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# A Tough and Efficient Self-Healing Supramolecular Materials modulated with WCNT-NH<sub>2</sub>

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**Abstract.** Self-healing polymers crosslinked by solely reversible bonds are intrinsically weaker than common covalently crosslinked networks. In this work, a self-healing materials with excellent mechanical properties was synthesized by a new design strategy, which is to introduce covalent into reversible networks to improve its mechanical properties. First, polyamidoamine dendrimer oligomers (PAMAM-Oligomers) was synthesized. Then amine functionalized carbon nanotubes (WCNT-NH<sub>2</sub>) reacted with PAMAM-Oligomers to form a polyamidoamine carbon nanotubes composite materials (PAMAM-WCNT-NH<sub>2</sub>). The synthesized materials behave as rubber and exhibit spontaneous self-healing behaviour at room temperature without external stimuli. The mechanical and self-healing properties are closely related to the content of WCNT-NH<sub>2</sub>. For 0.5wt% WCNT-NH<sub>2</sub> in the materials, the strain of the material is 330% and tensile strength is 0.6 MPa. Importantly it can improve the self-healing efficiency to 98% of its original tensile strength in 2h.

## 1. Introduction

Self-healing polymeric materials can revert to their original state with full or partial recovery of mechanical strength after damage. As such, they hold great promise to extend the lifetime of polymeric products in many fields[1]; examples include aerospace, automotive, civil, and medical engineering. Unlike classical polymer networks that are crosslinked by permanent covalent bonds, self-healing polymeric materials are often based on reversible associations, such as hydrogen bonds, metal–ligand coordination, host–guest interactions, ionic interactions, electrostatic interactions, hydrophobic associations,  $\pi$ – $\pi$  stacking, or polymer entanglements[2]. Such reversible associations can break and reform to enable self-healing ability, but they are nevertheless relatively weak compared to covalent bonds. Thus, the toughness of self-healing polymers does not match that of covalent polymer networks such as natural rubber[3].

Hyperbranched polymer, as one kind of three dimensional macromolecules with globular or dendritic architectures, is widely used in coatings, nanomaterials, drug release and other fields [4, 5]. Compared with common linear molecular structure, hyperbranched structure has some advantages; 1) unique molecules with uniform, repeated branching units, endows it with unique chemical and physical properties. 2) The abundant functional groups in the branched structures allow them to easily form covalent bonds or non-covalent bonds. We designed and fabricate a novel polyamidoamine dendrimer (PAMAM) with a new design strategy, which is to introduce permanent covalent crosslinks into a reversible network to improve its mechanical properties. And hyperbranched structure self-healing materials have few reports.

Here, we report a stiff, self-healing hyperbranched composite materials that contains both covalent and reversible networks. The preparation process is in Figure 1. Firstly, the polyamidoamine (PAMAM) dendrimer (G-0.5PAMAM, G-1.0PAMAM) were synthesized in the step1 and step 2. Then



G-1.0PAMAM and dimer acids form polyamidoamine oligomers (PAMAM-Oligomers) through condensation reaction. As illustrated step 3, the PAMAM-Oligomers contain multifunctional branched with a controlled distribution of shapes and lengths. The oligomers carry motifs that can form reversible bonds (green symbols) along the branched chains of polymers and form covalent bonds (red circles) at the end of branching arms. Then WCNT-NH<sub>2</sub> crosslinks with the end groups of the PAMAM-Oligomers to form a network containing both reversible hydrogen bonds and permanent covalent as described by Step 4. And the formation of reversible associations is illustrated by the change of a pair of empty green symbols to filled ones.

## 2. Experiment and methods

### 2.1. *Synthesis of G-0.5 PAMAM.*

Ethylenediamine (13.3 g, 0.2mol) was dissolved in 20 ml of anhydrous methanol and added drop wise to a solution of methylacrylate (144.0g, 2.4 mmol) in 50 ml of anhydrous methanol under nitrogen in an ice bath. The mixture was kept stirring for 24h at room temperature. The residual methylacrylate and solvent was evaporated under reduced pressure to afford the desired G-0.5.

### 2.2. *Synthesis of G-1.0 PAMAM*

G-0.5 PAMAM (25.0 g, 61.8mmol) was dissolved in 30 ml of anhydrous methanol. The solution was stirred under nitrogen for 30 min in an ice bath. Then, diethylenetriamine (75.4g, 714.6 mmol) was dropwise added to the solution and kept stirring for 24 h at room temperature. The residual diethylenetriamine and solvent were evaporated under reduced pressure to afford the desired G-1.0.

### 2.3. *Synthesis of PAMAM-WCNT-NH<sub>2</sub> composite materials*

Amine functionalized carbon nanotubes WCNT-NH<sub>2</sub> were synthesized according to the reported procedure[6], then the WCNT-NH<sub>2</sub> was dispersed in anhydrous DMF.

