Experimental investigation on self-activated healing performance of thermosetting polyurethane prepared by tungsten (VI) chloride catalyst

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Abstract

Polymers and polymeric composites are widely used for various applications due to their outstanding and wide range of properties. Polyurethanes, existing in different types, are novel and versatile polymers with excellent mechanical properties. Thermosetting polyurethane resins are among the most widely used polyurethanes wherein their manufacturing and developing have been introduced during the last few years. Self-healing materials have been inspired by biological systems in which damages provoke healing responses. It is almost cost-effective to use self-healing materials in commercial applications. This study investigates a novel self-activated approach in thermosetting polyurethane resins. A tungsten (VI) chloride (WCl₆) catalyst, a co-activator (phenylacetylene) and a dissolution agent (nonylphenol) were used for the onset of ring-opening metathesis polymerization of dicyclopentadiene. Here different percentages of a catalyst in polyurethane resins were used, the impacts of which on fracture toughness and healing efficiency were also studied. To examine healing efficiency, samples with tapered double-cantilever beam geometry were prepared and using the self-activated method, the development of thermosetting polyurethane self-healing was investigated. The results showed that the concentration of catalyst affects the basic properties of the material and healing efficiency of the composite. The highest healing efficiency of 97% was obtained for a 3 wt% catalyst.

1. Introduction

Self-healing materials are composed of some smart recently-developed materials capable of spontaneous self-healing by imitating the self-healing capability characteristic of most living organisms. Spontaneous self-healing is a requirement for the support and continuation of life. This capability provides for an appropriate idea in manufacturing and productivity of this technology in various industries [1]. Self-healing capability increases the life span of composite materials and opens up a promising perspective for the applications of these materials. Composite materials, especially polymer-based composites are sensitive to damages in the form of cracks since they can result in erosion and degradation of mechanical properties of the material. Furthermore, these cracks are sometimes so tiny that to identify and repair them is practically impossible [2]. Self-healing materials have been inspired by many biological models in which damages cause an initiation of self-healing processes [3].

Military, aerospace, sea transportation and other big industries such as oil and petrochemical industries require light composite pressure vessels. These materials are employed in satellite carriers, various types of airplanes and launchers in aviation industries. Self-healing materials are, in fact, composites capable of spontaneous self-healing of the cracks resulting from possible pressures. There are several different techniques for achieving self-healing properties in polymeric materials. Some of these techniques include the storage of healing agents by using microcapsules’ or hollow glass fibers containing healing agents [4], applications of
microvascular networks for presentation and delivery of healing agents in constructions [5], and applications of reversible cross-linking bondings [6]. Self-healing occurs when the monomer is released and combined with the catalyst phase embedded in the polymer matrix. Materials with polymeric self-healing compositions are ideal for long-term applications since micro-cracks inevitably created during usage and could be repaired without any manual interference [7]. Bao et al [8] employed nitrogen-coordinated boroxines to manufacture polymer composites capable of self-healing and recyclability and enriched mechanical properties. Most studies on self-healing polymers have been done on epoxy resins. Balazs et al [9] showed that nanoparticles in the polymeric matrix can be absorbed by the damaged spot due to the gravitational force existing between the nanoparticles and the damaged surface. Moll et al [10], studied the self-healing capability of woven glass/epoxy composites using microcapsules containing healing agent and catalyst. Sander et al [11] worked on polypropylene-polyglycerol sebacate (glycerol sebacate) composites with electrical conductivity produced by the free synthesis of the solvent and evaluated its self-healing capability. Keller et al [12] developed self-healing capability in elastomeric polydimethylsiloxane, under torsional fatigue and examined its efficiency. Wilson et al [13] utilized microcapsules containing dicyclopentadiene (DCPD) as the healing agent and wax micro balls containing Grubbs’ catalyst in epoxy vinyl ester matrix. Stojanovic et al [14] could prepare a self-healing acrylic thermoplastic material using a solution of the healing agent DCPD in dimethylformamide (DMF) and a solution of Grubbs’ catalyst in dichloromethane (DCM). Brown et al [12] investigated the fracture of self-healing polymer composites. They studied aspects of fracture mechanics, important for the development and optimization of self-healing materials. They examined epoxy polymer by injecting DCPD monomer and Grubbs’ catalyst mixture on the crack plane as well as microcapsules containing DCPD.

