Room-Temperature Self-Healing Elastomer based on Van der Waals Forces in Air and under Water

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Abstract. With the development of flexible wearable electronic devices, researches on self-healing conductive materials have become prevalent. However, the self-healing performance of most conductive self-healing materials is commonly achieved by the external stimulus that may cause damage to the equipment. Particularly, these self-healing materials may lose the self-healing properties when exposed to a high-humidity environment. Here, we adopted two hydrophobic monomers (2-methoxyethyl acrylate and ethyl methacrylate) to obtain a self-healing elastomer that could display self-healing properties in air or under water though van der Waals forces. The quality and mechanical properties of the elastomer material could keep stable after stored under water for half a month. This elastomer material was capable of self-healing in different environments with self-repair efficiencies more than 50% in deionized water, strong acid solution and strong alkaline solution. The self-repair efficiencies were up to 77% at room temperature(T=25℃) and 64% at low temperature (T=-20℃) in air.

Keywords: self-healing elastomer, van der Waals force, room temperature.

1. Introduction
Self-healing materials are a kind of smart materials that can repair their structural and functional characteristics autonomously when they suffer from mechanical damage [1]. At present, self-healing polymer materials with excellent mechanical properties and good stretchability are highly desirable in the field of flexible electronic devices. They usually repair themselves through dynamic covalent bonds or intermolecular interactions [2-6]. However, achievement of self-healing properties of these polymer materials usually requires external stimulation or external energy, which cannot self-heal at room-temperature [7, 8]. Dynamic covalent bonds and intermolecular interactions of self-healing polymers are also unstable in water, which can reduce the self-healing efficiency when those self-healing polymers are placed in wet environment [9]. Therefore, preparing a room-temperature self-healing polymer in air and under water without external stimulation in simple design principles is still a big challenge [10].

The van der Waals forces are universal and not easily affected by water molecules. The strong van der Waals forces have been achieved by constructing a key lock inter-matching structure, endowing the material with a good room-temperature self-repair without external force driving [11]. Here we employed van der Waals force as the driving force for self-healing performance and adopted hydrophobic 2-methoxyethyl acrylate (MEA) and ethyl methacrylate (EMA) as co-monomers to prepare...
a poly (2-methoxyethyl acrylate-co-ethyl methacrylate) elastomeric material (ME). This elastomeric material had good self-repairing properties at room temperature in air and under water.

2. Experimental section

2.1. Materials
Benzoyl peroxide (C.P, ≥ 95.0%) was purchased from Tianjin Kermel Chemical Reagents Development Center (Tianjin, China). 2-Methoxyethyl acrylate (MEA, 98%) and Ethyl methacrylate (EMA, 99%) were purchased from Beijing Innochem Technology Co., Ltd. (Beijing, China). The deionized water was used in all experiments.

2.2. Preparation of self-healing Poly (MEA-co-EMA) (MXEY) copolymer material:
Poly (MEA-co-EMA) was synthesized by the bulk copolymerization of 2-methoxyethyl acrylate (MEA) and Ethyl methacrylate (EMA). In a typical procedure, the monomers, MEA and EMA, and 1.5 wt. % (relative to monomer weight) benzoyl peroxide were sequentially added into a 20 mL glass vial and bubbled with nitrogen under stirring for 20 min at 25°C. Then, the mixture solution was transferred into a Teflon plate mold (10 cm × 10 cm, 2 mm thick) and polymerized at 65°C for 12 h to prepare poly-(MEA-co-EMA). In this work, MXEY and ME are short of poly-(MEA-co-EMA). X and Y respectively refers to the molar percentage of MEA and EMA in total monomers.

2.3. Characterization
The FTIR spectra were recorded on NICOLET IS10 (Thermo-Fisher, Germany) with the range of 500-4000 cm⁻¹. The glass of transition temperature (Tg) was measured by differential scanning calorimetry (DSC-60). The water contact angle was tested with a contact angle measuring instrument (Data-physics) produced by Germany Instrument Company. The tensile strength of the samples was measured on the AGS-J electronic universal testing machine (Shimadzu, Japan) at room temperature. A plate sample with a size of 50 mm×10 mm×2 mm was used for the tensile test with a speed of 100 mmꞏmin⁻¹.

2.4. Self-healing properties
The plate sample (50 mm×10 mm×2mm) was cut into two halves by a blade, then the damage interfaces are re-connected together for self-healing under different environmental conditions, and the AGS-J electronic universal testing machine was used for mechanical properties of the healed sample. The self-healing performance of the sample was mainly evaluated by stress recovery (Re) which were calculated by equations (1):

\[ R_e = \epsilon_1 / \epsilon_2 \times 100\% \]  

The \( \epsilon_1 \) and \( \epsilon_2 \) represented the breaking stress of the healed sample and the initial sample, respectively.
3. Results and discussion

3.1. Mechanical properties of the ME copolymer

Figure 1. a) Stress-strain curves and b) DSC curves of MxEy copolymers with different monomer ratios.

