Synthesis and Characterization of High Temperature Resistance Interpenetrating Polymer Network

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ABSTRACT: Interpenetrating polymer network (IPN) polymer has been prepared by blending silicone resin polymer with the organic polymers such as polypyrrole [PPy] and polythiophene [PTh]. The IPNs were characterized by FTIR, NMR, and TGA/DSC analysis. The heat resistance performance of these IPNs were evaluated as per ASTM D2485. The result indicates that the IPN based on silicone-PTh has got superior heat resistant property than silicone-PPy. The electrochemical impedance measurements showed that the corrosion resistances of both the IPNs was similar. AFM morphological study confirms the influence of PPy/PTh on silicone polymer in forming smooth heterogeneous micro-structured IPNs. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2339–2344, 2011

Key words: interpenetrating polymer network; heat resistance; impedance measurements; atomic force microscope; thermal analysis

INTRODUCTION

Interpenetrating polymer network technology is of importance for a wide gamout of applications especially in coatings. Most IPNs exhibit poor ambient temperature curing due to complex chemistry and physics of their alloying characteristics.[1–4] Kordomenes et al. who are pioneers in this field have confirmed that IPNs including full, semi- and pseudo-types provide improved film properties in all aspects as compared with conventional coatings.[5] Silicone-based coatings have received much attention in the field of protective coatings for high temperature applications.[6–8]

In recent years, conducting polymers have been used as inhibitors for corrosion protection. The protective mechanism of conducting polymers is ascribed to intelligent release of inhibitor anions. However, conducting polymers and pigments fail to protect large defective areas, although they offer excellent protection to small defect sites.[9] Electrodeposited conducting polypyrrole film protects mild steel substrate from corrosion and reduces the corrosion rate considerably.[10] Similarly, polythiophene is used as an inhibitive pigment for the protection of steel substrate in marine environment. It is concluded that such pigment incorporated coatings give a 10-fold protection as compared with coatings without this conducting polymer.[11] These conducting polymers are also stable in high temperature environments. Verge et al.[12] who studied the thermal stability of conducting IPNs reported that the protection ability of these coatings improved considerably. Conducting polymers based on polybutadiene and thiophene derivatives were used as an actuator. It has been found that the function of this single layer actuator was similar to a three layer actuator.[13] Conducting polymer based IPNs are widely used in actuators, but their use in protective coating industry is not well explained.

Thus, in this study, a series of IPNs have been prepared by systematic variation of the concentration of silicone resin, pyrrole, thiophene monomers, and additives. The characteristics of the IPNs using different modern techniques such as FTIR, electrochemical impedance spectroscopy (EIS), NMR, AFM, and thermal measurement have been extensively dealt with. The nature of IPNs assessed from their characterization has helped to formulate the coating system for protection of steel structures from corrosion and high temperature applications.

EXPERIMENTAL

Materials

Pyrrole and thiophene (E.Merck) were purified by distillation. Nondrying silicone polymer (Metro-ark), benzyl peroxide (Qualigens), dibutyl tin dilaurate

(Aldrich), and xylene (Qualigens) were used as received.

Synthesis of IPNs

The synthetic method for generating IPNs have been explained by many researchers.[14,15] Our method is a slightly modified version of Meet Kamal's procedures and it is given below.[16] A series of IPNs were prepared by *in situ* polymerization during which the concentration of the silicone polymer in xylene with pyrrole (Table I) and with thiophene (Table II) were systematically varied for 15 h at 413 ± 5 K. The unreacted monomer present in the IPN was removed by Soxhlet extractor using xylene as solvent. The IPN formed was collected in a dried vessel and a 60% volume solid IPN was prepared by using xylene as solvent.

Surface studies

Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} using NEXUS 670 (FTIR), USA. Thermal stability of these IPNs was ascertained through TGA/DTA analysis using universal V4 3A SDT 2600 under pure nitrogen at a flow rate of 25 mL/min. The sample and the references were heated at a rate of 20°C/min. The phase changes and the glass transition temperature of the resins were measured using Perkin-Elmer differential scanning calorimeter, DSC-2. NMR spectrum was recorded on a Bruker 400 NMR spectrometer. Morphology and interpenetration behavior of the IPNs were studied by atomic force microscopy (AFM) using PICOSCAN 2000. The temperature resistance performance of the IPNs was evaluated in a furnace as per ASTM D2485.

