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## Development studies of silver nanocomposite based sensors for acid penetration

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#### ABSTRACT

Polymer composites are widely used to store liquid chemicals. Recently, monitoring their structural health has attracted a lot of attention. The geometry of nanomaterial in polymer composites plays an important role in affecting the penetration progress, thus altering the durability of polymer composite. In this study, the silver nanocomposite-based structural health monitoring (SHM) sensors were designed to detect the progress of chemical diffusion and material degradation as a function of time. A comparison between the silver nanowire (AgNW) sensor and silver nanoparticle (AgNP) sensors was used to study the concentration and geometry of silver nanomaterial's effect on acid penetration. It appeared that the structural health monitoring sensors' resistance decrease in three stages with the diffusion time increase. Moreover, with the volume percentage of silver nanomaterial increase, the response time decrease. And the AgNW based sensors have shown a shorter response time. The conductive network that nanofillers formed in the sensors was studied its effect on the ion diffusion process. Modeling work based on Fick's second law was conducted using MATLAB to study the geometry effect of silver nanoparticle, silver nanoparticle aggregate, and silver nanowire on acid penetration progress. Copyright © 2022 Elsevier Ltd. All rights reserved.

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#### 1. Introduction

Polymeric composites are widely used as essential parts of numerous applications in our daily life, like the airplane wing, wind blade, chemical-resistance layer in pipeline and joints, etc [1–5]. Meanwhile, the demands on the safety and sustainability of these applications have increased. For aggressive chemical accidents, leaking is one of the major reasons, and the lifetime threatened hazardous can be caused [6-8]. Hence, the preventative measure is badly needed. Visual and smell inspection is the most common way for evaluating the condition of the chemical container due to its simplicity and low cost. However, the information about the composite condition is hard to achieve via periodic and simple inspection. Hence, embedded sensors into the structure for monitoring the health of the composite without any destruction become a standard preventative measure. Therefore, structural health monitoring (SHM) is critical in polymer composite application design [9,10].

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Ostachowicz et al. proposed that an ideal SHM system should fulfill some requirements: low cost, able to monitor the small level of damage, continuous assessment can be performed, sensitive to various types of damage, insensitive to environmental condition changes [11]. In real case, a general SHM system can only fulfill one or two requirements [12–14]. In the past, carbon nanotubesbased sensors were developed. These sensors were low-cost, sensitive to a more concentrated and aggressive chemical environment [15,16]. For the applications mentioned (airplane wing, wind blade, pipeline and joints), these composite structures are designed to work under aggressive and corrosive environment. Before the composite failure, it is important to monitor their health for locating the damage at early stage. Therefore, developing sensors for detecting the low-level damages caused by aggressive and corrosive environments is the focus of this study.

Acid diffusion in polymeric composites can be described as a process of various ion species diffusion [16]. For polymeric composite, the matrix and filler has different diffusion coefficient; thus, the ion diffusion is different in two components. Moreover, other studies showed that filler geometry, like graphene and clay, altered the ion diffusion process [17,18]. The diffusion process is also affected by polymer hydrolysis as water diffuses. The diffusion





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process is very dynamic and complex. Therefore, some current studies highlight the diffusion mechanisms as a function of filler geometry and its tendency to clustering into aggregates. For example, carbon blacks tend to form aggregates during nanocomposite fabrication. The aggregation structure significantly affects the conductive pathway formation, thus largely lowering the percolation threshold [19,20]. Moreover, according to the diffusion theory [21], the particle's shape changes and affects the diffusion process as the single sphere aggregate. In addition, the effect of particle aggregation on ion diffusion is not very well studied.

