# **CHAPTER IV**

## **RESULTS AND DISCUSSION**

## 4.1 Effect of Silane content on the Heat Resistance of the Epoxy-based Coating

The effect of silane content on the heat resistance and anticorrosion of epoxy resin-based coating was investigated in Section 3.4.1.1.

## 4.1.1 FTIR Analysis

The FTIR was used to investigate the siloxane crosslinking reaction. Figure 4.1 shows the FTIR spectra of epoxy resin coating, uncured silane (AEAPS as a control) that has a film thickness of 100  $\mu$ m, before and after being heated at 200, 250 and 300°C for 20 minutes. The characteristic peaks at 3460 cm<sup>-1</sup> (broad) indicated the OH stretching. The strong and sharp band at 1510 cm<sup>-1</sup> is assigned for the (=C stretching motion) of benzene nucleus. The band at 1035 cm<sup>-1</sup> indicates the aliphatic C-O stretching. The band at 828 cm<sup>-1</sup> corresponds to the vibration of adjacent hydrogens of benzene nucleus. At 300°C (Figure 4.1d) the broad band at around 1720 cm<sup>-1</sup> is associated with carbonyl group (C=O). Figures 4.2, 4.3 and 4.4 show typical FTIR spectra of epoxy/silane coating (AEAPS) (samples 1, 2, 3 and 4) compared to the epoxy coating (a control) with a film thickness of 100  $\mu$ m and heated at 200, 250 and 300°C for 20 minutes. Characteristic bands of the –OH stretching at 3460 cm<sup>-1</sup> and the bands at 1035 and 828 cm<sup>-1</sup> were originated from the epoxy resin. In each FTIR spectrum, there were an absorption peak, which corresponds to the broad band of the C=O stretching (carbonyl group) at around 1720 cm<sup>-1</sup>. Moreover, the effect of

elevated temperature on the cured epoxy resin was also observed. We found that there was formations of the carbonyl group generated through an oxidation in the epoxy resin. The rate of oxidation could be determined by the increase of absorbance of the carbonyl group at 1720 cm<sup>-1</sup>. In sample 4, the epoxy resin cured with the silane (AEAPS) has an stoichiometric amount of 7 phr (in a basic). In addition, the highly crosslinked siloxane network evidenced by the broad IR band at around 1103 cm<sup>-1</sup> is associated with the Si-O-Si band. The methoxy group was hydrolyzed and water is in situ released during the heat treatment by a condensation reaction to form a siloxane network structure, which is still observed at high temperature and high concentrate of silane as shown in Figure 4.5. Effect of film thickness on IR transmittance is shown in Figure 4.6. The results of sample 4 (AEAPS curing agent) having two film thickness of 50 and 100 µm indicated that increasing film thickness for the curing reaction does not affect the curing effeciency, because the IR absorption bands are almost identical. It was also observed that both film thickness in sample 4 still showing the broad band at around 1103 cm<sup>-1</sup>, which is associated with the Si-O-Si band ( the siloxane network).



Figure 4.1 FTIR spectra of epoxy coating, uncured silane (AEAPS) at heated temperatures of (a) room temperature, (b) 200°C, (c) 250°C and (d) 300°C.



Figure 4.2 FTIR spectra of epoxy/silane coating heated at the temperature of 200 °C, (a) control, (b) sample 1, (c) sample 2, (d) sample 3 and (e) sample 4



Figure 4.3 FTIR spectra of epoxy/silane coating heated at the temperature of 250 °C, (a) control, (b) sample 1, (c) sample 2, (d) sample 3 and (e) sample 4



Figure 4.4 FTIR spectra of epoxy/silane coating heated at the temperature of 300°C, (a) control, (b) sample 1, (c) sample 2, (d) sample 3 and (e) sample 4



Figure 4.5 FTIR spectra of epoxy/silane coating (silane as a curing agent) heated at temperature of (a) room temperature, (b) 200°C, (c) 250°C and (d) 300°C.