Coated panel preparation

Mild steel panels of 7.5 cm × 5 cm size were sand blasted to Sa 2.5 specification[17] over which the IPNs was coated with a brush and dried for 14 days. The thickness of the coatings was measured using micro tester and the dry film thickness was found to be 30 + 5 μm.

TABLE I
Synthesis of IPNs Using Silicone Polymer and Pyrrole

IPNs	Silicone polymer (mol)	Pyrrole (mol)	Catalyst dibutyltin dilaurate (mol)	Initiator (mol)
IPN1	0.25	0.250	0.0025	0.001
IPN2	0.25	0.427	0.0025	0.001
IPN3	0.346	0.569	0.0025	0.001
IPN4	0.346	0.711	0.0025	0.001

TABLE II
Synthesis of IPNs Using Silicone Polymer and Thiophene

IPNs	Silicone polymer (mol)	Thiophene (mol)	Catalyst dibutyltin dilaurate (mol)	Initiator (mol)
IPN5	0.25	0.250	0.0025	0.001
IPN6	0.25	0.427	0.0025	0.001
IPN7	0.346	0.569	0.0025	0.001
IPN8	0.346	0.711	0.0025	0.001

A.C. impedance studies

Impedance measurements were made at open circuit potential using a PAR model 6310. A.C. impedance system using a three-electrode configuration with 1 cm^2 area of the exposed panel as the working electrode, platinum as the counter electrode, and a saturated calomel electrode as the reference electrode. Aerated 3% sodium chloride solution was used as electrolyte. The impedance measurements were carried out over a frequency range of 10 mHz to 100 kHz with a 20 mV peak to peak sinusoidal voltage. A computerized data analysis was used for Bode plot acquisition.

RESULTS AND DISCUSSION

Heat resistance study

One set of the coated panels were subjected to heat treatment as per ASTM specification D2485. The experiment was conducted for different durations of exposure at different temperature as per the specification. The failure of the IPN coatings was observed visually by color change, crack formation, and loss of adhesion.

The control, silicone resin coated panels withstood up to 533 K,[18] whereas the IPNs based on this silicone resin withstood up to 643 K. The IPNs of both (b) formulations did not change the glass temperature (643 K), and therefore, the experiment was continued up to 698 K for 8 h. The results indicate that these two systems performed well at this temperature with a slight decrease in glass. These two systems were characterized by FTIR, TGA/DSC, and AFM methods.

FTIR study

The FTIR spectrum of silicone-PPy IPN is shown in Figure 1. A broad absorption peak at 3422 cm^{-1} is assigned to the ─OH group and the peak at 3062 cm^{-1} is due to the presence of ═CH stretching. The peak at 2963 cm^{-1} is due to the presence of C─H, methyl, and methylene groups in the polymer. The peaks observed at 1597 cm^{-1} and 1518 cm^{-1}
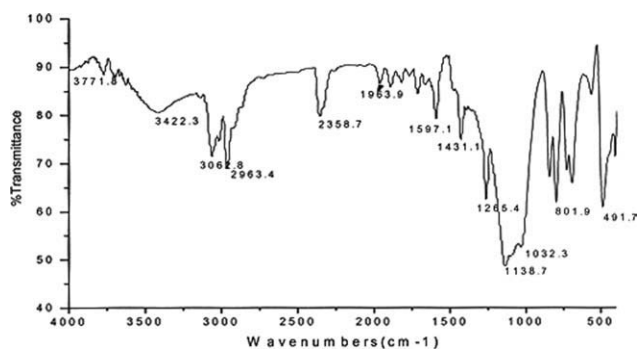
Figure 1 FTIR spectrum of silicone-PPy interpenetrating polymer network (IPN).