Most self-healing systems require a catalyst to complete a healing cycle. One of the catalysts for the DCPD system, reported in many studies [2, 13], is the Grubbs’ catalyst in which the healing material in the vicinity of the catalyst performs ring-opening metathesis polymerization (ROMP). Moll et al [15] showed a self-healing efficiency of 67% of the samples, mixing with microcapsules containing DCPD and wax-protected Grubbs’ catalyst. However, due to the scarcity and cost of Grubbs’ catalysts, in most researches, tungsten (VI) chloride catalyst (WCl₆) has been employed. Ghorbanzade et al [16] scrutinized self-healing capability in epoxy polymer samples containing carbon nanotubes (CNTs) and unfilled and CNT-filled epoxy. Using the DCPD healing agent and tungsten (VI) chloride catalyst (WCl₆), they evaluated the effects of self-healing. Employing microcapsules containing exo-DCPD and tungsten (VI) chloride catalyst (WCl₆), Jason et al [17] could examine the effects of self-healing on epoxy. Haiyan et al [18] studied epoxy resin-based self-healing using WCl₆ and DCPD healing agent. More convenient to produce and more industry-friendly, WCl₆ offers more advantageous properties than Grubbs’ catalyst. With a melting point of Tₘ = 275 °C, it has a higher temperature than Tₘ = 153 °C that of the Grubbs’ catalyst. Moreover, this material is potentially more capable of industrial production and business applications than Grubbs’ catalyst. WCl₆, alone, is not an active catalyst for self-healing activities and requires a co-activator called phenylacetylene and a dissolution agent called nonylphenol [17, 19].

Self-healing effects have been accomplished by using the DCPD system in various samples. The first method is the self-activated method, the sample containing a catalyst, there is no healing agent into the matrix and semi-manual healing is carried out by injecting the DCPD monomer mixture into the crack plane. The second method is the self-contained or in situ method, the sample containing both catalyst and microencapsulated DCPD in the matrix phase. In this case, healing agent delivery is achieved automatically through a fracture of healing agent-carrying microcapsules placed in the matrix. The third method is the manual method, there is no healing agent and catalyst into the matrix phase and manual healing is carried out by injecting both DCPD monomer mixture and catalyst into the crack plane [2, 17, 18].

Most self-healing studies have been carried out on epoxy polymers, and polyurethane polymers have rarely been subject to investigations. At present, polyurethanes (PUR) are perhaps the most diverse type of known plastics. They are of a very wide range of density, hardness and toughness allowing the production of different types of tensile fibers, tough elastomers and flexible light and tough polyurethane foams. Polyurethane materials are widely used in coatings, adhesives, furniture, textile fibers, artificial leather, etc [19]. The studies have mainly concerned colors, coatings and anti-corrosion investigations [20, 21]. Li et al [22] investigated mechanical performance and self-healing achieved by the induction of microwaves in thermoplastic polyurethane composites reinforced by Graphene- CNT. Jadhav et al [23] created microcapsules with phenol-formaldehyde resin shells and kernels containing drying and corrosion resistant agents and linseed oil. They observed that the roughness and toughness of the shell surface to provide better compatibility with the polymer matrix. Gosh and Urban produced polyurethane networks capable of self-healing as soon as they were exposed to ultraviolet light [24]. Xu et al [25] produced a mixture of thermoplastic polyurethane (TPU) and polycaprolactone (PCL) as a shape memory matrix with embedded multiwalled carbon nanotubes. They examined the performance, self-healing efficiency and shape recovery of resulting polymer blend. They stated that self-healing properties and shape memory could be appropriate options for various applications. By decreasing graphene oxide content in the matrix of waterborne polyurethane, Wan et al [26] produced self-healing waterborne polyurethane/reduced...
Zhiguo et al \cite{27} tried to synthesize biodegradable body temperature-responsive shape memory polyurethanes, with self-healing function, from different chain extenders and polycarbonate diol, which exhibited a good memory behavior for medical applications.

