

## Research Article

# Investigations of Self-Healing Property of Chitosan-Reinforced Epoxy Dye Composite Coatings

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Chitosan has a very wide application range in different parts of life such as in biomedical and antimicrobial areas. In recent years the self-healing property of chitosan becomes more of an issue. In the study chitosan was used to obtain a self-healing composite material. An epoxy dye was converted to a self-healing coating. Different types of samples were prepared by coating the glass substrates with a polymer matrix reinforced with various amounts of chitosan. The samples were characterized by fourier transform Infrared (FTIR) and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS). In addition, self-healing test was applied as a primary objective of this research. In this respect, the samples were scratched with a very thin pin, and they were analyzed by SEM periodically. It was observed that chitosan-reinforced dyes showed self-healing property. Mechanism of the self-healing process was also scrutinized.

## 1. Introduction

A self-healing material is a material that has the built-in ability to partially repair damage occurring during its service life time. Self-healing is the ability of a material to restore mechanical properties, which were earlier perturbed by a plastic deformation or failure involving cracks and voids. Usually, certain properties of any engineering material such as metals, polymers, ceramics, cementitious, and elastomeric and fibre-reinforced composite materials degrade over time due to environmental conditions or fatigue or due to damage incurred during operation. This damage is often on a microscopic scale, requiring periodic inspection and repair to avoid them growing and causing failure [1]. Self-healing materials address this degradation through the inclusion of an “active” phase that responds to the microdamage by initiating a repair mechanism, and several mechanisms have been proposed for the engineering materials. Investigation of possible self-healing mechanisms is an important emerging

field of nanotechnology [2]. The inspiration of self-healing materials comes from biological systems, which have the ability to heal after being wounded. Initiation of cracks or other types of damage on a microscopic level changed thermal, electrical, and acoustical properties and eventually led to whole scale failure of the material. Usually, cracks cannot be mended by hand because it is hard/difficult to detected. A material that can intrinsically correct damage can lower production costs of a number of different industrial processes, can reduce the inefficiency over time caused by degradation, and can prevent costs incurred by material failure [3].

Different strategies and approaches to devise self-healing materials in metals, ceramics, and polymers have been investigated. These materials possess different intrinsic properties, and self-healing is based on the same common general principle in all of them. Self-healing can take place on the microscopic to macroscopic level. The prerequisite for a self-healing of a (mechanical) damage is the generation of

a mobile phase, and the mobile phase can close the crack (Figure 1). If a material is damaged (Figures 1(a) and 1(b)), a crack can occur. Then subsequently a “mobile phase” (Figure 1(c)) which is triggered either by the occurrence of damage (in the ideal case) or by external stimuli was generated. Following the mobile phase generation, the damage can be removed due to the directed mass transport towards the damage site and the subsequent local mending reaction (Figure 1(d)). The latter assures the (re)connection of the crack planes by physical interactions and/or chemical bonds. After the healing of the damage the previously mobile material is immobilised again, resulting in the best case in fully restored mechanical properties (Figure 1(e)) [4].

The first report of a completely autonomous man-made self-healing material belongs to a group [5]. They reported an epoxy system containing microcapsules, and the microcapsules were filled with a (liquid-thermosetting) monomer. If a microcrack occurs in this system, the microcapsule will rupture, and the monomer will fill the crack (Figure 2) [6]. Subsequently it will polymerise by the initiation of catalyst particles dispersed through the system. This model system of a self-healing particle proved to work very well in pure polymers and polymer coatings [7].

SiC/C/SiC model composites and Si-Ti-C-O fiber-bonded ceramics are the examples that show self-healing features under heating at high temperatures [8]. In addition, semiorganic and ceramic protective coatings, silicate nanocomposites, and SiC/SiC fibrous composites may reveal chemical mechanisms of self-healing on exposure to oxygen [9]. Generally speaking, very high local temperatures are required to repair most current ceramics, due to the high activation energies of the diffusive mass transport in the covalent or ionic structures of ceramics (e.g., SiC/Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> composite: 1300°C). In Figure 3, the healing reaction is initiated by the heat of combustion, and a self-healing oxidation and corrosion protection coating on SiC ceramic (burner nozzle) occur. A reactive filler (MOSi<sub>2</sub>) embedded in a SiOC matrix is oxidized by permeating oxygen, and the formed SiO<sub>2</sub> closes the crack completely (Figure 3) [4].