Many groups have studied the acid diffusion mechanisms, and various sensors were used to monitor the structural health monitoring of polymer composite [22–25]. For studies focus on carbon nanotube (CNT) and carbon black (CB) nanocomposites' sensing behavior, the experimental results of CNT could not be well interpreted [16,26]. One of the assumptions was that the CNT was so flexible and entangled then formed a complex electrical network. Thus, the simulation results on a simple geometry-formed electrical network were difficult to explain the complex experimental result. In this study, we were using silver nanowires (AgNWs) and silver nanoparticles (AgNPs) to study the effect of nanofillers' geometry on sensing behavior. The AgNP aggregation is a low structure that has a much simple geometry in comparison to CB. AgNW is much stiff about CNT, and its geometry is simple, thus a better choice to study this problem. Moreover, the sensors were applying the electrical property on SHM. The conductive network that nanofillers formed in the sensors was studied its effect on the ion diffusion process. Furthermore, this work studied AgNW and AgNP nanocomposites-based sensors at various concentrations experimentally and numerically. Modeling work was based on Fick's second law and applied the Fricke-Hamilton-Crosser model. The simulation results helped for better understanding the effect of nanofillers' geometry and concentration on sensing behavior.

#### 2. Experimental study

#### 2.1. Materials

For silver nanofillers synthesis, anhydrous ethylene glycol (EG  $\geq$  99.8%), silver nitrate AgNO<sub>3</sub>, Polyvinylpyrrolidone were purchased from Sigma-Aldrich. Copper(II) Chloride Dihydrate (CuCl<sub>2</sub>,  $\geq$  99.8%) was purchased from Acros Organics. Acetone was purchased from Alfa Aesar. For sensors manufacture, Epon 862 (epoxy) was purchased from Hexion. Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>  $\geq$  99.0%) was purchased from Sigma-Aldrich.

#### 2.2. Preparation of nanofillers

AgNWs and AgNPs were synthesized separately by a polyol reduction method [27]. The typical steps for AgNW synthesis are as follows. First, the synthesis system was set up. Flask heating mantles were used to heat the EG in a 250 ml three-neck flask, and a thermometer was used to monitor the solution's temperature. A stirring plate and stir bar were used to stir the flask contents after the heat was turned off. A condenser was used to condense the EG vapors. The flask was wrapped with glass wool to provide thermal insulation. Second, 150 ml of EG was added to the three-neck flask and heated at 150 °C for 60 min. A stir bar was added to the EG with a spin rate of 260 rpm. Third, 20 mM CuCl<sub>2</sub> in EG, 0.882 M PVP in EG, and 0.564 M AgNO<sub>3</sub> in EG were prepared. PVP and CuCl<sub>2</sub> solutions were shaken and ultrasonicated to obtain homogeneous mixtures. The 0.564 M AgNO<sub>3</sub> solution was shaken by hand every five minutes and then stored in the dark to prevent light reduction. Fourth, once the 150 ml EG solution was heated, 0.16 ml of CuCl<sub>2</sub> was added to the flask for 15 min. Fifth,

5 ml of the PVP solution and 5 ml of the AgNO<sub>3</sub> solution were injected into the heated solutions for 90 min. After reactions ended, the solutions were cooled to room temperature, and 100 ml of acetone was added to the products to dilute the solutions. Next, the products were centrifuged three times. The first centrifugation was at 4000 rpm for 30 min to separate AgNWs from EG/PVP. After removing the clear solution, acetone was added, and this solution was ultrasonicated for 5 min. The second centrifugation was at 2000 rpm for 30 min. The third centrifugation was done at 1500 rpm for 15 min. After centrifugation, a small amount of acetone was added to the centrifuge tubes and ultrasonicated for 5 min. The last step was to collect the AgNWs by pipette and store them in acetone. The synthesis of AgNPs was carried out in a similar manner. The major differences were that no CuCl<sub>2</sub> was added, and the PVP and AgNO<sub>3</sub> concentrations in EG were 0.932 M and 0.72 M, respectively. In addition, the AgNP centrifugations were done at a rate of 4000 rpm for 30 min.