Here we investigated a self-healing system and its development on thermosetting polyurethane resins with tungsten (VI) chloride (WCl$_6$) catalyst, phenylacetylene co-activator, and nonylphenol dissolution agent. Different percentages of the catalyst in polyurethane resins were used and the effects of which on fracture...
toughness and healing efficiency were also studied. To examine healing efficiency, samples with tapered double-cantilever beam geometry were prepared and using both self-activated and manual methods, the impacts of self-healing on thermosetting polyurethane were investigated. Moreover, the effect of catalyst concentration was examined on the material’s basic properties and healing efficiency of composites.

2. Experimental processes

2.1. Materials
The polyurethane resin, two parts of A and B, TASK 4, was purchased from Smooth-on (USA) company and used as received. This type of polyurethane system has a lot of applications such as making prototype and architectural models, model toys, durable miniatures, ultra-thin mechanical parts, and special effect props. The polyurethane samples (TASK 4) were formed using equal quantities of part A and B, the pot life of this system is about 20 min. The tungsten (VI) chloride (WCl₆) catalyst was purchased from Sigma-Aldrich. The DCDP (Merck, Germany) as a healing agent and nonylphenol (Sigma-Aldrich, Germany) as a dissolution agent and phenylacetylene (Merck, China) as a co-activator were used. All of the aforementioned materials were without further purification.

2.2. Sample preparation
The fracture of samples was accomplished using the tapered double-cantilever beam (TDCB) model and the geometry of which was adopted by Brown et al [2] to study and evaluate healing efficiency since the tapered geometry fracture toughness measurement is independent of crack length. TDCB geometry is shown in figure 1.

Fracture toughness is calculated as

$$K_{IC} = \alpha P_C$$ (1)

Where $\alpha$ is a scaling parameter dependent on the sample’s geometry with the value set to $11.2 \times 10^3 \text{ m}^{-3/2}$ for the considered geometry. Also, $P_C$ is the critical fracture force. The healing efficiency is now calculated as follows.
Where, $P_{C_{\text{virgin}}}$ is the virgin critical fracture force (before healing) and $P_{C_{\text{healed}}}$ is the critical fracture force after healing. To ensure the growth of the crack in the same direction with the sample’s central line, two grooves have been devised at both sides in the TDCB geometry.

To manufacture a TDCB silicone mold, first, a metal sample was prepared using laser cutting equipment. Then, using a CNC milling machine, channels were created on both sides of the sample’s central line. Then, smooth finishing on the surface and desired thickness were achieved using grinding with extreme accuracy and precision. Finally, to prepare a 2-piece mold, reverse molding of the sample was accomplished using silicone rubber (figure 2). Samples were tested under the control displacement rate. Using pin loading and fixtures specially designed for the purpose, the samples were tested in mode-I under 0.3 mm min$^{-1}$ displacement rate with the STM-20 tensile testing machine (figure 3).
2.3. Composite preparation

To examine self-healing in the said polyurethane resin, four different tungsten (VI) chloride (WCl₆) catalyst weight percentages, (1, 3, 5 and 7 wt%) were used. Furthermore, to compare fracture cross-section, three neat samples were prepared for each weight percentage to allow for repeatability. Thus, a weighed amount of part A

![Figure 5. Crack propagation with a tensile test using pin-loading fixture after healing.](image)

![Figure 6. Healing efficiency diagram for different tungsten (VI) chloride (WCl₆) catalyst concentrations.](image)