Although metals and ceramics have been investigated for self-healing studies, polymers (and composites) are by far the most studied material class in the context of self-healing behaviour. This may be due to easy achievement of functionalisation and modification of the polymeric systems that require low temperatures to induce mobility and need the large volume of mobile molecules in comparison to the volume of mobile atoms [4].

Chitosan is one of self-healing materials which has been investigated in polymer technology. It is a linear polysaccharide obtained by extensive deacetylation of chitin (Figure 4(a)). It is mainly composed of two kinds of (1 → 4) linked structural units, namely, 2-amino-2-deoxy-d-glucose and *N*-acetyl-2-amino-2-deoxy-d-glucose. The chemical structure of a completely deacetylated chitosan is represented in Figure 4(b). Nonetheless, as much as it is virtually impossible to completely deacetylate chitin, what is usually known as chitosan is a family of chitins with different but always low degrees of acetylation. The capacity of chitosan

to dissolve in dilute aqueous solutions is the commonly accepted criterion to differentiate it from chitin [10, 11].

Chitosan has a very wide application range everywhere in life. It is a very useful polymer for biomedical applications in terms of its biocompatibility, biodegradability, and low toxicity [12]. The well-established antimicrobial properties of chitosan and chitin against a wide spectrum of bacteria, fungi, and viruses can lead to a potentially large reduction in the amount of synthetic food preservatives currently used. Despite of this, the precise mechanisms of antimicrobial action of chitosan and chitin are yet to be elucidated [10].

Recently the self-healing properties of chitosan have been investigated. A group of scientists completed a research on a self-healing coating which repairs small scratches after being exposed to sunlight. The sunlight causes the chitosan molecules to react with split oxetane rings (a combination of polyurethane paint, chitosan molecules, and a ring-shaped molecule) which in turn closes the split, essentially healing the surface [13].

Ghosh and Urban [14] reported the development of polyurethane networks that exhibit self-repairing characteristics upon exposure to ultraviolet light. The network consists of an oxetane-substituted chitosan precursor incorporated into two-component polyurethane. Upon mechanical damage of the network, four-member oxetane rings open to create two reactive ends. When exposed to ultraviolet light, chitosan chain scission occurs, which forms cross-links with the reactive oxetane ends, thus repairing the network. These materials are capable of repairing themselves and can be used in many coatings applications, ranging from transportation to packaging or fashion and biomedical industries [14].

In our study, an epoxy dye was converted to a self-healing coating by using chitosan. First homogeneous chitosan colloids were obtained within acid solutions, and sundry amounts of those were loaded to the polymer matrix. The glass substrates were coated with the polymer matrix, and different coated glasses were obtained. Characterizations of the samples were performed by Fourier Transform Infrared (FTIR) and scanning electron microscope (SEM). In addition, self-healing tests were performed for the samples scratched with a very thin pin, and the samples were analyzed by SEM periodically.

## 2. Experimental Procedures

**2.1. Preprocessing.** Chitosan (MW 150 kDa, degree of deacetylation 84.5%) was purchased from Sigma (St. Louis, USA). Different amounts of chitosan were dissolved completely in two different acetic acid solutions (1% and 3% by v/v) under stirring. Then, chitosan solutions were stirred in ultrasonic cleaner. Finally the solutions were stirred for 20 min in air by using magnetic balls, and homogeneous solutions were obtained. The percentages of chitosan and acid solution are presented in Table 1.