#### 2.3. Preparation of nanocomposite sensors

Epon 862 (epoxy) and Jeffamine D230 (hardener) were used as the epoxy resin system, where the ratio of epoxy to hardener was 20:7 by weight. Each sensor was comprised of five layers. Lightweight cellulose veil (Kimwipes paper, KCC 34155, Kimtech) layers were used in constructing the laminate structure in order to keep the copper electrode in the middle, shown in Fig. 1. The areal weight of the nonwoven fabric was 2.03 mg/cm<sup>2</sup>. The procedure for preparing sensors was strictly followed as below: (1) The desired amount of Ag nanofillers and 5 g acetone were added to 20 g epoxy and stirred for 180 min; (2) the solution was transferred to the vacuum oven for 30 min at 40 °C in order to eliminate most of the acetone; (3) 7 g Jeffamine D230 was added to the mixture and stirred for another 75 min; (4) over the course of 20 min, the mixed solution was used in a wet layup process to form a laminated structure with a copper electrode inserted in the middle, as shown in Fig. 2 and described in more detail below, and (5) the sensors were cured in a vacuum bag for 72 h at room temperature, shown in Fig. 3 Generally, 15 to 20 sensors could be produced at a time, and the final cured thickness of the sensor was controlled around 0.5 mm.

The wet layup and vacuum bagging process details are as follows. Each sensor was comprised of two layers of lightweight veil. To each 1.5 cm  $\times$  4 cm stack of veil, approximately 0.4 g of resin was applied. The copper electrode was pure copper foil with 0.5 cm  $\times$  3.5 cm. The wet layup stack was surrounded by a nonporous Teflon coated release film (Release Ease 234 TNFP, Airtech International). The vacuum bag was nylon (Wrightlon WL6400, Airtech International). A Gast <sup>1</sup>/<sub>4</sub> HP oil-less vacuum pump was used to pull a vacuum of approximately 0.9 atm on the vacuum bag throughout the cure. Some excess resin squeezed out of the release film during the cure cycle. Gel time for this resin system is typically 6–12 h at ambient. The final composite was mostly nanocomposite resin, with the veil comprising approximately 10 vol% of the structure. The purpose of the veil therefore was to help maintain the electrode position in the center plane of the sensor.

#### 2.4. Testing method and characterization

A Phenom desktop SEM (Phenom, Pro X, 15 kV) was used to characterize the morphology of the silver sensors. The wideangle X-ray diffraction (Rigaku, Smartlab X-ray diffractometer, WAXD) was used to examine the crystallinity of raw AgNW and AgNP. A vacuum oven (Model 282A, Fisher Scientific) was used to mostly decrease the acetone in the mixed solution. As shown in Fig. 4, a testing system was built by connecting a KEITHLEY 2700 Multimeter, a signal recording software, and the sensing sec-



Fig. 1. Illustration of the sensor structure and the optical image of the sensor's cross-section. The X-direction is the assumed ion diffusion direction.

tion. The sensing section consisted of the nanosilver sensor (cathode), the copper electrode (anode), and a beaker with 1 M  $H_3PO_4$  solution. With the sensors inserted in the acid, the recording started with a one-second interval. 180 to 300 min was needed for testing a sample. Until the resistance decreased to the lowest value, the sensor was completely degraded, and the recording stopped.

#### 2.5. Theoretical and modeling study

The modeling work was based on Fick's second law [26]. The transient diffusion was assumed to be in 1 dimension, which was the X-direction defined in Fig. 1. The modeling work did not consider the effect of polymer degradation, swelling, nanofiller oxidation, or reduction. Moreover, the concentration of ions was assumed to be constant. Eq. (1) is shown below:

$$\frac{\partial \varphi}{\partial d} = D_e \frac{\partial^2 \varphi}{\partial t^2} \tag{1}$$

 $\phi$  is the concentration of ion (mol/L), d is the thickness of a calculated layer (cm), t is the time (second),  $D_e$  is the effective diffusion coefficient of ion in the composite (cm<sup>2</sup>/s).