| WCl₆ concentration wt% | Virgin | Healed | Healing efficiency % |
|------------------------|--------|--------|----------------------|
| 0                      | 2.51   | —      | —                    |
| 1                      | 2.29   | 1.77   | 77.9                 |
| 3                      | 2.24   | 2.16   | 97.1                 |
| 5                      | 2.09   | 1.73   | 83.5                 |
| 7                      | 1.80   | 1.56   | 84.5                 |
polyurethane resin, poured into a container, was kept in the desiccator for 10 min to carry out initial degassing. Then, weighed amounts of WCl₆ catalyst were added based on the required weight percentage, mixed up manually and again kept in the desiccator for 15 min for degassing. Part B was polyurethane resin, afterward, added to the mixture. After final degassing, the mixture was poured into the silicone mold and left at ambient temperature for 7 days for final curing and obtaining mechanical properties.
All tests were carried out using tensile test equipment at ambient temperature. To begin the testing process, a pre-crack was first made at the edge of the notch using a razor blade. Then, using constant displacement rate, load-displacement values were recorded and its curve was plotted, while loading continued for a short time after the propagation of the crack. The amount of load dropped considerably at the moment of crack propagation, which is known as virgin critical fracture load value $P_{C,\text{virgin}}$. The loading was then stopped and using the Hamilton syringe, about 100 μl of healing solution was injected into the crack plane. The healing solution, composed of 1g DCDP and 12 mg nonylphenol and 6 mg phenylacetylene, had previously been prepared. Then fractured two pieces were joined to each other (by the reverse movement of the tensile testing machine), and the samples were kept stationary for 48 h at ambient temperature to allow for healing. After healing, the samples were tested again in the same way with the difference that this time, no pre-cracks were made in the edges of sample notches. Afterward, the curve for load-displacement was again plotted and healed critical fracture load value $P_{C,\text{healed}}$ was obtained. The healing efficiency was calculated based on equation (2). All steps were carried out for the different catalyst weight percentages with the repeatability of three samples. The steps mentioned above are for the self-activated method.

In the manual method, firstly the neat polyurethane sample with TDCB geometry was brought under loading in the direction of the crack propagation in the same way as the self-activated method, and after virgin critical load value $P_{C,\text{virgin}}$ was obtained, firstly, tungsten (VI) chloride (WCl₆) catalyst and then healing agent were injected on to the crack plane. The samples were then left under ambient conditions for 48 h to allow for the healing process. Then, the samples were again changed in the pre-test similar conditions, so that post-healing critical load value could be obtained.

The samples were named in this way: as an example, in T4SA-TD-3W-B1 from left to right, T4 is manufacturer material code (TASK 4), SA stands for self-activated, TD means TDCB geometry, 3W refers to 3 catalyst weight percentages, B signifies before healing (A signifies after healing) and number 1 shows number of repeatability of samples and tests.

### 2.4. Morphological characterization preparation

To examine the fracture plane after healing, elemental investigation of the healing process and also impacts of catalyst on fracture morphology, all polyurethane neat samples, those with 1% to 7% weight catalysts (self-activated method)
and those with manual method samples were investigated via field emission scanning electron microscope (FESEM, MIRA3 TESCAN). Afterward, to produce conductivity on the surfaces of the samples and to avoid static electric charge accumulation during electron irradiation, all samples were sputtered with gold using a sputter coater. All images have been taken using the FESEM device operating at 15 kV. A back-scattered electron (BSE) detector was used to differentiate the WCl₆ catalyst from the samples’ cross-section. Also, an EDS device was coupling to FESEM used in an investigation of quantitative and elemental values.

3. Results and discussions

For the self-activated method, The Crack propagation test, as well as healing processes, were carried out for different catalyst weight percentages with three times repeatability, and load-displacement values, as well as critical load value at the moment of crack propagation, were obtained. In figures 4(a) and (b) before healing and after healing load-displacement curves with three times repeatability are plotted for samples containing 3 wt% catalyst, respectively. Figure 5 shows the sample under test after the healing process.

The virgin and healed fracture toughness values were obtained via finding the average for repeatability and calculated using equation (1) for the neat specimens and four different weight percentages samples. The
healing efficiency is also presented in table (1) as well as the curve in figure 6 shows changes for efficiency. As it is shown, the highest healing efficiency of 97.1% was obtained for 3 wt% tungsten (VI) chloride ($WCl_6$) catalyst, while the lowest healing efficiency of 77.9% was obtained for 1 wt% catalyst concentration. It seems this is because of the existence of the greater amount of catalyst in the resin matrix due to the catalyst increase from 1% wt to 3%wt, leading to a greater polymerization reaction of the catalyst with the healing agent, allowing for a higher healing efficiency. It is true that by using higher weight percentages of a catalyst such as 5%wt and 7%wt, there would be a greater amount of catalyst in the resin matrix; however, it does not always result in higher

Figure 11. Cut off part of the TDCB sample after healing for the FESEM analysis.