**2.2. Fabrication of Composite Materials.** Epoxy dye has been used as a composite matrix that is known as polyepoxide, a thermosetting copolymer formed from reaction of

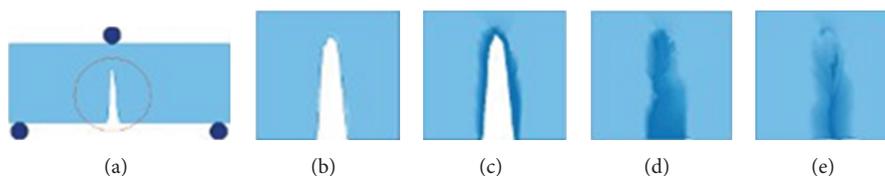


FIGURE 1: Basic principle of self-healing process. (a) induction of a crack by the mechanical loading, (b) view of the crack in details, (c) inducing a "mobile phase," (d) closure of the crack by the "mobile phase," and (e) immobilisation after healing [4].

TABLE 1: Sample codes and definitions.

Sample code	1	2	3	4	5	6	7
Acid	3%	3%	3%	3%	3%	1%	Pure dye
Chitosan in the composite	0.05%	0.5%	2.5%	5%	1.25%	1.25%	

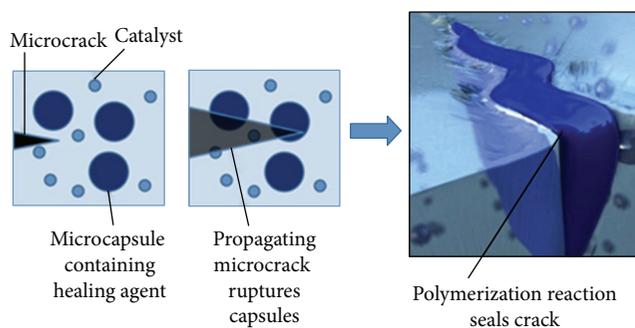


FIGURE 2: Schematic representation of crack propagation through microcapsule-embedded material [6].

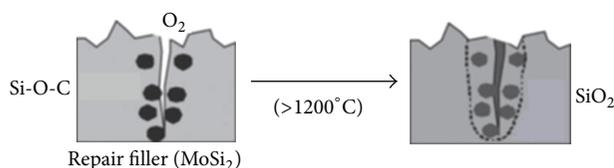


FIGURE 3: Self-healing of cracks in SiOC/MoSi<sub>2</sub> oxidation protection coatings on SiC ceramics [4].

an epoxide "resin" with polyamine "hardener." The resin consists of short-chain polymers with an epoxide group at either end. Epoxy resin is produced from a reaction between epichlorohydrin and bisphenol-A. The hardener consists of polyamine monomers, triethylenetetramine.

The obtained chitosan solutions were added to epoxy dye as a polymer matrix with different loading levels to see the concentration dependence of material's self-healing effect. Then glass substrates were coated with those polymer composites. Sample codes and descriptions are shown in Table 1. After coatings are obtained, they were dried for 24 hours at the room temperature; no more curing job has been done. After coated samples are obtained, they were scratched by a very thin pin to get thin splits/cracks.

All of the prepared samples were characterized by FTIR by which % transmittance and % absorbance as a function of wavelength curves can be obtained. FTIR (PerkinElmer)

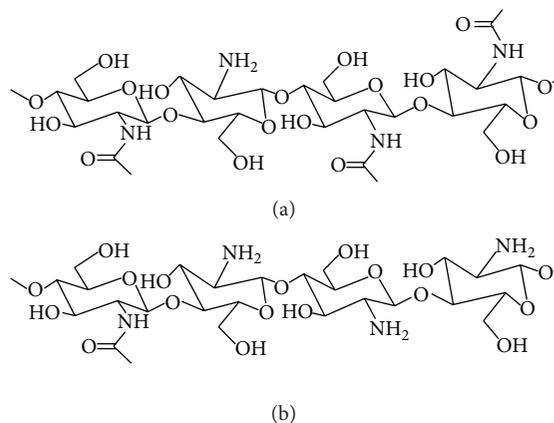


FIGURE 4: Structure of (a) chitin and (b) chitosan [11].

absorption spectra of the composites were taken over the range from 4000 to 400 cm<sup>-1</sup> at room temperature.

