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Original Paper

Strategic design and self-healing by using modified PVC-Cu(II) complex

Dina S. Ahmed[1], **Amamer M. Redwan**[2], **Shams A. Ismael**[3], **Khalid Zainulabdeen**[3], **Amani Husain**[4], **Ahmed Ahmed**[4], **Omar Al-Obaidi**[5], **Salam Mohammed**[6], **Emad Yousif**[3*]

[1] Department of Chemical Industries, Institute of Technology-Baghdad, Middle Technical University, Baghdad, Iraq
[2] Department of Chemistry, Faculty of Science, Bani Waleed University, Bani Waleed, Libya
[3] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
[4] Polymer Research Unit, College of Science, Mustansiriyah University, Baghdad, Iraq
[5] Chemistry Department, College of Science, University of Anbar, Al Anbar, Iraq
[6] Department of Chemical and Petrochemical Engineering, College of Engineering and Architecture, University of Nizwa, Nizwa, Oman

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Corresponding author
Emad Yousif
emad_yousif@hotmail.com

ABSTRACT

Advanced functional polymers have attracted significant interest in science and technology. However, microstructural damage and variations in chemical composition are often introduced during manufacturing and use, leading to degradation or even loss of functionality. To address these issues, self-healing functional polymeric materials have been developed to autonomously restore non-structural functions, thereby extending service life and durability. Recent work has emphasized such materials with capability of independently recover function without external repair. Unlike structural self-healing systems that prioritize strength restoration, functional self-healing targets recovery of specific properties. In modern polymers and hydrogels, temperature, pH, and light commonly act as external stimuli to trigger recovery. Biomimetic self-healing systems may also rely on chemical or mechanical interactions to repair critical cracks and restore functional performance. At the molecular level, $\pi-\pi$ interactions, metal-ligand coordination, and hydrogen bonding are frequently exploited to reinforce weakened regions. These capabilities have driven demand across materials science and engineering. Moreover, they were used in biomedical fields such as localized drug delivery, skin grafting, implantation, dentistry, and bone and tissue regeneration. Self-healing polymers can regenerate damaged surfaces and often show favorable biocompatibility, faster healing, and improved tensile strength, supporting use in medical devices and other applications. As an example, a modified poly (vinyl chloride)/Cu(II) (PVC/Cu(II)) film were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive X-ray (EDX) analysis, and optical microscopy.

Keywords: *Biocompatible materials, Biomedical applications, Molecular interactions, Self-healing polymers, Stimuli-responsive hydrogels*

1 INTRODUCTION

Poly (vinyl chloride) (PVC) is a widely used thermoplastic polymer, with annual production exceeding 31 million tons [1]. Its extensive use across transportation, construction, packaging, and healthcare stems from its chemical and biological durability, affordable price, and ease of processing [2]. Currently, PVC accounts for approximately 30% of all disposable polymeric devices used in medical diagnosis, screening, health care, and treatment [3, 4].

Research on PVC surface modification aims to minimize the environmental release of additives and improve recyclability [5], enhance interfacial and mechanical properties for applications involving contact with biofluids [6,7], and reduce biofouling, goals that are particularly important for medical-grade PVC [8]. Approaches include argon and oxygen plasma treatments [9], exposure to UV radiation [10], graft polymerization to produce polymer brush layers [7], and nucleophilic substitution via wet-chemical processes [11].

Aromatic thiols have been used as nucleophilic reagents to replace chlorine atoms on the PVC backbone in various media, including solutions, aqueous suspensions, and during melt processing [12]. Surface grafting modifies only the outer layer of a material while preserving the properties of the inner core. The effects of surface modification can arise from chemical changes that extend into the bulk polymer or from alterations confined to the surface that leave bulk composition and properties unchanged [13]. Outdoor photodegradation driven by ultraviolet (UV) radiation causes color fading and mechanical deterioration, drastically shortening a substrate's useful life [14]. Applying a UV-blocking coating can shield the surface from harmful radiation. However, even slight mechanical scratches can compromise coating integrity and reduce protection. For instance, in cable applications, small cracks in the outer layer generated by dragging or installation promote UV-induced photo-aging, enable moisture and oxygen ingress, and reduce service life [15, 16]. A UV-blocking coating with self-healing properties can mitigate such damage by autonomously repairing microdefects, resulting in prolonging resistance to UV aging and enhancing overall durability. Self-healing materials are advanced materials capable of autonomously repairing damage [17–19]. The primary types, based on healing mechanism, are the extrinsic (filling) type, which incorporates carriers such as microcapsules, hollow fibers, or micro-vasculatures dispersed within a polymer matrix, and the intrinsic type, which relies on reversible intermolecular interactions among its components to facilitate healing [20–22].