Figure 4.6 FTIR spectra of sample 4 with a film thickness of 50 and 100  $\mu$ m heated at 300 °C, (a) 50  $\mu$ m, (b) 100  $\mu$ m

# 4.1.2 Evaluation of coating film by colorimetry

The siloxane network formed on the steel surface can protect the film from deterioration of heat. The results of color difference ( $\Delta E^*$ ) of epoxy coating at different silane concentrations, film thickness and temperatures were presented in Table 4.1

Temperature	Dry film	$(\Delta E^*)$ of sample						
(°C)	thickness	Control	1	2	3	4		
	(D.F.T.) (µm)							
	25	12.5	12.3	12.4	12.3	13.1		
200	50	12.2	12.1	12.9	13.6	13.2		
	75	12.0	12.6	12.5	12.5	12.7		
	100	10.1	10.0	10.5	10.5	10.2		
	25	40.4	39.7	39.9	40.0	37.9		
250	50	41.3	41.1	40.8	40.6	38.4		
	75	40.3	40.1	40.1	39.9	37.7		
	100	40.9	39.9	40.3	40.1	37.7		
	25	43.1	42.8	42.6	42.1	40.7		
300	50	42.5	42.7	42.4	42.4	40.5		
	75	42.1	41.6	41.7	41.2	39.1		
	100	42.1	41.6	41.7	40.9	38.7		

**Table 4.1** Color difference ( $\Delta E^*$ ) of the color changes caused by heat exposure at<br/>various film thickness

Color difference ( $\Delta E^*$ ) slightly decreased with increasing film thickness. All films became yellowish, which was attributed to the type of curing agent (amine). When amine curing agent was heated, the effectiveness of the color of reaction is shown in the yellowing of the coated film. At a low heating temperature, yellowing of the coated films was observed in terms of  $\Delta E^*$ . At the higher temperature, the epoxy coating was somewhat decomposed to give yellowing as well. For sample 4, it contains inorganic silane that is thermally stable. This contributed to the increased heat resistance, especially when inorganic silane content and its film thickness were increased. Figure 4.7 shows the color changes of epoxy/silane coating at various silane concentrations heated at 300°C for 20 minutes.





It was observed that the color shade of the low content silane is darker than that of high content silane, which is described in color difference ( $\Delta E^*$ ). Color difference ( $\Delta E^*$ ) decreased with increasing film thickness and concentration of silane (AEAPS). Sample 4 that had the lowest  $\Delta E^*$  values gave the good heat resistance.

## 4.1.3 Thermogravimetric Analysis (TGA)

TGA data were analyzed to evaluate thermal stability of the coating films. The coated films were heated from  $100^{\circ}$ C to  $600^{\circ}$ C. The thermogravimetric curves are shown in Figure 4.8



Figure 4.8 Thermogravimetric curves of epoxy/silane coating (a) control,(b) sample 1, (c) sample 2, (d) sample 3 and (e) sample 4

The result in Figure 4.8 shows the decomposition of the coating in terms of weight loss. This oxidizing thermal decomposition has two consequences: The weight loss observed at the temperatures ranging from  $350^{\circ}$ C to  $550^{\circ}$ C was attributed to the decomposition of organic network (epoxy). After being heated, the change in weight loss was observed, the residues of thermally stable ash were 10.3%, 12.5%, 17.4%, 19.7% and 25.7% for the controlled silane, samples 1, 2, 3 and 4 respectively. In the

presence of inorganic siloxane the residue from the thermal degradation increased with increase in the concentration of silane (AEAPS), especially in sample 4 that had the higher thermal stability than the epoxy coating. This siloxane network was thermally stable up to 600 °C. Thermal stability of the polymer is related to the silicon backbone. The silicone-based polymers containing the Si-O-Si linkage have superior heat and ultraviolet resistance (based on bond energy and oxidation resistance) compared to polymers based on only C-C linkages. The Si-O-Si linkages are similar to the silicon atoms of sand and rocks, which are very durable inorganic materials. The epoxy/silane coatings are effective because they possess the strong bonding and higher energy required to cleave the siloxane bonds. The Si-O-Si bonds are superior in strength to the C-C bond. The Si-O-Si bond provides an energy of about 106 kcal/mole, while a C-C bond has only 82-83 kcal/mole [26, 27]. The higher the content of silicone in a formulation, the stronger the bond energy in a coating, and the greater the heat resistance. The organic groups, methyl and phenyl are most commonly used in high temperature coating. To increase the organic coating in superior heat properties, silane should be included in the formulation.