The microstructural cross-sectional areas of composites were examined by using a JEOL JMM 6060 SEM with an EDS attachment. Size factors and wettability properties were examined in the composites using SEM-EDS.

On the other hand, to see the self-healing property of chitosan, scratched coatings were analyzed with a Philips XL 30S FEG scanning electron microscope (SEM). SEM images of each sample were taken at different days, and improvements of self healing of the samples were investigated by the time.

### 3. Results and Discussions

Figure 5 depicts SEM micrographs of chitosan-reinforced epoxy dye composite coatings. Chitosan was incorporated into the coatings. Generally homogeneous composites were produced, and smooth surfaces were obtained. As it was mentioned earlier, two different acid solutions were used. Different acid rates will lead to different dissolution for chitosan. Acid rate is 3% for sample 5 and 1% for sample 6; the chitosan quantity was the same as 1.25%. As it can be seen from the Figure 5, there is not so much difference between

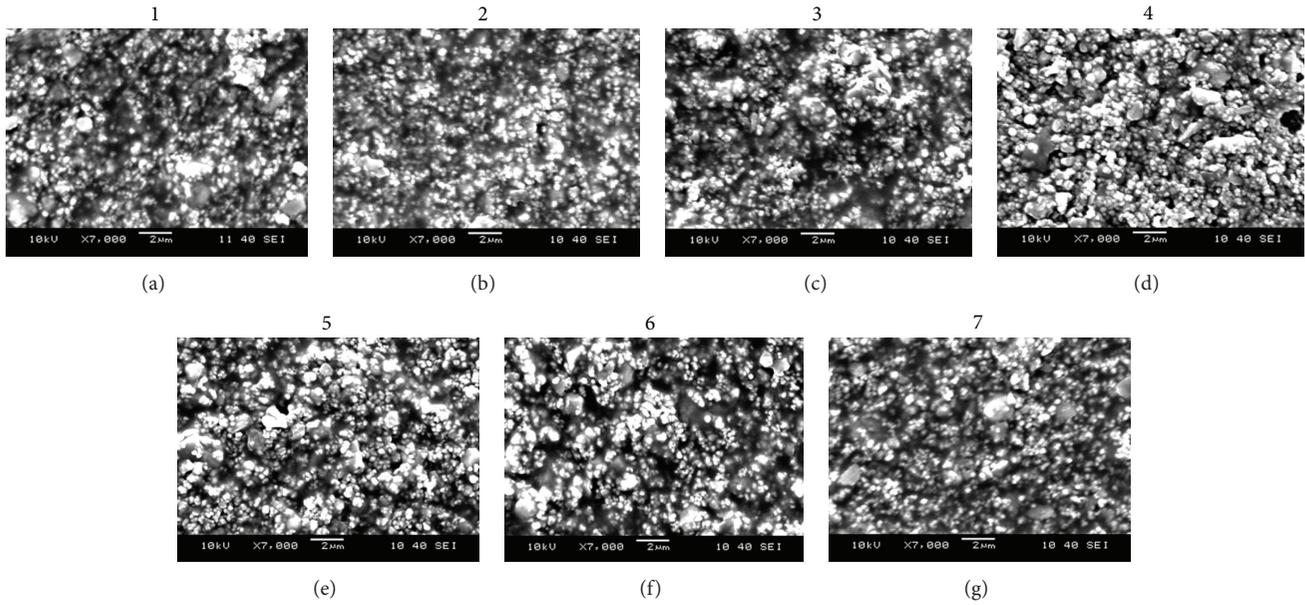


FIGURE 5: SEM micrographs of chitosan-reinforced composite coatings.

samples 5 and 6 in terms of surfaces. So it can be said that using different concentration acid solutions do not affect the morphology of the coatings.