correspond to the C—C and C—N stretching vibrations in the pyrrole ring, respectively. The peak at 1597 cm^{-1} is also attributed to C=N stretching vibration of pyrrole ring present in the polymer. The peaks between 779 cm^{-1} and 850 cm^{-1} denotes the vibration of C—H stretches and the broad band between 750 cm^{-1} and 500 cm^{-1} indicates the C—C bond in the pyrrole without the plane ring deformation one similar at the same position, which is also explained by Ping.[19] The bonds characteristic of silicon atom attachments are reflected at 1265 cm^{-1} and 491 cm^{-1}, which correspond to the presence of Si—CH$_3$ and Si—O—Si bonds in the silicone resin. It can be seen that the major groups, namely, —CH$_3$ and —OH are directly attached to the silicone resin. The peaks at 1138 cm^{-1} is due to Si—O linkage and the band at 1032 cm^{-1} is due to —OH group of the silicone polymer.[20,21]

The FTIR spectrum of silicone-PTh IPN is shown in Figure 2. Absorption band at 1429 cm^{-1} belong to C=C symmetric stretching vibration of thiophene ring. The bands at 842 cm^{-1} and 693 cm^{-1} are assigned to C—S stretching of thiophene ring present in the IPN polymer.[13] The characteristic C—H stretching of thiophene at positions 2 and 5 are represented by the sharp peaks at 3050 cm^{-1} and
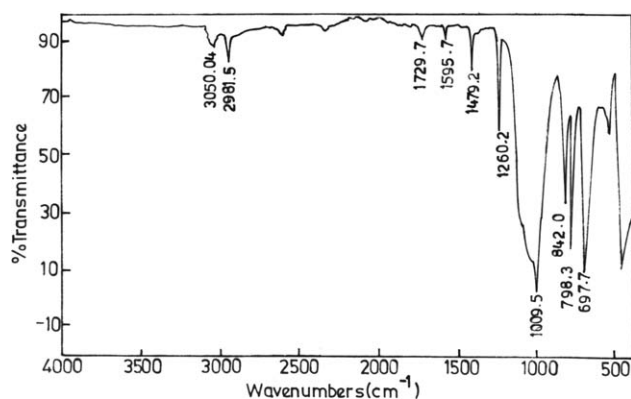

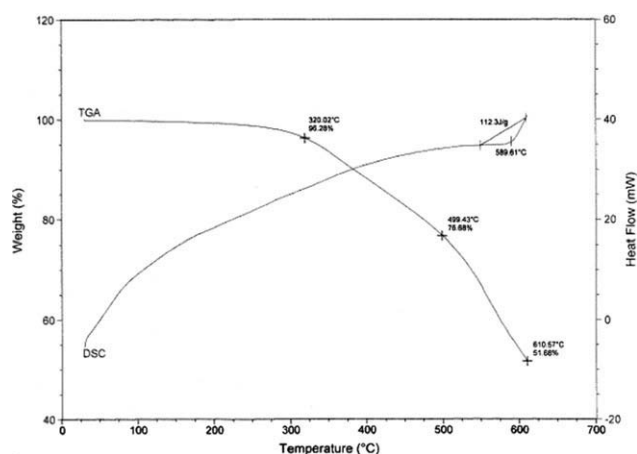**Figure 2** FTIR spectrum of silicone-PTh interpenetrating polymer network (IPN).

Figure 3 TGA/DSC analysis of silicone-PPy IPN resin.

763 cm^{-1}. These two peaks disappear in the spectrum of IPN polymer, but a small broad peak is seen in this position. This indicates that the formation of IPN occurred in this position of the thiophene moiety of the monomer. Two new bonds related to C—H out of plane bending of 2,5-disubstituted thiophene stretchings appeared at 842 cm^{-1}. The other characteristic peaks of silicone resin appearing in this case are also similar to the IPN of silicone-PPy.

Thermal stability

Figure 3 shows the TGA and DSC curves of silicone-Ppy IPN. The TGA for the IPN shows an almost horizontal line up to 593 K with a weight loss of 3.72%. This indicates that there is no change in the physical or chemical nature of the polymer up to 593 K. This small weight loss is due to evaporation of superficial water molecules and traces of unreacted monomers present in the IPNs. This initial degradation temperature (593 K) is higher than that of polypyrrole (433 K) synthesized by the electrochemical method.[15] Further, this delay in degradation of siloxane moiety
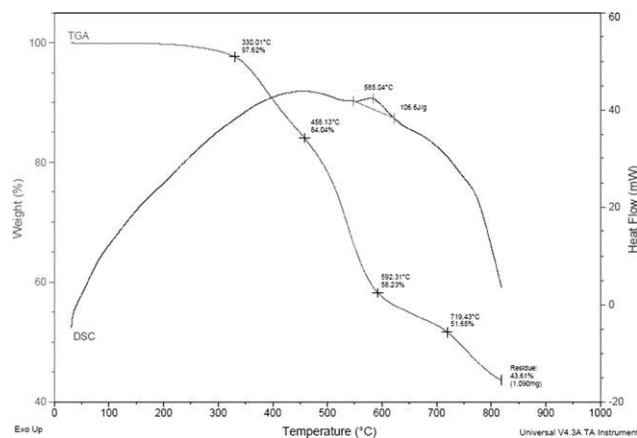