Materials whose self-healing mechanisms rely on dynamic covalent bonds can break and reform those bonds under external stimuli such as heat [23], light [24], or pH changes [25], thereby facilitating repair of damaged regions. Conversely, materials that employ noncovalent interactions can activate self-repair without external triggers, using hydrogen bonding [26], $\pi - \pi$ interactions [27], metal coordination [28], or topological entanglements [29] to build stable supramolecular networks. A key advantage of such noncovalent systems is their capacity for repeated, cyclic self-healing without dependence on embedded carriers. Among supramolecular strategies, host-guest systems often exhibit particularly strong self-healing performance. For example, research teams have reported supramolecular gels based on host-guest interactions that heal rapidly even after extreme deformation [30], and gels combining clay with telechelic dendritic macromolecules that achieve complete recovery [31]. Similarly, elastomers have been developed that regain up to 90% of their mechanical strength after damage [32].

To combine self-healing with UV shielding, one approach employs a host-guest inclusion polymer in which cyclodextrin (modified with TiO_2 nanoparticles as a UV-shielding agent) serves as the host, and adamantane, functionalized with a reactive monomer, acts as the guest. After assembly, the host-guest complex is co-polymerized with additional monomers to yield a self-healing, UV-protective coating.

In this work, a new polymeric system for self-healing is synthesized and designed by preparing modified PVC films using an appropriate aldehyde and copper (II) acetate. We characterize the resulting PVC/ Cu(II) films by Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, and optical microscopy.

2 MATERIALS AND METHODS

2.1 Materials and devices

Ethylenediamine (98%) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Poly(vinyl chloride) (PVC) with a degree of polymerization (DP) reported as 3000 was obtained from Petkim Petrokimya (Turkey). Fourier transform infrared (FTIR) spectra of the polymer films were recorded on a Shimadzu 8400 spectrophotometer over 400-4000 cm^{-1}. Surfaces of irradiated and surface-modified PVC films were examined by scanning electron microscopy (SEM) using a ZEISS SIGMA 500 VP microscope. Additional morphological analysis was performed by atomic force microscopy (AFM) with a Veeco instrument and a MEIJI TECHNO microscope.

For AFM, samples were maintained under nitrogen to prevent distortion; three-dimensional images were acquired in tapping mode at a scan rate of 0.8 Hz.

2.2 Fabricated PVC films preparation

2.2.1 PVC (blank) film preparation

Uniform PVC films were prepared by solvent casting. For blank films, 5 g of PVC was dissolved in 100 mL of tetrahydrofuran (THF) with constant stirring for 3 h.

2.2.2 PVC containing schiff base preparation

PVC films modified with ethylenediamine were prepared by dissolving PVC (5 g) and ethylenediamine (30 mg) in tetrahydrofuran (THF, 50 mL), then adding salicylaldehyde (30 mg). Acetic acid (1 mL) was subsequently added, and THF was brought to a final volume of 100 mL. The mixture was stirred for 3 h, the solvent was removed, and the modified PVC was dried for 24 h at room temperature.

2.3 Synthesis of PVC containing schiff base and copper acetate

PVC-Schiff base (0.4 g) and copper acetate (0.1 g) were mixed in THF (4 mL). The mixture was sonicated for 1 h and was cast onto glass plates to yield a 40 µm-thick film. The film was dried for 24 h at 25 °C and then placed under vacuum for 3 h to remove residual solvent (SchemeSelf-healing test 1).

2.4 Self-healing test

The film was further dried in a vacuum oven at 50 °C. The blend was then scratched and exposed to UV light with a specific wavelength at 25 °C for a duration between 50 and 300 hours.

3 RESULTS AND DISCUSSION

Aminolysis of PVC was carried out to generate amino-functionalized films. This approach, commonly used to introduce amine groups onto PVC surfaces, involved reacting PVC with ethylenediamine in THF (Scheme 1). The reaction proceeds via nucleophilic substitution (S_N2) to yield an amino-functionalized PVC surface. The modified PVC was then reacted with salicylaldehyde to form Schiff bases along the polymer chains. Finally, the PVC-Schiff base was mixed with copper(II) acetate in THF to afford the corresponding PVC/Cu(II) material (Fig. 1).