Figure 6 shows FTIR analysis results of the samples. It can be seen from the figure that chitosan exhibits main characteristic bands of carbonyl ( $C=O-NHR$ ) and amine group ( $-NH_2$ ) at  $1450\text{ cm}^{-1}$ . However, this band can correspond to  $C-H$  bending from epoxy matrix. In the same way,  $CH_3COH$  group band can be observed at  $748\text{ cm}^{-1}$  related to the chitosan, but this may come from the epoxy also, because the characteristic peaks of epoxy indicate the formation of  $Si-O$ ,  $Si-O-Si$ , and  $Si-C$  at  $751$ ,  $1084$ , and  $1270\text{ cm}^{-1}$ , respectively. The broad band due to the stretching vibration of  $-NH_2$  and  $-OH$  group from chitosan can be observed at  $2950\text{ cm}^{-1}$ , but it may be related with epoxy alkyl groups ( $-CH_3$ ,  $-CH_2$ ) stretching [16, 17].

Both chitosan and epoxy are polymers, and they have organic bands. As epoxy dye is formed by different materials and having different bands, some of its bands can overlap with chitosan bands in the FTIR analysis. Therefore, sometimes it can be difficult to separate the peaks and their corresponding bands.

Figure 7 depicts SEM micrographs of scratched coatings. As mentioned earlier, the micrographs were taken from the samples in 0 min, 30 min, 7 days, 20 days, and 35 days after the scratching to watch the improvement on healing. From all chitosan-reinforced samples self-healing properties were obtained just after 30 min, and no more improvement has been found after that time. Therefore there were not any differences between the SEM micrographs taken 7, 20, and 35 days after scratching. Due to this they are not displayed in this paper.

Generally from all figures, self-healing property can be determined as branches of the tree and fill and seal the open

cracks. As, there is not any healing behaviour in sample 7: chitosan rate is 0.00% and it can be said that chitosan's self-healing effect appeared clearly with spanning the gap of a thin scratch. Epoxy polymer composites at room temperature far below the glass transition temperature tried to diffuse across those gaps. It is clear if this can be a cross-linked network of epoxy composites working by the agency of chitosan. Otherwise sample-7 also should have that kind of healing property. This is important for the possible diffusion processes. On the other hand, the distinctions on the crack tips were measured and written on the micrographs, and the self-healing may not be determined according to those values. Because as mentioned previously, branches were developed like the arms for a wound heal. That is to say that self-healing mechanism might be operated with those branches.

The self-healing results are in agreement with Kessler et al. When they allowed the specimens to heal, partially cured poly (DCPD-dicyclopentadiene), strands were observed bridging the crack behind the crack tip. Present on the surface are several strands of poly (DCPD) that bridged the two surfaces of the delamination before ultimately rupturing and collapsing in a folded film on the fracture surface [18]. On the other hand, as it is explained in detail in [19], the healing mechanism is similar to molecular interdiffusion method. This method is that when two pieces of the same polymer are brought into contact at a temperature, the interface gradually disappears and the mechanical strength at the polymer-polymer interface increases as the crack heals due to molecular diffusion across the interface. Visual healing of the fracture surfaces was found to occur before a significant recovery in strength was achieved, with the interdiffusion of numerous chain segments being reported as the most likely healing mechanism [19]. This agrees with our results that the thin cracks were healed better than the wide ones. Such that,