The Fricke-Hamilton-Crosser model was used to study the diffusion process in the composite system, which consisted of two components. First, the model assumed that the dispersion of nanofillers is homogenous. Second, it was assumed that each component had its diffusion coefficient. Third, an empirical equation was used to relate the anisotropic property of the component to the diffusion coefficient. Thus, the effective diffusion coefficient of the composite system can be affected [26]. This study used the Fricke-Hamilton-Crosser model to study the nanofiller's shape effect on the acid penetration process. In the Fricke-Hamilton-Crosser model,  $D_a$  is the diffusion coefficient of the polymer matrix, and  $D_b$  is the diffusion coefficient of nanofiller. For the ion diffusion on nanofiller, the experimental result showed the nanofiller could make the ion diffuse faster in the nanocomposite, so the  $D_b$  should be bigger than  $D_a$ . The mechanism of ion diffusion on nanofiller is still not clear. One hypothesis is that the ion can diffuse along the conductive nanofiller, and the anisotropic of the nanofiller affects it a lot. Effective diffusion coefficient  $D_e$  consists of  $D_a$  and  $D_b$  in the model, and the  $D_e$  can be interpreted as Eq. (2) shows:

$$D_e = \frac{x\nu_a(\phi-1) + \phi + x}{\nu_a(1-\phi) + \phi + x}D_b$$
<sup>(2)</sup>

Subscript a represents the polymer matrix. Subscript b represents the nanofiller.  $D_b$  is the diffusion coefficient of part b, v is the volume percentage of each content. x is a function of  $D_a/D_b$ , and  $\phi$  equals  $D_b/D_a$ .  $\phi$  was set as 100 to obtain a clear observation on geometry effect on effective diffusion coefficient in this study. An empirical equation on determining x was applied, and the sphericity of a particle was used to describe x. For a single sphere particle, the x = 2; for the particle aggregation and wire, the shape was considered as a prolate spheroid for simplifying the simulations, and x is expressed as Eq. (3) shows:



Length: around 4 cm.

Curing, 72 hours

Fig. 2. Schematic illustration of silver nanocomposite sensor.

$$x = \frac{3}{\psi^2} - 1 \tag{3}$$

The  $\psi$  is the sphericity of a particle, and the definition is the ratio of the surface area of a sphere and a particle. Meanwhile, the sphere and the particle have the same volume. The simple illustration of  $\psi$  is shown in Fig. 5.

Avoid hyphenation at the end of a line. Symbols denoting vectors and matrices should be indicated in bold type. Scalar variable names should normally be expressed using italics. Weights and measures should be expressed in SI units. All non-standard abbreviations or symbols must be defined when first mentioned, or a glossary provided.

Consider AgNP aggregate as a prolate spheroid, for AgNP aggregation, the  $\psi$  is expressed as Eq. (4) shows:

$$\psi = \frac{2(r_1^2 \mathbf{A} \cdot \frac{l_1}{2})^{\frac{4}{3}}}{r_1^2 + \frac{r_1 \hat{\mathbf{A}} l_1}{2\sqrt{1 - (\frac{2r_1}{l_1})^2}} \mathbf{A} \cdot \arcsin\sqrt{1 - (\frac{2r_1}{l_1})^2}$$
(4)

 $r_1$  is the equatorial radius of the prolate spheroid;  $l_1$  is the length of the prolate spheroid, which is twice the distance from center to pole along the symmetry axis. The single sphere radius was set as 0.1 µm. In order to study the effect of aggregate geometry on effective diffusion coefficient, the aspect ratio of aggregation was simulated from 4 to 20, with an interval of 2.

Consider AgNW as a prolate spheroid, for AgNW, the  $\psi$  is expressed as Eq. (5) shows:

$$\psi = \frac{2(\frac{3r_2^2 \hat{A} \cdot l_2}{4})^{\frac{2}{3}}}{r_2^2 + r_2 \hat{A} \cdot l_2} \tag{5}$$

 $r_2$  is the radius of AgNW,  $l_2$  is the length of AgNW. The aspect ratio of AgNW was simulated from 30 to 100 with an interval of 10, which confronted the range of the AgNW used in this study. The primary purpose of the simulation was to determine the geometry's effect on the effective diffusion coefficient, thus the diffusion rate of ions

#### 3. Results and discussion

#### 3.1. Materials and morphology

The silver nanofillers were characterized by using SEM and XRD. The morphology of the raw silver nanomaterial was shown in Fig. 6a (AgNP) and Fig. 6b (AgNW). For AgNP, the average diameter