Figure 12. Crack propagation path for the self-activated method, (a) Neat polyurethane, (b) 1 wt% $WCl_6$ concentration, (c) 3 wt% $WCl_6$ concentration, (d) 5 wt% $WCl_6$ concentration, (e) 7 wt% $WCl_6$ concentration.
healing efficiencies, since in the first place, pot life time is shortened, so there could be a shorter time for deoxidization, and in the second place, increasing the catalyst agglomeration rate might account for reduction in healing efficiency. Similar behavior was observed in [18], in which optimal healing efficiency at a certain catalyst weight percentage starts to reduce after adding more catalyst.

As it is seen, adding the catalyst to polyurethane resin decreases fracture toughness, considering the curve of which was given in figure 7. The load-displacement curves for before and after healing for all 1%, 3%, 5%, and 7% tungsten (VI) chloride (WCl₆) catalyst weight percentages are given in figure 8.

Sensitivity analysis and correlation coefficient for the self-activated method and for all data obtained from repeatability were carried out using SPSS Statistic software that the results of which are shown in table 2. As indicated in table 2, the P-Value or Sig. (2-tailed) for the relation between the catalyst’s concentration to fracture toughness before healing and healing efficiency is smaller than 0.05 which is actually a confirmation of the meaningful relationship between catalyst weight percentage and healing efficiency. This sensitivity analysis also supports the results obtained in table 1.

The crack propagation test, as well as the healing process with the same conditions as the self-activated method, were also carried out for the manual method; the before and after healing load-displacement curves of which are plotted in figure 9. The healing efficiency of 63.6% was obtained from this method which is 18% lower
than the lowest value obtained in the self-activated method. The self-activated method is better than the manual method in healing efficiency because of better dispersion of catalyst into the crack plane.

According to the experimental tests and resin manufacturer (Smooth-on Co.) instructions, the pot-life time for the neat resin is about 20 min. However, the addition of 1% and 3% weight catalyst, increased this time to about 50 and 35 min, respectively. Yet, the addition of 3% and 7% weight catalyst, decreased this time to about 15 and 7 min, respectively. Samples were made for the weight percentages higher than 7% weight catalyst, but the pot-life time, then significantly decreased (about 1 to 2 min), therefore there was not enough time for casting resin into the mold and the final product was very porous as shown in figure 10(a). The pot-life (min) variations of polyurethane versus WCl$_6$ concentration were shown in figure 10(b). The reason behind this issue is that there is very little change in the viscosity of the resin for 1% wt catalyst, while for higher weight percentages, the resin viscosity increases significantly causing reductions in pot life time [28]. On the other hand, because the composition of the two parts of polyurethane resin tested is thermogenic, by increasing the weight percentage of tungsten (VI) chloride (WCl$_6$) catalyst, the rate of heat distribution in the resin is increased due to the presence of the catalyst. The literature survey shows that the temperature is the most important parameter in pot life time or gelation of resins [28–30]. Therefore, the greater the amount of the catalyst, the faster and more uniform distribution of temperature in the resin, therefore less gelation time.

Figure 14. The FESEM Images from the cross-section of the TDCB samples after healing in self-activated method, (a) Neat polyurethane, (b) 3 wt% WCl$_6$ concentration, (c) 5 wt% WCl$_6$ concentration, (d) 7 wt% WCl$_6$ concentration.
To take FESEM images, all polyurethane neat samples, those with 1% to 7% weight catalysts (self-activated method) and those with manual method samples were cut through about 20 mm as shown in figure 11.

Figure 15. The FESEM image of neat polyurethane, after a fracture.

Figure 16. The EDS Analysis of neat polyurethane at zone A in figure 15.