3.1 FTIR spectroscopy

The FTIR spectrum of aminated PVC showed two new absorption bands. The symmetric and asymmetric N-H stretching vibrations of the primary amine (–NH_2) appeared at 3361 and 3322 cm^{-1}, respectively. In addition, a band at 3288 cm^{-1} could be assigned to the N-H stretching of a secondary amine. Peaks at 2972 and 2910 cm^{-1} indicate aliphatic C-H stretching, and the band at 1248 cm^{-1} was assigned to C-N stretching.

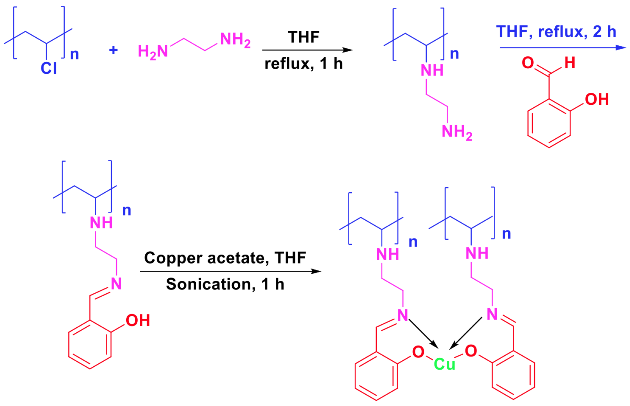

Fig. 1 Synthesis steps of modified PVC/Cu(II).

A strong absorption band at 1639 cm^{-1} corresponds to the imine (C=N) group, which represents PVC containing the Schiff base. Additional stretching bands were observed at 3064 cm^{-1} (aromatic C-H), 2900 cm^{-1} (aliphatic C-H), and 3290 cm^{-1} (secondary amine N-H).

3.2 Morphological study of polymeric surface

3.2.1 Scanning electron microscopy (SEM)

Analyzing polymer surface morphology provides critical insight into damage arising from changes in particle size and shape. SEM is a valuable tool for evaluating surface distortions, heterogeneity, and particle morphology [5], as shown in Figure 2.

3.2.2 Energy dispersive x-ray spectroscopy (EDX)

EDX was used to investigate the chemical composition of the materials. The three-dimensional resolution of EDX is governed by the interaction volume of the electron beam with the polymer films [6]. EDX patterns were acquired for two purposes: identification of the major elements present and to assess compositional homogeneity. Figures **??** and 10 show new peaks in the regions corresponding to nitrogen, copper, and oxygen, indicating that the PVC was successfully modified.

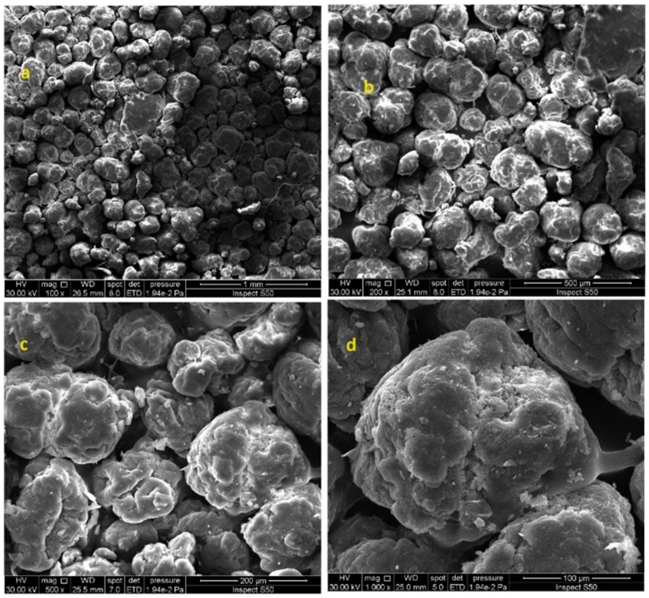

Fig. 2 Different magnifications of modified PVC/Cu(II) (a) 1mm, (b) 500µm, (c) 200 µm, (d) 100 µm.