#### Set up



Fig. 3. Schematic illustration of vacuum bag arrangement.

of a silver nanoparticle sphere was 200 nm. The silver nanoparticles were stored in acetone, and the aggregation is distinct, shown in Fig. 6a. To achieve a great dispersion of nanofillers in nanocomposite and eliminate the unfavorable aggregation. The following approaches were made. First, the silver nanomaterial was sonicated well before it was mixed with epoxy. Second, severe aggregation can be formed if the AgNP was stored for a long time, thus the AgNP was used in 24 h right after it was synthesized. Moreover, to prevent the unpredictable effect on experimental results, surfactant for preventing aggregation was not added. After these pretreatments, the silver nanoparticle dispersed as very small aggregate in the nanocomposite, shown in Fig. 7a. For AgNW, the average length was 10  $\pm$  5  $\mu$ m and the diameter was 150 nm. The aggregation of AgNW was easy to be solved compare to AgNP aggregation. After 3 h stirring, the AgNW dispersed uniformly and individually, shown in Fig. 7b. Due to the big amount AgNW synthesis, very small amount silver nanoparticles appeared with the AgNW. The XRD results of silver nanofillers are shown in Fig. 6c. Three peaks of both silver nanofillers corresponded to (111) at 38.09°, (200) at 44.3° and (220) at 64.4°. The peaks of the synthesized silver matched with the face centered-cubic silver (JCPDS file No. 04-0783) [38]. Moreover, these results are similar to other published studies [28–29]. The difference between AgNP and AgNW at (111) peak was dominant. The higher peak of AgNW could be attributed to the bigger particle size and nanowire growth direction [30].

Fig. 7 is shown the surface of AgNP sensors and AgNW sensors. As shown in Fig. 7a, compared to raw AgNP, most AgNP were dispersed uniformly, and only tiny aggregations were still apparent. However, the aggregation size was much smaller than before mixing. The shape of AgNP aggregation was irregular, similar to a prolate spheroid. The aspect ratio of this aggregation was around 3, and the whole size was around 2  $\mu$ m. It is challenging to prevent aggregates due to many factors: lower interaction energy barrier between particles due to their small size; higher temperature seems to increase the aggregation rates; even the gravity force and light will affect the nanoparticle aggregate formation [31]. In Fig. 7b, the AgNW dispersion showed a partially ordered arrangement, which formed a net structure. In Byoungchoo Prak's study, they used the horizontal-dip coating method to achieve a highly ordered AgNW arrangement, and the key was to control the flow direction of AgNW suspension [32]. In this case, one hypothesis is that the sensor was made by a vacuum bag, and the uncured polymer solution was flowing in the vacuum bag during the curing; thus, the flow resulted in AgNW ordered arrangement.

#### 3.2. Experimental result

Various samples were fabricated at different volume % and tested. Their sensing behavior was shown in Fig. 8. The resistance was shown in logarithmic scale as y-axis, and the x-axis was the time in second. As shown in Fig. 8a and b, the silver nanocomposite



Fig. 5. Illustration of the  $\psi$  definition.

sensors exhibited three stages in the electrical resistance-time curve. One hypothesis is that the three stages can be caused by different ion diffusion processes. The size of the ion could affect the diffusion rate, and with the water ion diffused in the nanocomposite, the swelling and hydrolysis would make more space for the bigger ion diffusion. As a result, the resistance-time curve showed three stages. For example, in Fig. 8a, the 0.1 vol% AgNW sensors started to have a signal around 1400 s, then the resistance sharply



Fig. 6. SEM image of (a) AgNP, (b) AgNW; (c) XRD patterns of silver nanofillers.



Fig. 7. SEM image of nanosilver sensors surface (a) AgNP/Epoxy and (b) AgNW/Epoxy.