Figure 4 TGA/DSC analysis of silicone-PTh IPN resin.

Figure 5 ^{13}C NMRSpectra for silicone-PPy IPN resin.
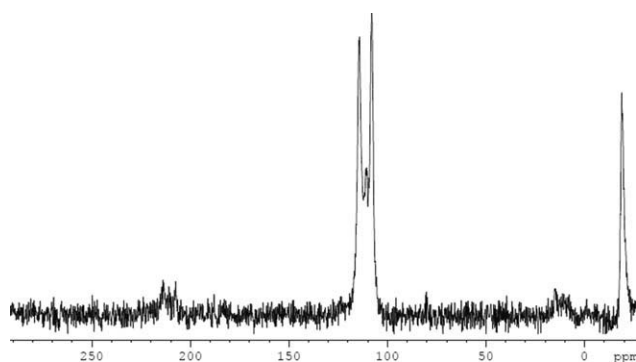

Figure 6 ^{13}C NMRSpectra for silicone-PTh IPN resin.

is also caused by the partial ionic nature of the IPN, high bond energy, and thermal stability of —Si—O—Si-linkage. Degradation of the IPN starts at 593 K stabilizing at about 772 K with a weight loss of 24%. This indicates that the bonding in the IPN gets weakened upon liberation of pyrrole molecules. At 883 K, the IPN changes into a powder with complete liberation of pyrrole from the IPN, the attendant weight loss being 49%. The higher weight retention of IPNs compared with the individual system was the characteristic phenomenon of IPNs.[17,22]

Similar behavior was also observed from the DSC studies. It is observed there is that no thermal reaction takes place up to 823 K. An endothermic reaction is seen between 823 K and 898 K with the absorption of 142.8 J g^{-1} of energy. This indicates that the IPN absorbed this much of energy to break the bonding between the silicone polymer and pyrrole linkages in the IPN and to disintegrate. The stable residue of 51% by weight indicates that the
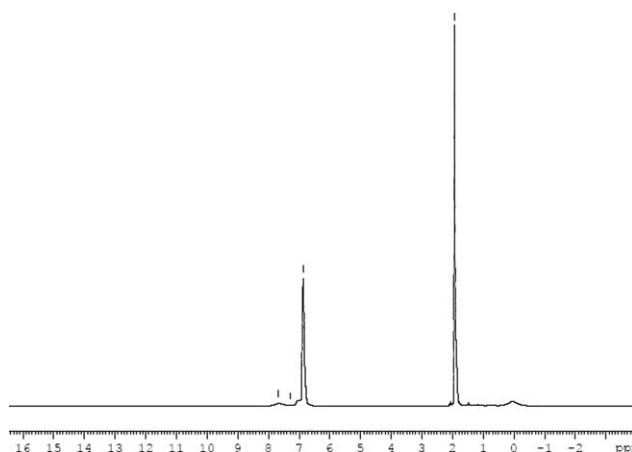
silicone-based polymers are thermally stable at high temperatures.