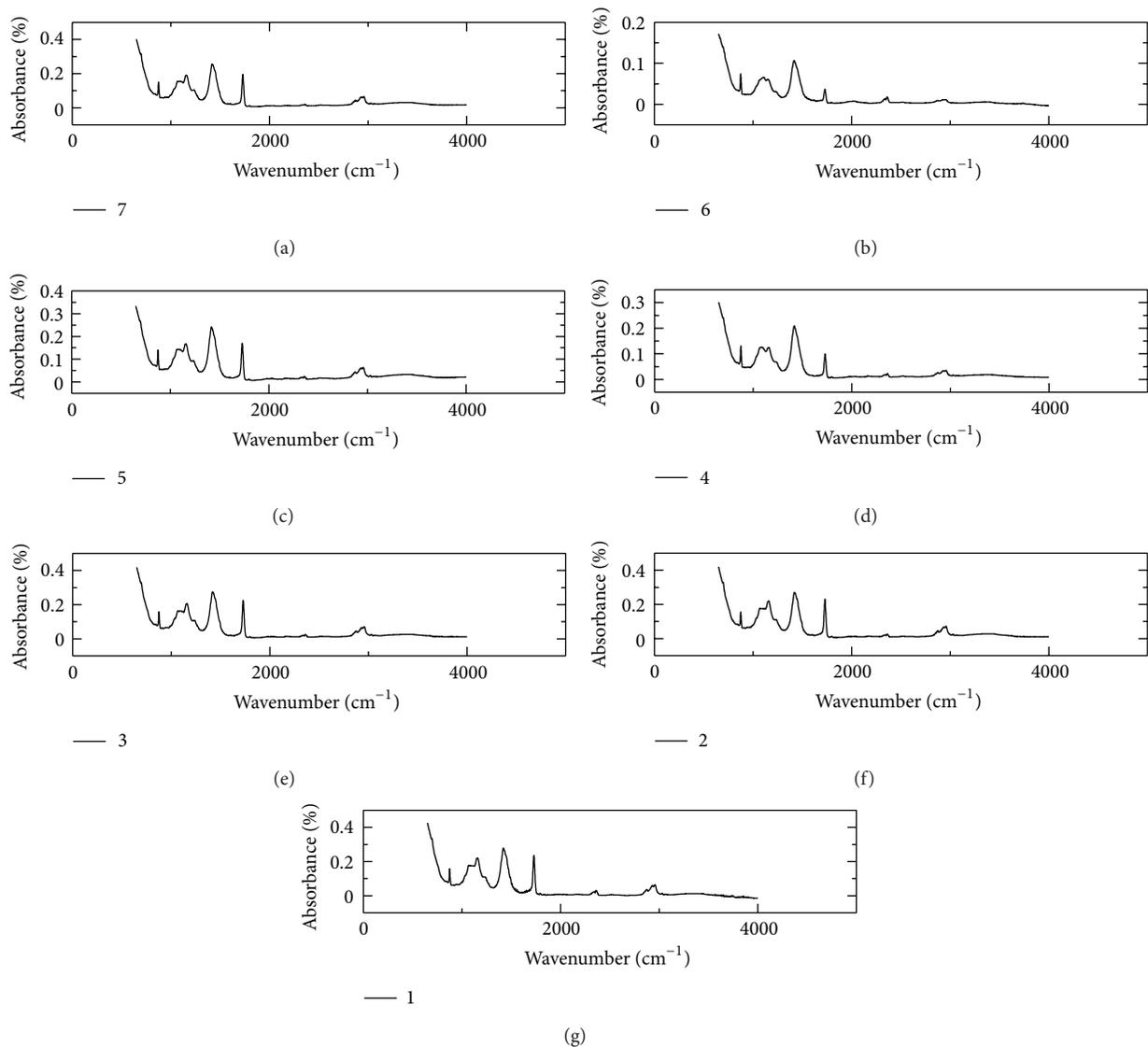


FIGURE 6: FTIR analysis results of chitosan-reinforced composite coatings.

there are much more branches in the samples of 3 and 6 than sample 4 (Figure 7).

Additionally, the mechanism of the self-healing is explained by Wool [20] as the healing of polymer-polymer interfaces. This can occur due to softening of the surface layer below glass transition temperature. They treated the surface layer softening as a gradient rigidity percolation issue. They obtained the healing after cracks are formed in the coating revealing the presence of excess healing fluid on the coating surface. The optical image of self-healing structure shown in their article is very similar to our study [20].

Wool and O'Connor [21] suggested a five-stage model to explain the crack healing process in terms of surface rearrangement, surface approach, wetting, diffusion, and randomization [19]. When it is compared with the SEM photographs, the similarity can be seen. Some researches [15, 22] also presented a microscopic theory for the diffusion and

randomization stages. They observed that the development of the mechanical strength during the crack healing process of glassy polymers is related to interdiffusion of the molecular chains and subsequent formation of molecular entanglements. The research carried out by Wool and O'Connor [23] and McGarel and Wool [24] confirmed that the phenomena of crack healing in the thermoplastics occur most effectively at or above the  $T_g$  of these materials [19]. However, the self-healing study in this article was obtained in the room temperature.