Fig. 8. The recorded resistance of (a) AgNW sensors, (b) AgNP sensors; The response time of (c) AgNW sensors, (d) AgNP sensors.

decreased with time. The first signal could be caused by H<sup>+</sup> diffusion. The size of H<sup>+</sup> was small, so H<sup>+</sup> was easy to diffuse in the nanocomposite, bridge the nanofillers, and brought conductivity to sensors. The electrical resistance was high in the first stage due to the slow diffusion speed and a small amount of H<sup>+</sup> ions. With the ion diffusion processing, the electrical resistance kept decreasing slowly until 6000 s. At the beginning of stage two, the electrical resistance sharply decreased first then reached a resistance value of  $1.6 \times 10^5 \Omega$ . This could be caused by the water molecules, which were larger than H<sup>+</sup>. However, the electrical resistance kept decreasing over time until 9000 s. In stage three, the sensing behavior was similar to stage two. With the larger ions, like the phosphate ion group, diffused in the nanocomposite, the electrical resistance finally kept at a certain value, around  $1.0 \times 10^4 \Omega$ . Moreover, after the experiment, nanosilver sensors were replaced by a pure copper electrode to measure the direct resistance, and the value was around  $1.0 \times 10^3 \Omega$ , which was lower than the certain value in stage three.

On the other hand, with the nanofiller's concentration increased, the sensing behavior showed some difference. In comparison to 0.1 vol% AgNW, the 0.5 vol% AgNW showed a slowly decrease of the electrical resistance in stage three. For the 1.0 vol % AgNW sensor, its resistance-time curve was much complex, the electrical resistance curve was much flat in stage one and stage two, and the curve became less smooth compared to the lower vol% AgNWs sensors. The electrical resistance curve of 1.0 vol% AgNP sensor showed a similar change: the resistance slowly decreased in each stage, and the curve became less smooth compared to lower vol% AgNP sensors (Fig. 8b).

In Liu's work, for the sensors fabricated using carbon nano additives, the second and third stages were not presented as carbon nanomaterial's concentration increased [16]. The disappearance of the second and third stages was attributed to the entanglements and aggregations of CNT and CB. According to Xing's study, the 3D carbon conductive network could favor the diffusion of lithium ions in the composite [33]. Zhou et al. used carbon nanofiber (CNF) to construct a necklace-like conductive network which was beneficial for the fast Li<sup>+</sup> diffusion [34]. Thus, the conductive network formed by nanofillers could be an important factor that may affect ion diffusion. In contrast to CNT, the AgNW was stiff, and the conductive network of AgNW was formed by wire overlapping without any entanglements. In other words, the network structure was simple. Compared to CB, AgNP formed low structure aggregations, which were much difficult to build a conductive network compared to high structure CB aggregations [26]. Due to these differences, the conductive network's effect on sensing behavior could be better observed in this study. The second and third stages appeared with the silver nanofiller's concentration increased, which highly approved the ion stages model. The experimental result has confirmed our hypothesis that conductive networks affect ion diffusion, thus the sensing behavior of the nanocomposite sensor.

#### 3.3. Modeling result

The modeling only focused on the nanofillers' geometry and concentration effect in altering the effective diffusion coefficient ( $D_e$ ). The higher diffusion coefficient means the ion can move faster on nanofiller or go through it [35,36]. As shown in the experimental result, the addition of nanofiller resulted in a faster response; thus, the effective diffusion coefficient of silver nanofillers was higher than that of the epoxy resin. In other words, the  $\phi$  was bigger than 1 in this sensor. In our group previous work, the effect of nanofiller geometry on forming specific conductive networks was discussed [37]. AgNW nanocomposite had a much lower percolation threshold than AgNP nanocomposite. However, the AgNP aggregation exhibited irregular shapes that benefited the conductive network formation with anisotropic properties.



Fig. 9. The nanofiller's geometry effect on effective diffusion coefficient. The arrow shows the aspect ratio of AgNP aggregation increment and aspect ratio increment of AgNW. (a) AgNP aggregation's aspect ratio 4 to 20 with an interval of 2; (b) AgNW's aspect ratio 30 to 100 with an interval of 10.