## 4.2 Effect of Silane content on the Adhesion of the Epoxy Coating

The adhesive tape test is used as a qualitative adhesion test method. The silane concentrations, thickness and cure time were studied. The result in Table 4.2 shows that the adhesion was assessed qualitatively on the 0 to 5 scale (ASTM D 3359).

D.F.T.	Control		Sample 1		Sample 2		Sample 3		Sample 4	
(µm)	cure time									
	24 hrs.	20 mins	24 hrs.	20 mins	24 hrs.	20 mins	24 hrs	20 mins	24 hrs	20 mins
	Room	105 °C								
	temp.									
25	3B	5B	5B	5B	5B	5B	4B	5B	4B	5B
%area	12	0	0	0	4	0	4	0	4	0
removed										
50	2B	5B	5B	5B	5B	5B	4B	5B	3B	5B
%area	20	0	0	0	0	0	4	0	12	0
removed										
75	2B	5B	5B	5B	5B	5B	2B	5B	2B	5B
%area	24	0	0	0	0	0	20	0	20	0
removed								1		
100	1B	5B	5B	5B	5B	5B	2B	5B	2B	5B
%area	40	0	0	0	0	0	28	0	20	0
removed										

 Table 4.2
 Adhesive tape test on epoxy/silane coated film

For the 5B rating, the edges of the cuts are completely smooth. In the 4B rating, the areas were defected less than 5%. In the 3B rating, percent area removal was 5-15%. In the 2B rating, the percent area was removed 15-35%. In the 1B rating, the coating became flaked along the edges of cut and the percent area removed was 35-65% of the lattice. In the 0B rating, the defected area was greater than 65% of the lattice.

In Table 4.2, the results show that the adhesion of control (no silane) is lower than those of epoxy/silane coating (samples 1, 2, 3 and 4) cured for 24 hours. The data in Table 4.2 indicate that silane is markedly effective in improving adhesion after 24 hours cure. The mechanism for such a result is rather complex. However, organosilane is used as a primer or an integral blend to promote adhesion of the resin to the metal

substrate. Silane coupling agent produces the highly reactive silanols, these silanols begin to condense, and form oligomeric structures, and also to form weak hydrogen bonds to the surface of inorganic materials. After drying, the inorganic material leads to further condensation and dehydration between the coupling agent and the surface. This process yields multiple strong, stable ether linkages, covalent bonds to the surface [3, 28]. Figure 4.9 illustrates this type of chemical bonding.



Figure 4.9 Idealized structure of a silane reaction with a reactive substrate [3]

Sample 4 used silane (AEAPS) as the curing agent for substitued poly(amide amine), so the adhesion of coating film decreased with increaseing film thickness. The trialkoxy silyl group is attached to a short hydrocarbon chain, the other end of which has the amine functional group. Epoxy-silane (AEAPS) cure is accomplished through silyl methoxy groups. It can react with water to produce silanol groups that can, in turn, react with remaining silyl methoxy groups to generate polysiloxane at the surface. The terminal amine groups can, of course, react with epoxy groups in the resin. Because the adhesion is decreased, the selection of solvents affects the relative rates of reaction. In this work ketone was used as solvent, which can react with primary amines to give ketimines and water (as shown in the reaction 4.1).

$$R_2C=O + H(HNR)_aNH_2$$
   
ketone amine  $R_2C=N(RNH)_aH + H_2O$  (4.1)

The ketimine formed in the reaction will not readily react with epoxy group and will remain in the ketimine form until additional water is introduced to reverse the reaction. In the presence of hydrolyzable silanes, the water so formed irreversibly reacts to hydrolytically condense the silane groups [7,19]. However, if these reactions can increase film thickness to give multiple interfacial bonds, then at least some of the bonds are expected to remain on the intact coating. Furthermore, hydrolysis is reversible, so that the hydrolyzed bonds can reform. In epoxy coating (control), the adhesion decreased with increase in film thickness. The use of ketone solvent must be carefully considered that it may react with primary amines (as shown in reaction 4.1). However, ketimines are hydrolyzed by water to release the free amine and the ketone, which is the reverse reaction of ketimine formation and water. This situation takes place, when thick film was difficultly dried out all components in a coating. The improved adhesion is accomplished when all formulations were cured at 105°C for 20 minutes. Adhesion of all formulations were very good (as shown in Table 4.2). For every resin/silicone combination, there is an optimal usage level of the silicone. The overdosage of silicon molecules, which may remain in the interfacial layer could be undersirable side effects such as loss of adhesion. The silicone additive will relatively quickly migrate into the liquid/gaseous interface due to their interfacial activity. It is still mobile and does not chemically react with other components. This is very important to adjust the level of silane as an optimal amount [27].