TGA/DSC profile of silicone-PTh is given in Figure 4. The thermogram shows that the degradation temperature of this IPN is slightly higher than that of silicone-PPy IPN. The IPN of silicone- PTh starts to decompose at 603 K with a weight loss of 2.2%. This weight loss is mainly due to loss of moisture in the IPN. After 603 K, the IPN decomposes with the loss of 41.8% at 865 K. The degradation temperature is also much above that of pure polythiophene (473 K) synthesized by an electrochemical method.[15] Thus, it is clear that the thermal stability of the silicone resin (decomposition temperature 533 K) is enhanced by the incorporation of polythiophene, which forms ionic linkages to siloxane moiety. Above 865 K, the IPN further disintegrates
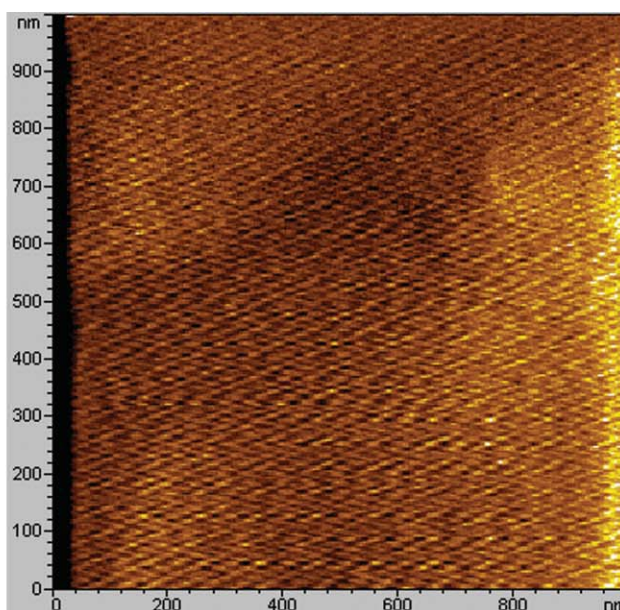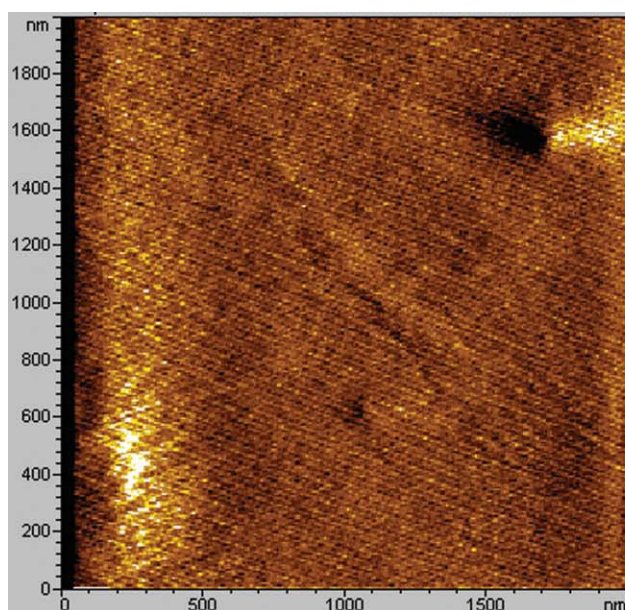

Figure 7 AFM image of silicone-PPy and silicone-PTh IPN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Impedance Data of Interpenetrating Polymer Network Coatings

Duration	Si-PTh IPN		Si-PPy IPN	
	R_t (Ω)	C_{dl} (F cm^2)	R_t (Ω)	C_{dl} (F cm^2)
1 h	1.438×10^7	5.685×10^{-8}	5.239×10^7	8.999×10^{-11}
1 day	2.810×10^6	1.208×10^{-6}	1.045×10^5	3.340×10^{-6}
7 days	2.368×10^6	6.448×10^{-11}	2.545×10^4	1.662×10^{-7}

leaving a 43.6% residue at 1088 K. It has been observed that the residual material is a brittle and glassy powder. In the DSC analysis, an exothermic peak is observed between 823 and 923 K accompanied by the liberation of 106.5 J g^{-1} of energy. This shows that the breaking of the siloxane-thiophene linkages takes place with the liberation of energy. Further more, the DSC study shows that the —Si—O— and —C—S— linkages in the IPN can be oxidized at around 858 K.

NMR spectroscopy

An NMR spectrum of the silicone-PPy IPN is shown in Figure 5. A sharp broad peak at 108.06 confirms that there is a branching in the third or fourth position of the pyrrole ring. The peaks at 114.48 and 114.19 indicate that the carbon atoms in the pyrrole ring are in two different environments. This result confirms the penetration of the pyrrole with the reactive sites of silicone to form the IPN. An NMR spectrum of the silicone-PTh IPN is shown in Figure 6. The solvent peaks can be seen at 1.942 and 1.938. The peaks at 7.670 and 7.287 confirm that there is a

branching in the second or fifth position of the thiophene ring. The peak at 6.866, 6.878, 6.886, and 6.891 confirm that there are four different types of carbon atoms in the IPN. This result indicates that the thiophene moiety penetrates into the siloxane reactive sites to form interpenetrated polymer network. In a similar manner, Kobayashi et al.[23] explained the NMR of silicone based IPN and confirmed the formation of IPN through intermolecular diffusion.

