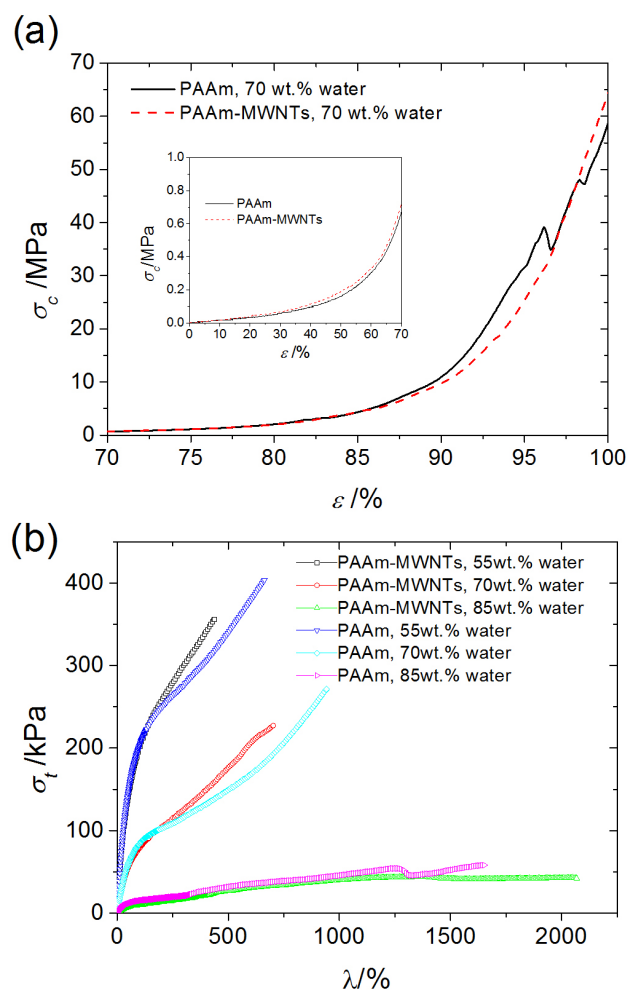


Figure 2: The compressive (a) and tensile (b) stress–strain curves of the PAAm hydrogels without MWNTs and surfactant and PAAm-MWNTs hybrid hydrogels. The PAAm-MWNTs hybrid hydrogels contained 0.2 wt.% MWNTs (10–20).

Table 1, the mechanical strengths of the Triton X-100 contained PAAm hydrogels without MWNTs were a little lower than those of the PAAm hydrogels synthesized without surfactant and MWNTs. These results suggest that the enhancement in the mechanical strengths of PAAm-MWNTs hybrid hydrogels is due to the effect of MWNTs or the combinational effect of MWNTs and surfactant, rather than surfactant alone.

Evaluating from both compressive and tensile mechanical properties, the PAAm-MWNTs hybrid hydrogel is one of the strongest hydrogels even made.

The PAAm-MWNTs hybrid hydrogels swelled faster and had higher equilibrium swelling ratios than the PAAm hydrogel in acidic, neutral and basic environments (Figure S6). And the PAAm-MWNTs hybrid hydrogels could keep their original shapes better in the swelling process than the PAAm hydrogels (Figure S7).

Discussion

We developed a new way of synthesizing hybrid hydrogels containing CNTs. The former hybrid hydrogels containing CNTs were usually fabricated by physical mixing CNTs into aqueous polymer solution. Our hybrid hydrogels were synthesized for the first time through radiation-induced *in situ* polymerization and crosslinking of the aqueous monomer solution and well-dispersed CNTs. Although both are radiation methods, this method is completely different from that in our previous paper [6]. This one is a simultaneous method in which the hydrogel is formed by the direct radiation-induced polymerization and crosslinking of monomer [32]. Whereas, the one in our previous paper is a pre-irradiation method, in which the MMS emulsion is irradiated with ^{60}Co γ -rays in oxygen to form peroxides on the surface of macromolecular microspheres (MMS), the polymerization is initiated by the peroxides formed and the gelation is mainly due to the entanglement of the grafted polymer chains on vicinal MMS.

The simultaneous radiation method has been used to synthesize many kinds of hydrogels for a long time [33–35]. However, surprisingly, less attention has been paid to the mechanical properties of the hydrogels obtained. The possible reason is that the mechanical strength of hydrogel became a topic concerned by scientists only in recent years after the development of several hydrogels with high mechanical strength. We found that the hydrogels synthesized by the radiation method are usually much stronger than those by normal chemical methods using initiator and crosslinking agent. The minimum fracture compressive stress of the PAAm hydrogel was 29.5 MPa which is much higher than those of PAAm hydrogels synthesized by a traditional chemical method (usually less than 1 MPa) [4]. The strategies used for the fabrication of hydrogels with high mechanical strength are usually quite complicated. However, the simultaneous radiation method is very convenient and the final mechanical strengths of the hydrogels are comparable to those strong hydrogels even made [1, 4–7]. We believe that the finding has some potential industrial applications.