The mechanical properties of self-healing materials played an important role in their practical application. The stress-strain curves of MxEy copolymers with different monomer ratios were evaluated in Figure 1a. It could be seen that the mechanical strength of the MxEy copolymers increased while the tensile strain decreased with the increase of the EMA monomer proportion. These results could be attributed to the glass transition temperature of the MxEy copolymers (Figure 1b). PEMA had a high glass transition temperature (Tg = 64.25℃), which was the hard segment in the MxEy copolymer. The increase of the PEMA segment content would increase the rigidity of the molecular chain in the MxEy copolymer, endowing the MxEy copolymer with a higher glass transition temperature and stronger mechanical strength. On the contrary, PMEA had a low glass transition temperature (Tg = -34℃), which was the soft segment in the MxEy copolymer. The increase of the PMEA segment content would make the molecular chains softer in the MxEy copolymer, endowing the MxEy copolymer with a lower glass transition temperature and more molecular chain migration. Although M30E70 copolymers showed the optimal mechanical strength, they could not self-healed at room-temperature because of the high glass transition temperature. So, the M40E60 copolymers was the most suitable for the self-healing study with an excellent mechanical property and a glass transition temperature lower than room temperature.
3.2. Self-healing mechanism of the ME copolymer

![Figure 2. a) The Schematic diagram of ME polymers for self-healing under water b) The schematic diagram of self-healing mechanism of ME polymers](image)

Recently the commodity copolymers which could self-heal upon mechanical damage was reported [11]. In the commodity copolymers, van der Waals forces were used instead of dynamic covalent bonds or intermolecular interactions to achieve multiple recovery upon mechanical damage without external intervention. According to this ideal, we chose hydrophobic monomers 2-methoxyethyl acrylate (MEA) and ethyl methacrylate (EMA) to prepare ME self-healing elastomer materials by in-situ free-radical copolymerization. The self-repairing process under water at room temperature of ME polymers was shown in Figure 2a. Two freshly cut ME polymer samples were placed under water and dyed by different colours. Then the damaged ME polymer interfaces were re-contacted closely to self-repair under water at room temperature. After healing for 3 h the healed sample could be stretched to 200% strain. The good self-healing properties of the prepared ME copolymer at room temperature in air and under water were attributed to van der Waals forces between molecular chains which could be illustrated as the δ⁺-δ⁻ induced dipole interaction on the side chain of the molecular chains as shown in Figure 2b. When the ME materials suffered from damages, the cross-linking structure between the molecular chains was destroyed. When the damaged interfaces were re-contacted, the cross-linking structure would be restored with the δ⁺-δ⁻ induced dipole interaction between the side chains of the molecular chain due to van der Waals forces.
3.3. Self-healing properties of the M40E60 copolymer in air

Figure 3. The self-healing properties of M40E60 copolymer in air a) at room temperature b) at low temperature. c) The optical microscope images of M40E60 polymers self-healed for different times.

The mechanical self-repairing property of M40E60 copolymers in air at room temperature was shown in Figure 3a. It could be seen that the mechanical strength of the M40E60 copolymer could be recovered to 78% after self-healing for 24 h in air at room temperature. From the optical microscope images of healed M40E60 copolymers self-healed for different time, it could be seen that the scars at the damaged location became lighter obviously after healing for 3 h. Within 24 h of self-healing, the scars almost disappeared, further confirming M40E60 copolymers had a good self-healing property at room temperature in air (Figure 3c). The self-repair efficiency of M40E60 copolymers was significantly decreased, only 64% after self-healing in air at low temperature (-20°C) for 24 h (Figure 3b). The migration of molecular chains was reduced at low temperature, leading to a poor self-repair performance.

3.4. Self-healing properties of the M40E60 copolymer under water

Figure 4. a) Water contact angle of M40E60 copolymers. b) The stability of M40E60 copolymers under water. c) Self-healing properties of M40E60 copolymers in different aqueous solutions.

The ME copolymer prepared by bulk polymerization of ester monomers showed a water contact angle of 92°, which was a hydrophobic material (Figure 4a). The M40E60 copolymer could not be infiltrated in water and not affected by the hydrogen bonds of water molecular because of hydrophobicity. Therefore, it was speculated that M40E60 copolymer was stable under water. In order to confirm this speculation, M40E60 copolymer was placed under water for 15 days. After 15 days, the mechanical properties and weight of the M40E60 polymer were evaluated. It was found that the mechanical strength of M40E60 polymer only decreased from 1.45MPa to 1.3MPa, and the stretchability still remained about 500%; while the mass of M40E60 copolymer only increased by 1.5% (Figure 4b). These findings confirmed that the M40E60 copolymer had a good stability underwater, which was a prerequisite for self-healing under water. The damaged M40E60 copolymers were placed under water to self-heal for 24 h at room temperature (Figure 4c). It could be seen that the M40E60 copolymer had a self-healing efficiency of 53% in pure water. And M40E60 copolymer could self-heal not only in pure water, but also in harsh aqueous solutions. When the M40E60 copolymer was self-healed in strong acidic solution...
(pH=1) and strong alkaline solution (pH=13) for 24 h, the self-healing efficiencies respectively reached 55% and 53%, which was closed to the self-healing efficiency in pure water (53%). These results indicated that M₄₀E₆₀ copolymer was still effectively self-healed in harsh water environments.

4. Conclusion
We successfully prepared room-temperature self-healing ME copolymer elastomers by the facile bulk copolymerization of two hydrophobic monomers. The self-healing mechanism was contributed to the δ⁺-δ⁻ induced dipole interaction between neighboring chains in ME copolymer, which were conducive to the formation of strong van der Waals force as the driving force to achieve self-repair. The mechanical strength of M₄₀E₆₀ was up to 1.41MPa, and its self-repairing efficiency could respectively reach 77% in air at room temperature, 64% in air at low temperature (-20℃). The ME copolymer as a hydrophobic material was not easily affected by water molecules, and the van der Waals force between polymer molecular chains would not interact with water molecules, so it could be self-repaired under water. The self-repairing efficiencies of M₄₀E₆₀ in pure water, acid solution (pH=1) and alkaline solution (pH=13) were more than 50%. These results proved that the ME copolymer had a good self-healing performance under a variety of extreme conditions.

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