G-1.0 PAMAM (15g, 21.8mmol) was mixed with dimer acid (48.8g, 87.2mmol), and the mixture was stirred at 120 °C for 2 h until a homogeneous dispersion was obtained. After a further 4 h stirring at 150°C, the PAMAM-Oligomers was allowed to reach room temperature and dispersed in DMF. 0.5wt%, 1.0wt% or 1.5wt% WCNT-NH<sub>2</sub> was respectively added to the oligomers solution and stirred for 30min. The mixture was heated to 150°C and kept stirring for 8h while DMF was removed under N<sub>2</sub>. Finally, the product was poured into template to obtain a testable sample for test.

### 2.4. *Characterization*

Mechanical tensile-stress were performed on a LLOYD LR30k pulls tensile testing machine. Four samples were completely cut perpendicular to the tensile direction and then jointed immediately by contact the fracture surfaces. The healing was lasted for variable times (1h, 2 h, 24h) at room temperature of 25 °C. The tensile tests were performed at a stretching rate of 5 mm / min at the ambient temperature of 25 °C. Electron microscopy (TEM) images are collected by using a JEOL JEM-1400 Microscope with an accelerating voltage of 100 kV.

### 3. Results and Discussion

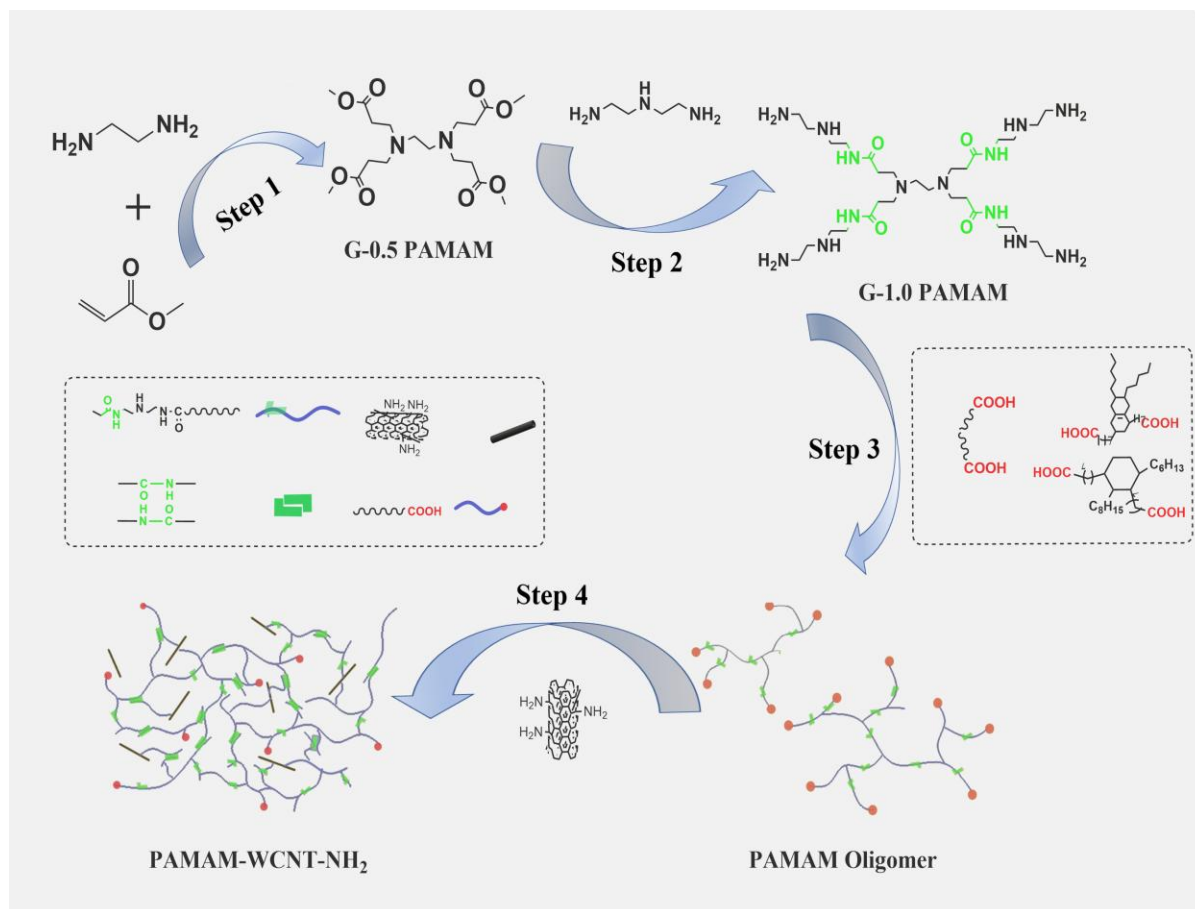


Figure 1 Concept and synthesis of hybrid networks.