# 4.3 Effect of Silane content on the Corrosion Resistance of the Epoxy-based Coating

In this study, we investigated the effect of the silane coupling agent in epoxy coating for cold mild steel plates on the corrosion resistance via an accelerating corrosion test. In a corrosion study, tests progress in the improvement of corrosion protection by epoxy/silane coating. The corrosion evaluation is operated by mass loss measurements. The performance of epoxy/silane coating on test is evaluated by visual observation and appearance of rusts. The photographs shown in Figures 4.10 to 4.13 indicate various degrees of degradation, which serve as observational standards greatly reduce variation between observers. The use of standardized evaluation and to give numerical ratings to test specimens are a common practice in paint testing. Rating systems for the evaluation of corrosion and blistering on coated metal panels have been standardized (as described ASTM D 1654, ASTM D 714 and ASTM D 610, see Appendix A).



Figure 4.10 Effect of salt spray after 500-hour exposure on epoxy/silane coating samples against control with D.F.T. 50 μm



**Figure 4.11** Effect of salt spray after 500-hour exposure on epoxy/silane coating samples against control with D.F.T. 100 μm



**Figure 4.12** Effect of salt spray after 1000-hour exposure on epoxy/silane coating samples against control with D.F.T. 50 μm



Figure 4.13 Effect of salt spray after 1000-hour exposure on epoxy/silane coating samples against control with D.F.T. 100 μm

In Figures 4.10 to 4.13, at the same time, the rusting of x-cuts on the epoxy coating (control) was larger than epoxy/silane coatings (samples 1, 2, 3 and 4). For the longer exposure time of 1000 hours, the rusting of x-cuts on the epoxy/silane coating and epoxy coating (control) was larger. A degree of rusting can be used to assess corrosion on a coating as shown in Table 4.3.

Type of	D.F.T.	500-hour exposure					1000-hour exposure			
coating	(µm)	x-cut		Surface		x-cut		Surface		
		Scribe	Blistering	Unscribe	Blistering	Scribe	Blistering	Unscribe	Blistering	
	25	6	10	8	10	5	4 MD	7	4 MD	
	50	7	10	8	10	7	4 MD	8	4 MD	
Control	75	8	10	9	10	7	2 M	9	4 MD	
	100	8	10	9	10	7	2 M	9	4 MD	
	25	7	10	8	10	6	4 MD	8	10	
	50	8	10	9	10	7	4 MD	9	10	
Sample 1	75	8	10	9	10	7	4 M	9	10	
	100	8	10	10	10	7	4 M	9	10	
	25	8	10	9	10	6	4 MD	8	10	
Sample 2	50	8	10	9	10	7	4 MD	9	10	
	75	9	10	10	10	7	4 M	9	10	
	100	9	10	10	10	8	4 M	9	10	
	25	8	10	9	10	6	4 MD	8	10	
Sample 3	50	8	10	9	10	7	4 MD	9	10	
	75	9	10	10	10	7	4 M	9	10	
	100	9	10	10	10	9	4 M	9	10	
	25	8	10	9	10	8	4 M	8	10	
	50	8	10	9	10	7	4 M	9	10	
Sample 4	75	9	10	10	10	7	4 M	9	10	
	100	9	10	10	10	9	4 M	9	10	

# Table 4.3 Effect of salt spray exposure time and coating thickness on cut rusting and surface appearance

Rusting Rating 10 = No change, 0 = Complete failure, Blistering standard No.10 = No blistering, No.8 = the smallest size blister, Nos. 6, 4 and 2 = larger sizes, Frequency at each step in size was designated as follows: Dense (D), Medium dense (MD), Medium (M) and Few (F).