To take FESEM images, all polyurethane neat samples, those with 1% to 7% weight catalysts (self-activated method) and those with manual method samples were cut through about 20 mm as shown in figure 11.
As shown in figure 12, in the self-activated method, crack propagation started at the beginning of the sample (upper part) in which the primary crack is seen, and secondary cracks have been created due to the existence of tungsten (VI) chloride (WCl₆) catalyst which has scattered secondary cracks.

Figure 13 shows the backscattering analysis of polyurethane containing 1% to 7% catalyst weight percentages in the self-activated method. As indicated, by the signs in this figure, lighter spots are particles of tungsten (VI) chloride (WCl₆) catalyst, being of a lighter color and more easily seen since they contain heavier elements than the elements in the matrix and they are dispersed in proportion to the rise in their weight percentage of the catalyst.

The FESEM images of neat polyurethane and those healed with various catalyst weight percentage in the self-activated method are demonstrated in figure 14. As it is obvious in figure 14(a), the fracture plane of pure polyurethane has approximately smooth regions with the cleavage pattern which are related to the cracks propagation. In return, the presence of the catalyst within the polyurethane structure changes the fracture pattern significantly. As seen in figure 14(b), for 3 wt% catalyst, the fracture pattern has become more uneven and irregular with signs of micro cracks and show quasi cleavage pattern. In detail, the existence of the catalyst together with the healing agent causes the cracks to be healed. Moreover, catalyst dispersion resulted in the branching of the cracks into some micro-cracks after the healing test. The branched regions are marked in figure 14(b). Another point is that because of the branching mechanism, the newly initiated micro-cracks are propagated in various directions and this resulted in new fracture planes with different levels. So, the fracture

| Elt | Int    | K     | Kr    | W%   | A%    | ZAF  | Pk/Bg | LConf | HConf |
|-----|--------|-------|-------|------|-------|------|-------|-------|-------|
| C   | 333.6  | 0.8625| 0.4232| 58.12| 63.77 | 0.7281| 339.37| 57.17  | 59.07  |
| N   | 10.2   | 0.0370| 0.0182| 14.78| 13.91 | 0.1229| 10.54 | 13.40  | 16.16  |
| O   | 79.3   | 0.1004| 0.0493| 27.09| 22.32 | 0.1819| 110.68| 26.19  | 28.00  |
| Total| 1.0000 | 0.4907| 100.00| 100.00|       |       |       |       |       |

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plane has more roughness and uneven fracture planes with respect to the pure polyurethane and gets a quasi-cleavage pattern. This state becomes more intense by increasing the catalyst weight percentage. As is clear in figures 14(c)–(d), the surface roughness and the new micro-cracks are more impressive, especially for 7 wt% catalyst. The specified arrows in figures 14(c)–(d), illustrate the catalysts and the new micro-cracks initiated around it.

Table 4. Quantitative results of the neat polyurethane at zone B in figure 17.

| Elt | Int   | K      | Kr      | W% | A%  | ZAF   | Pk/Bg | LConf | HConf |
|-----|-------|--------|---------|-----|-----|-------|-------|-------|-------|
| C   | 306.8 | 0.7781 | 0.3600  | 62.15 | 72.65 | 0.5792 | 297.85 | 61.09 | 63.21 |
| N   | 8.7   | 0.0308 | 0.0142  | 11.91 | 11.94 | 0.1195 | 7.94   | 10.70 | 13.11 |
| O   | 52.1  | 0.0647 | 0.0299  | 16.08 | 14.11 | 0.1862 | 41.39  | 15.41 | 16.74 |
| Cl  | 49.8  | 0.0305 | 0.0141  | 1.73  | 0.68 | 0.8173 | 7.34   | 1.65  | 1.80  |
| W   | 5.8   | 0.0959 | 0.0444  | 8.14  | 0.62 | 0.5452 | 2.77   | 7.13  | 9.14  |
| Total | 1.0000 | 0.4627 | 100.00  | 100.00 | 100.00 |

Figure 18. The EDS Analysis of neat polyurethane at zone B in figure 17.