#### 3.1. Tensile Properties of the Composites Materials

To investigate the influence of WCNT-NH<sub>2</sub> as a filler on materials, we synthesized three PAMAM-WCNT-NH<sub>2</sub> with different weight percentages of WCNT-NH<sub>2</sub> at 0.5wt%, 1.0wt% and 1.5wt% which we termed PAMAM-0.5wt%WCNT-NH<sub>2</sub>, PAMAM-1.0wt%WCNT-NH<sub>2</sub>, PAMAM-1.5wt%WCNT-NH<sub>2</sub>. Stress-strain curves are shown in Figure 2a. For PAMAM-1.5wt%WCNT-NH<sub>2</sub>, although its tensile strength reaches 2.80 MPa, the elongation at break is only 114%, which is different from a conventional elastomer. However, for PAMAM-1.0wt%WCNT-NH<sub>2</sub>, the elongation at break exceeds 275%, the tensile strength is 1.8 MPa. And it behaves as soft rubber. Similarly, for PAMAM-0.5wt%WCNT-NH<sub>2</sub>, the elongation at break exceeds 330%, and the tensile strength decreases to 0.60MPa. Tensile stress increases and the strain decreases with the WCNT-NH<sub>2</sub> content increasing. The result means that the hybrid network disturbs the orientation of the polymer chain at high elongation, while increasing WCNT-NH<sub>2</sub> to improve the crosslinking degree of the network. So, the WCNT-NH<sub>2</sub> is the key factor in tuning the mechanical properties of the composite materials. And with only 0.5wt%WCNT-NH<sub>2</sub>, the tensile strength of the composite materials is superior to the hydrogen bond self-healing material previously reported[7].

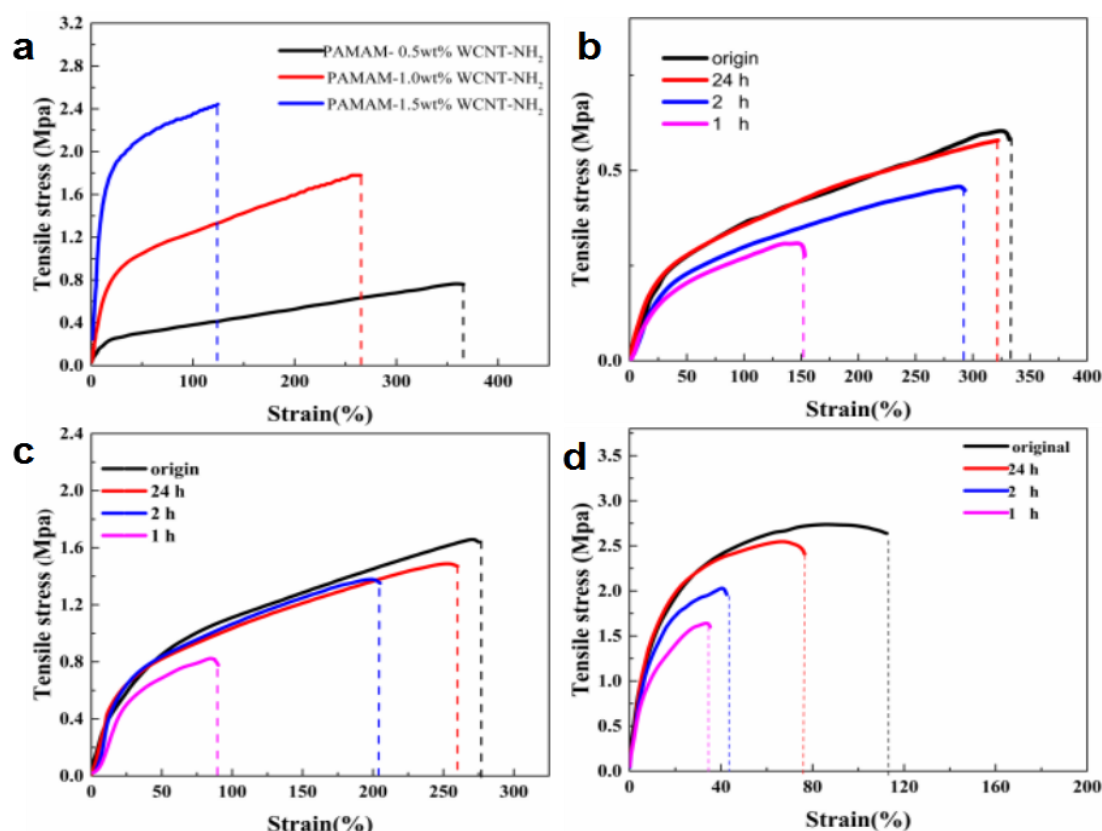


Figure 2. a) Strain-stress curves of the PAMAM-WCNT-NH<sub>2</sub> with different WCNT-NH<sub>2</sub> percentages. Strain-stress curves of the PAMAM-WCNT-NH<sub>2</sub> with WCNT-NH<sub>2</sub> at b) 0.5wt%, c) 1.0 wt% and d) 1.5wt% upon different healing time at room temperature;