In Fig. 9a, the red line at the bottom is the single sphere AgNP, and with the arrow's direction, the AgNP aggregation's aspect ratio increased from 4 to 20 with an interval of 2. First, with the vol% increased, the effective diffusion coefficient increased. Second, the effective diffusion coefficient increment was dominant as the aspect ratio of AgNP aggregation increased to a specific concentration. The modeling result clearly showed that the single sphere geometry had the lowest effective diffusion coefficient compared to the AgNP aggregation. Thus, a lower acid penetration rate and longer response time were expected. Moreover, the AgNP aggregation increased the ion diffusion rate. The simulation results proved that the aspect ratio should be an essential parameter in affecting ion diffusion. However, ion diffusion is dependent on many factors, like the conductive network. But in general, at a certain concentration, with AgNP aggregation size increases, the number of particles decreases. According to the previous work, the probability of forming a conductive network increased and decreased with the aggregation size increased. The anisotropic property of aggregation became dominant while the aggregation size was very small. It is difficult to draw a comprehensive statement for aggregation's effect on acid diffusion. However, it seems that if the nanofiller is spherical, the dispersion into the polymer is more uniform and displays better durability.

In Fig. 9b, the increment of the effective diffusion coefficient was significant as the aspect ratio of AgNW increased. The higher effective diffusion coefficient value at 1 vol% leaded to a faster diffusion rate. The difference in response time between AgNW and AgNP became significant as concentration increased. The modeling result gave a reasonable explanation on this issue. For example, in Fig. 9, the effective diffusion coefficient of 0.1 vol% AgNP single sphere was  $1.003 \times 10^{-9}$  cm<sup>2</sup>/s, and the effective diffusion coefficient of 0.1 vol% AgNW (aspect ratio 50) was  $1.012 \times 10^{-9} \text{ cm}^2/\text{s}$ , the percentage difference was 0.897%. At 1 vol%, the effective diffusion coefficient difference percentage between 0.1 vol% AgNP single sphere and 0.1 vol% AgNW (aspect ratio 50) increased to 9.71%. In this study, the D<sub>e</sub> was regarded as an indicator to describe the geometry's effect on ion diffusion, and the  $D_b/D_a$ , which is the  $\phi$ , was set as 100 to have a clear observation on the increment of D<sub>e</sub>. Furthermore, the diffusion coefficient ratio of the two components could be varied in other cases. Gomasang's work showed that graphene could be used as an effective additive for reducing moisture permeability in the polymer [17]. In Liu's work, the  $\phi$  was set as 0.01, which means the nanofiller has a much lower diffusion coefficient than the polymer matrix. In his study, the simulation results showed that, with the concentration of nanofiller increased, the De decreased. The simulation results based on the Fricke-Hamilton-Crosser model helped understand the graphene's hindering effect better [16]. These results indicate that the effective diffusion coefficient is an important parameter in explaining the sensing behavior.

#### 4. Conclusion

In this study, the electrical conductivity of nanocomposite was used as an important indicator for structural health monitoring. Various nanocomposite sensors were fabricated with different concentrations of AgNW or AgNP. The differences in sensing behavior between 0.1 vol%, 0.5 vol%, and 1 vol% nanosilver sensors were observed. The experimental result showed that both silver nanocomposite sensors responded in a shorter time with the concentration increased. Meanwhile, the AgNW sensor had a shorter response time than the AgNP sensor at the same vol%, and with the concentration increased, the difference became significant. At 1 vol%, the AgNW sensors responded immediately as contacting the acid. By analyzing the resistance curve, we found that the addition of nanofiller slightly affected the curve, and the resistance curve became less smooth.

The modeling work showed that the ideally dispersed AgNP had a lower effective diffusion coefficient. Thus, a longer response time was expected. Meanwhile, a higher aspect ratio of AgNP aggregations could accelerate the acid penetration due to a higher effective diffusion coefficient. For AgNW, the higher effective diffusion coefficient gave a promising explanation of the sensing behavior. Moreover, it seems that the acid diffusion process can be affected by the nature of the conductive network. The 1 vol% AgNW responded immediately due to its conductive network formation.

#### **CRediT authorship contribution statement**

**Qichen Fang:** Conceptualization, Methodology, Software, Formal analysis, Writing – original draft, Visualization. **Khalid Lafdi:** Validation, Resources, Writing – review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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