Figure 19. The FESEM image of fractured samples, (a) neat polyurethane, (b) polyurethane containing 3 wt% WCl₆ concentration after healing, (c) polyurethane containing 7 wt% WCl₆ concentration after healing.
Figure 15 shows images from a cross-section after the fracture of neat polyurethane with TDCB geometry. In the center of the image, the crack propagated under tensile test can be seen and the even fracture plane is confined by micro cracks. The EDS analysis of zone A of this image is given in figure 16 and its quantitative values and elemental analysis are presented in table 3.

Figure 17 shows the fracture cross-section after healing for polyurethane containing 3 wt% tungsten (VI) chloride (WCl₆) catalyst in the self-activated method. A visual comparison of this image with the image of figure 15 evidently shows the difference between the visual pattern and the fracture plane after healing, which in the image of figure 17, the surface plane healed by the polymerization of the chemical reaction of the healing agent with the catalyst placed in the resin is visible. Furthermore, in the shown part by a yellow arrow, the crack is propagated due to loading after healing. The EDS analysis in zone B, presented in figure 18 that demonstrates the existence of healing. The EDS analysis shows that DCDP exists on the surface of the sample and is fully polymerized and combined with the catalyst.

Moreover, the comparison between the EDS analysis in figure 18 and the given EDS analysis in reference [16] clearly validate the polymerization of the healing agent with the catalyst.

Quantitative values and elemental analysis of zone B of image 17 are presented in table 4. Comparison of tables 3 and 4 shows the existence of tungsten and chlorine elements (related to catalyst). In figure 19, the fracture planes for neat polyurethane and polyurethane containing a catalyst at a magnification of 20kx are presented in the comparison of visual pattern. Figure 19(a) belongs to neat polyurethane, 19b belongs to polyurethane containing 3 wt% WCl₆ concentration after healing and 19c belongs to polyurethane containing 7 wt% WCl₆ concentration after healing for the self-activated method. By comparing them, we can notice evidence of changes in the appearance of the polymeric chains in the neat plane and those in the healed plane due to polymerization of DCDP with the catalyst. The indicated arrow in image figure 19(b) indicates a propagated micro-crack after healing as well as loading.

Figure 20 illustrates after healing fracture cross-section for the manual method. In figure 20(b) which is the magnified part of region C in figure 20(a), the upper right of the image is the part healed due to the polymerization of DCDP with the catalyst dispersed within the crack plane and the lower left is a part of the neat polyurethane sample lacking DCDP polymerization due to the inappropriate catalyst dispersion and its absence in this part of crack plane. As indicated by FESEM images, inappropriate catalyst dispersion in the crack plane accounts for the lower healing efficiency of the manual method compared to the self-activated method. It is because the catalyst is in the form of powder, so for an appropriate dispersion, it cannot appropriately penetrate through the crack. However, in the self-activated method, the catalyst is evenly and properly dispersed within the whole matrix and consequently the crack plane. Therefore, polymerization occurs and the crack heals sufficiently well as soon as DCDP comes in contact with the catalyst.
4. Conclusions

In this paper, we synthesized self-healing polyurethane composites with the ability to heal cracks using both the self-activated and manual methods. We used tungsten (VI) chloride (WCl₆) as the catalyst in the matrix with four different weight percentages to evaluate the effect of weight percentages of WCl₆ on healing efficiency. We used tapered double-cantilever beam (TDCB) geometry to evaluate healing efficiency. We found that the maximum healing efficiency is about 97% with 3 weight percentages of catalyst concentrations in the self-activated method and about 63% in the manual method. We also found that we couldn’t synthesize self-healing polyurethane composites with higher than 7wt% of catalyst concentrations. Furthermore, we noticed that an increase in the tungsten (VI) chloride (WCl₆) content in the matrix reduces the fracture toughness of samples. The backscattering FESEM images showed that the dispersion of catalyst into the matrix is appropriate. Moreover, we showed that because of better dispersion of catalyst into the crack plane, the self-activated method is better than the manual method in healing efficiency. The FESEM micrographs and EDS analysis showed that DCDP is completely polymerized with WCl₆ approving successful healing of the samples.

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