The high mechanical strength of the hydrogels synthesized by radiation method can be attributed to their unique microstructure. Firstly, there are less crosslinking points between the polymer chains, since there was no chemical crosslinking agent used. Mahmudi et al calculated the average molecular weight ($\overline{M}_c$) between cross-links of low swelling (swelling ratio=3–5) acrylamide based hydrogels obtained by radiation synthesis, the $\overline{M}_c$ s are about 10,000 [36]. Our hydrogels have much

higher swelling ratios (about 50), hence possibly much higher $\overline{Mc}$ s. The low crosslinking density and the high $\overline{Mc}$ allow the polymer chains can be stretched to a higher extent. Secondly, irradiation is an effective way to initiate grafting, and hence grafting reactions can occur on the PAAm chains once they are formed. The grafted chains attached to one PAAm chain may get entangled with vicinal PAAm chains and the grafted chains on them. The grafted structure provides the mechanism to dissipate stress on the hydrogel effectively by all polymer chains.

The mechanical and swelling tests indicate that the microstructure of the PAAm-MWNTs hybrid hydrogels is different to that of the PAAm hydrogels. It is widely recognized that the fabrication of high performance nanotube-polymer composites depends on the efficient load transfer from the host matrix to the tubes. The load transfer requires homogeneous dispersion of the filler and strong interfacial bonding between the two components [37-38]. This principle must also be applicable to hybrid hydrogels containing CNTs. The homogeneous dispersion of MWNTs in aqueous solution and finally in the hydrogel has been proved by the experiments. Although there are no direct evidences for the strong interfacial bonding between MWNTs and PAAm yet, the extremely high mechanical strengths of the hybrid hydrogels indirectly prove that strong interfacial bonding between MWNTs and PAAm exists. Our experiments showed that the mechanical strengths of the Triton X-100 contained PAAm hydrogels without MWNTs were a little lower than those of the PAAm hydrogels synthesized without surfactant and MWNTs. This fact also, from the reverse side, suggests there should be strong interfacial bonding between MWNTs and PAAm. The surfactant molecules are adsorbed on the surfaces of the MWNTs by van der Waals forces [26]. The surfaces of the MWNTs were fully covered with surfactant molecules due to its higher weight ratio (Figure S8). Radiation-induced grafting reactions can occur on the surfactant molecules. As there are many surfactant molecules on the MWNTs surfaces, thus there are many grafted polymer chains attached to the MWNTs through surfactant layer as a medium. These grafted chains can physically entangle with the PAAm chains formed. Thus strong interactions are formed between MWNTs and PAAm hydrogel. The MWNTs in the network can dissipate the energy by their distortions and transfer the load from one end to the other one, and possibly from one MWNT to other ones if they are closely interwound. Of course, the strong interactions between MWNTs and PAAm hydrogel exist only when the water content is not too high. When the hydrogels are swelled to an equilibrium state, the polymer chains grafted on the surfactant molecules which are physically attached to

MWNTs might be dissolved in water and the MWNTs can be found (Figure 1b). The higher elastic modulus of the hybrid hydrogel is due to the high modulus of MWNTs and the strong interactions between MWNTs and PAAm hydrogel.

The hybrid hydrogels of PAAm and MWNTs synthesized by *in situ* radiation-induced polymerization combine the unique microstructure of radiation synthesized hydrogels and the load transfer mechanism of nanotube-polymer composites, both are effective in dissipating energy to slow crack propagation. This is the reason for the extremely high mechanical strengths of the hybrid hydrogels.

Conclusion

In summary, we have developed a novel hybrid hydrogel with extremely high mechanical strength. The new method of fabricating CNTs contained hydrogel is very simple and effective, in which MWNTs are evenly dispersed into water by utilizing a surfactant and sonicating, followed by the addition of aqueous monomer solution, finally irradiated with γ -rays. Other hydrophilic monomers can also be used to prepare hybrid hydrogels containing CNTs, however, great attention must be paid to the match between surfactant and monomer. Very possibly, other kinds of nanotubes or nano-fibers can also be used. The hybrid PAAm-MWNTs hydrogels show extremely high compressive and tensile strengths. The hybrid hydrogels with water contents more than 80 wt.% usually did not fracture even at compressive strengths close to or even more than 60 MPa and strains more than 97%. And the hybrid hydrogels had very high elongations (more than 2000% in some cases), especially when the water content was high. The tensile strengths are in sub-MPa. The hybrid hydrogels may have more applications than other strong hydrogels.

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