As no differences obtained from the morphological analysis of 30 min, 7 days, 20 days, and 35 days after scratching, it can be said that the self-healing occurs in the first 30 minutes in those coatings. This agrees with the literature of [18, 25] that the self-healing behaviours were obtained in the first 30–60 minutes. However, in [26] self-healing was investigated in 1 day and 2 days.

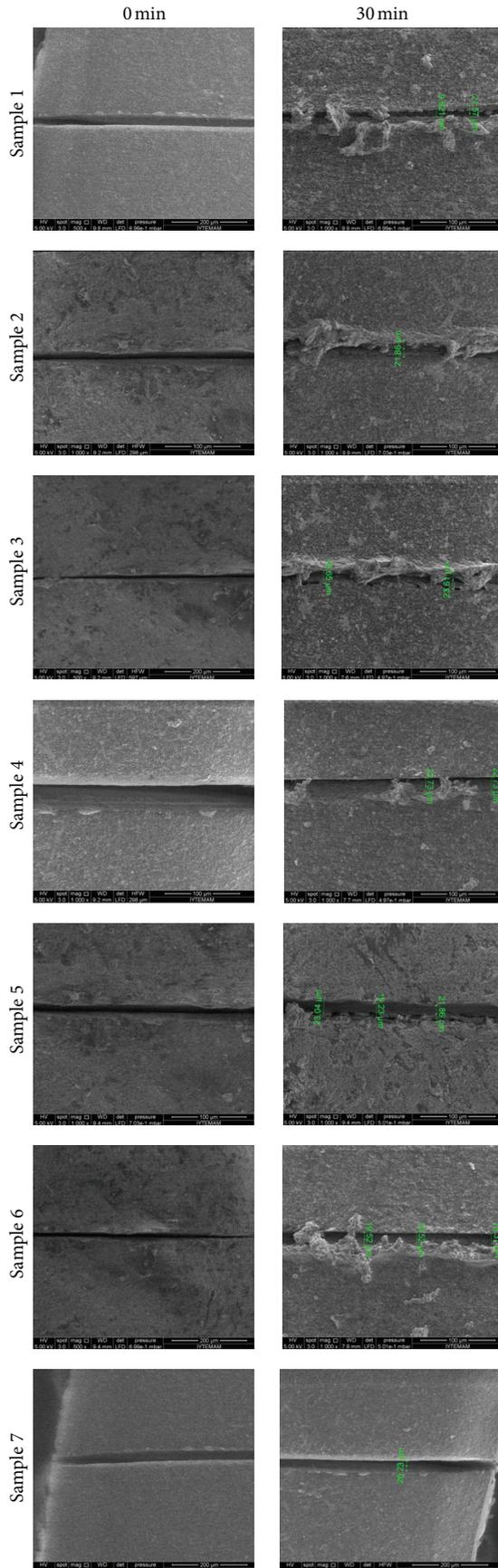


FIGURE 7: Self-healing of chitosan-reinforced composite coatings.

## 4. Conclusions

The glass substrates were coated with the epoxy dye loaded with different acid dissolved chitosan. The prepared samples were characterized by FTIR and SEM-EDS. EDS and FTIR analysis results were similar for all samples, as all samples have the same elements with different concentrations.

Self-healing test was performed, in this respect, after scratching the samples with a very thin pin, and they were analyzed by SEM periodically. Self-healing property was determined as putting forth branches like a tree, and splits are packed with the composite. Chitosan's self-healing effect appeared clearly. For comparing the samples by means of self-healing, measuring the distances on the top of the splits did not help. However, it needs to look the braches numbers, shapes, orders, or thicknesses to evaluate any self-healing occurrence. On the other hand, there is no big difference in the SEM analysis done by the time. Self-healing occurs in the first 30 minutes.

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