In Table 4.3, epoxy/silane coatings (samples 1, 2, 3 and 4) offer better corrosion performance than the epoxy coating (control) alone. After 500-hour salt spray exposure, the corrosion could only occur on the steel at the x marks, the rating of corrosion of the control is worse than those of samples 1, 2, 3 and 4. Very satisfactory result, no blisters were found on these samples. In general, hydrogen atom on the amine group of polymer backbone can be bond strongly with oxide surface of the steel. If the interaction is strong enough, the amine group would not be displaced by water. In a long exposure time of 1000 hours, rusting and blistering at the x-cuts of the epoxy coating wihtout silane were larger than those epoxy/silane coating (samples 1, 2, 3 and 4). Rusting and blistering on epoxy coating are caused by sodium chloride solution that passed through the damage and diffused into the interface between the coating and the metal substrate. The corrosion process could occur on the steel at the x-cuts. The adhesion between the vehicles of the coating and the steel surface is normally enchanced by the polar interaction and by hydrogen bonding. These hydrogen bond interactions could be displaced by water, which can introduce hydrogen bond with all of the groups on the surface of the steel. Water diffuses under the coating and causes swelling of the coating. Therefore, the coating and the metal substrate would lose their adhesion. The coating thus became softer. This mode of failure, is illustrated in Figure 4.14 [28]. However, the rate of water displacement can be reduced, because the adsorbed polymer molecules have a rigid chain structure and sufficient number of polar groups on each molecule. For instance, the epoxy/silane coating (samples 1, 2, 3) and 4) have rigid chain structures, interpenetrating polymer network (IPN) more than the epoxy coating (control).

In this work, the corrosion product is red rust  $(2Fe_2O_3H_2O)$ . The mechanism of corrosion started, when water and oxygen had permeated through the film and water displaced some of the adsorbed groups of the coating from the surface of the steel. In

this process, all the components of an electrochemical cell are present. Electrochemical reactions begin in the absence of oxygen, the initial reactions are [29]:

At the anode (oxidation): the formation of ferrous ions by the loss of electron,

$$2Fe \longrightarrow 2Fe^{2+} + 4e^{-1} \qquad (4.2)$$

At the cathod (reduction): the formation of hydroxyl ions,

$$O_2 + 2H_2O + 4e$$
  $\longrightarrow$  4OH (4.3)

The initial product of redox is thus the yellow rust of ferrous hydroxide,

$$2Fe + 2H_2O + O_2 \longrightarrow 2(Fe(OH)_2)$$

$$(4.4)$$

In the presence of excess oxygen, the ferrous hydroxide is oxidized to hydrated ferric oxide, rest rust:

$$4Fe(OH)_2 + O_2 \longrightarrow 2Fe_2O_3.H_2O + 2H_2O$$
(4.5)

The method for predicting corrosion of coated steel material exposed to the mist of salt solution is by a corrosion rate method (as shown in Figures 4.14 and 4.15)



Figure 4.14 Stage of corrosion at a scribe and blistering through a film [28]



Figure 4.15 Corrosion rate of the epoxy coating (control), samples 1, 2, 3 and 4 for 500 hour exposure time





The relative corrosion resistances are expressed as mils per year, when mpy < 1 =Outstanding, mpy 1-5 = Excellent, mpy 5-20 = Good, mpy 20-50 = Fair, mpy 50-200 = Poor, mpy 200+ = Unacceptable [30] The variation in silane coupling agent, film thickness and time were studied. The results in Figures 4.16 and 4.17 show that the corrosion rates of epoxy coating (control), samples 1, 2, 3 and 4 were decreased when the concentrations of silane and film thickness increased. The corrosion range classified was mpy 0-5. Moreover, the classification of corrosion range implied excellent corrosion resistance. The corrosion protective performance is improved, because the diffusion of molecules and ions could not be deeper to the interface between the epoxy/silane coating and the substrates. Thus, thicker films will delay the attack of water and oxygen at the interface.

# 4.4 Effect of Silane content on the Mechanical Properties of the Epoxy-based Flooring

The flooring system is used in civil engineering. Several performance properties of the floor systems were determined, including hardness, compressive strength and chemical resistance. The mechanical property measurements were made after 1, 3, 5 and 7 days of cure.

## 4.4.1 Hardness

Hardness was measured using a modified version of the methodology described in ASTM D 2240/shore D. The results of the hardness are reported in Table 4.4.