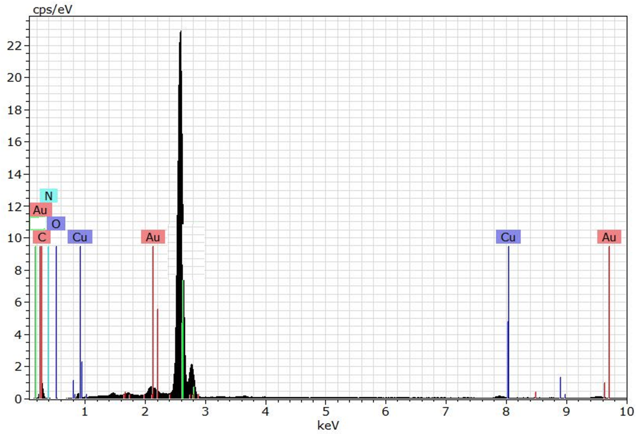

Fig. 3 EDX spectra obtained for modified PVC/Cu(II).

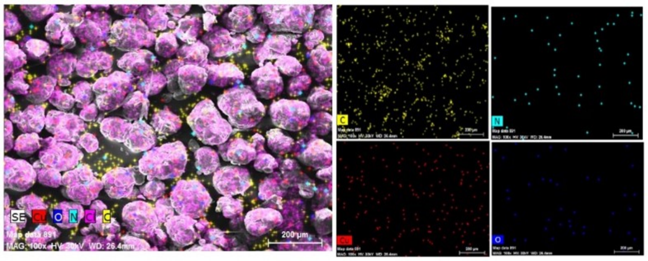

Fig. 4 EDX mapping analysis for modified PVC/Cu(II).

3.2.3 Atomic force microscopy (AFM)

AFM was used to obtain high-resolution topographic images of polymeric surfaces. The roughness factor (Rq) quantifies surface smoothness. AFM provided two- and three-dimensional topography for further evaluation of surface roughness [7]. Figure 5 shows AFM images of the modified PVC/Cu(II).

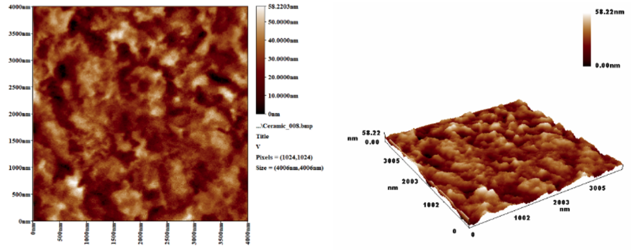

Fig. 5 AFM images for modified PVC/Cu(II).

3.2.4 Optical microscope

The effect of ultraviolet radiation on the self-healing properties of modified PVC/Cu(II) was evaluated by introducing controlled scratches on film surfaces. Surface features such as spots, grooves, cracks, and discoloration were examined to assess damage and recovery. After UV exposure, the modified PVC/Cu(II) surface appeared smoother and more orderly as indicated in Figure 6. Notably, PVC integrated with the Cu(II) complex exhibited the greatest smoothness and the fewest defects compared with its pre-exposure state.

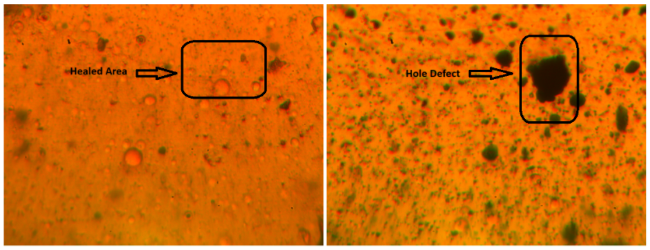

Fig. 6 Optical microscope images for modified PVC/Cu(II) film before and after UV exposure.

4 CONCLUSIONS

Research on self-healing polymeric materials, driven by scientific and technological needs, has focused on restoring non-structural functionalities compromised by microstructural damage and chemical change. These materials show strong regenerative behavior and broad utility, particularly in medical and biomedical contexts. Functional recovery is commonly triggered by external stimuli such as temperature, pH, and light. Whereas structural self-healing emphasizes restoration of mechanical integrity. Regeneration is enhanced by molecular interactions including $\pi - \pi$ stacking, metal-ligand coordination, and hydrogen bonding. With favorable biocompatibility, accelerated healing, and improved tensile strength, these polymers are promising candidates for drug delivery, tissue engineering, and medical devices. In this study, the modified PVC/Cu(II) film examination results by FTIR, SEM, AFM, and EDX provide a comprehensive characterization that supports its potential for specific biomedical applications and future development.

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DECLARATIONS

Conflict of interest

Authors declare that there is no any relevant conflict of interest.

Consent to publish

All authors consent to the publication of this work. Written informed consent for publication was obtained from the participants.

Ethical approval

N/A

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