### 3.2. Self-healing Properties Composites Materials

The hydrogen bond type self-healing mechanism of polymer networks has been reported. Upon a mechanical damage event, the weaker hydrogen bonds are more likely to break as opposed to the stronger covalent bonds. When the ambient temperature is above the glass transition temperature ( $T_g$ ), the dynamic hydrogen bonds found in the supramolecular components of the fracture area can be re-established as soon as the damaged surface resumes contact[7]. Based on results from the tensile test, we focused on the self-healing ability of the materials. First, we cut the self-healing materials into two separate pieces. Then bring them together with different healing times. As shown in Figure 2b, 2c and 2d, the curves indicate that the PAMAM-0.5wt%WCNT-NH<sub>2</sub>, PAMAM-1.0wt%WCNT-NH<sub>2</sub> and PAMAM-1.5wt%WCNT-NH<sub>2</sub> were able to recover 90%, 78% and 45% of their original elongation at break in 2h. Particularly, the healing time of PAMAM-0.5wt%WCNT-NH<sub>2</sub> and PAMAM-1.0wt%WCNT-NH<sub>2</sub> are significantly shorter than other previously described hydrogen bonding self-healing supramolecular materials which generally need more than 48 h heal to 75% of its original strain[8]. As the healing time increased to 24 h, the self-healing efficiency increased to 98.6%, 92.1% and 66%, respectively. Increasing the amount of WCNT-NH<sub>2</sub> lead to more covalent cross-linking and more restricted movement of polymer chains, which may explain the observed trend for increased time for the self-healing process. The self-healing experiment of the PAMAM-1.0wt%WCNT-NH<sub>2</sub> in Figure 3a demonstrates that the broken ends are recombined just by simply bringing them together at room temperature. The SEM images confirm that fracture surface is sufficiently healed with time in the Figure 3b.

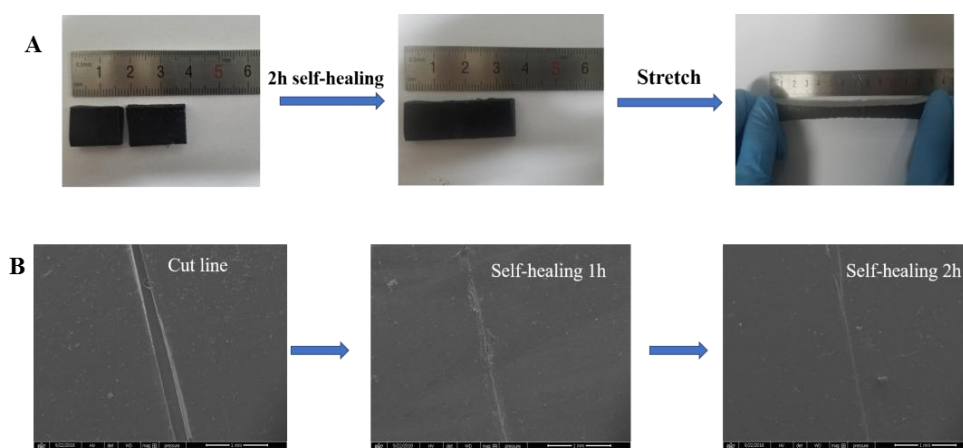


Figure 3. a) Stretching of the PAMAM-1.0wt%WCNT-NH<sub>2</sub> sample after cut and subsequent 2h self-healing at room temperature. The sample can be stretched to 260% while retaining a modulus similar to pristine sample. b) SEM images of the PAMAM-1.0wt%WCNT-NH<sub>2</sub> surface after 1 and 2h.

#### 4. Conclusions

In summary, this research introduces a self-healing materials based on crosslinking hyperbranched structure. Then we described concept of using WCNT-NH<sub>2</sub> as both cross-linkers and fillers to improve the mechanical strength. And by adjusting the content of WCNT-NH<sub>2</sub>, the degree of crosslinking and mechanical strength of the materials can be modulated. The final synthesized composite materials are similar to rubber and can spontaneously heal at room temperature in 2 h. In addition, due to the excellent conductivity of WCNT-NH<sub>2</sub>, the PAMAM-WCNT-NH<sub>2</sub> is also electrically conductive, making it practical for use in stretchable self-healing conductive elements.

#### 5. References

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