Days of cure	Hardness of flooring of						
	Control Sample 1		Sample 2	Sample 3			
1	69	74	78	78			
3	71	80	83	88			
5	75	83	86	95			
7	76	84	86	95			

#### Table 4.4 Hardness of epoxy/silane flooring

It was observed that hardness increased with increase in silane coupling agent. The hardness of epoxy/silane flooring (samples 1, 2 and 3) was higher than that of epoxy flooring (control). The epoxy/silane flooring has rigid chains; by the curing of the epoxy resin with cycloaliphatic amine to form a cured epoxy polymer, and such a reaction of silane (AEAPS) produce the component hardness. The amine moiety of the silane (AEAPS) undergoes the epoxy-amine addition reaction and is condensed by catalytic function of the amine functional group within itself. In sample 3, the silane coupling agent is used as a curing gent, substituted cycloaliphatic amine curing agent. The hardness was higher than the epoxy/silane flooring, where cycloaliphatic amine was used as a curing agent, because the silane can form polymeric structures by condensation of the silanol group to become siloxane (Si-O-Si) linkages. These structures have been extending into the resin matrix and the Si-O linkages are strong and the rigid chain structure, which cannot move beyond the dimension of molecular segments, such as Si-O bonds in quartz, glass, ceramic are more rigid than the organic C-C bond. Therefore, higher levels of the silane used in epoxy resin can increase the hardness of the coating [8, 11].

#### 4.4.2 Compressive Strength

Compressive strength was measured using a modification of ASTM C 579. Floor samples which are cast out in the diamension described (cylinder shape  $1\pm 1/32$  inch), have a cross section area of  $1\pm 1/32$  inch. The result of the mechanical properties is reported in Figure 4.17.



Figure 4.17 Compressive strength of epoxy/silane flooring

The results in Figure 4.17 show the compressive strength of epoxy/silane coating (samples 1, 2 and 3) and the control (no silane). It was observed that the compressive strength increased with increase in silane (AEAPS) and curing time. One day compression of epoxy/silane flooring is higher than that of epoxy flooring (control). The additonal silane (AEAPS) is hydrolyzed and easily condenses by a catalytic function of the amine function group, that gives a very rapid cure resulting in the mechanical properties. Further increases in the silane content up to 3 wt% (sample 1), the compressive strength was increased to an optimum value, which indicates that the level of silane affects the increase of compressive strength. However, increases of

the silane content to 5 wt% (sample 2), the compressive strength was slightly increased, which was lower than that at 3 wt% silane content. This observation is attributed to the excessive amount of amine from cycloaliphatic amine and silane (AEAPS), which caused the incompletion of the epoxy curing reaction. The demand on the curing process is to obtain the best balance of properties with polyfunctional epoxides. For the reaction curing agents, it is desirable to react with the resin and curing agent at approxiamtely stochiometric quantities.

# 4.4.3 Chemical Resistance

The effects of chemical immersion were studied on epoxy flooring. Shore D hardness was measured of the cured floor prior to chemical immersion and after the immersion. Hardness retention is relevant to the flooring application where it indicates the durability of the floor. Specimens were cured for 7 days at room temperature before testing and after 7-day immersion. The reagents were removed and the surfaces were dried. Shore D hardness of each sample was re-measured and the percent hardness retention was then calculated. The results of this study are presented in Figure 4.18.



Figure 4.18 Chemical resistance of epoxy flooring

The result indicates that the epoxy/silane floorings (samples 1, 2 and 3) are resistant to water and solvent such as toluene. The immersion in ethanol and MEK showed a marked softening of the floor, due to the absorbed solvent. The epoxy flooring (control) was swollen especially at the floor when immersed in ethanol. Epoxy resins are usually soluble only in highly polar solvents such as ketones, esters and alcohols. The results indicates that silane (AEAPS) helps improve the chemical resistance through the highly crosslinked network. It is interesting to note also that, when the concentrations of silane (AEAPS) was 5 wt% (sample 2), after immersion in solvent, hardness retention was less than that of silane (AEAPS) containing 3 wt% (sample 1). This may be caused by the excess amine curing agent. Unreacted amine functionalities apparently are hydrophilic enough to favor entrance of water and polar solvent such as ketone and alcohol, to the interphase region [4]. Sample 3 (silane AEAPS curing agent) obtains a balance of properties with polyfunctional epoxide and reactive coating agent. In the case of sample 3 (silane AEAPS curing agent), the high reactivity leads to improvement in properties of the epoxy resin, which provides good chemical resistance and hardness retention with the highly crosslinked network [8].