Morphology

Figure 7 shows the AFM surface morphologies of the silicone-PPy and silicone- PTh, IPNs. It is seen from the images that the surface is glossy with heterogeneous microstructures. The AFM surface profile of silicone-PTh is much more regular than that of silicone-PPy, suggesting that the silicone containing polymer matrices form new hybrid structured polymer systems when compared with the silicone resin. The heterogeneity of silicone-PTh IPN is higher when compared with that of the silicone-PPy IPN. Morphology and heterogeneity are among the most important characteristics of IPN polymers.
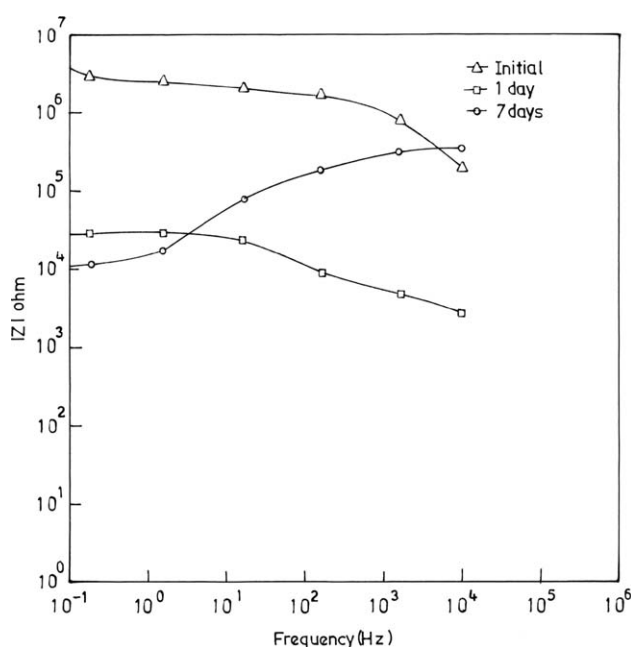

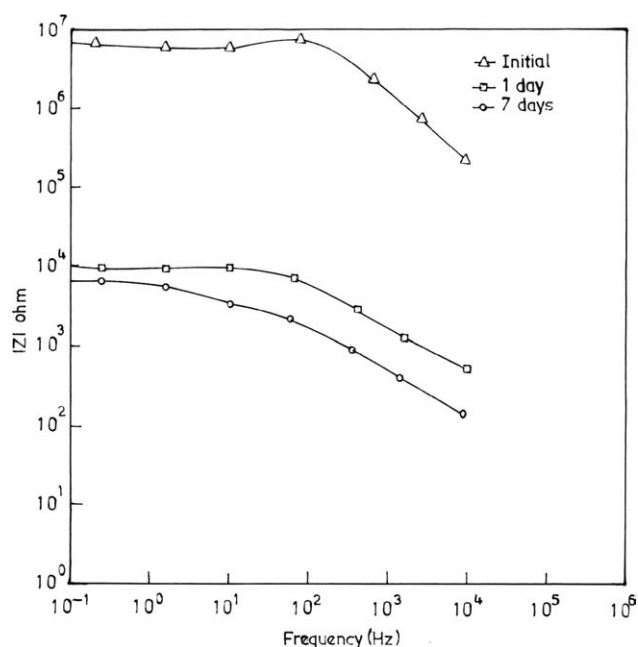**Figure 8** Impedance spectra of IPN$_3$ on M.S substrate in 0.5M NaCl solution.

Figure 9 Impedance spectra of IPN$_7$ on M.S substrate in 0.5M NaCl solution.

Addition of the conducting polymers alters the morphology of the silicone resin, as is reflected in our AFM study. Similarly, the morphological study of transparent IPNs film by Borsig et al. leads the correct composition of the crosslinking agent gives perfect domain of sphere structure for the IPNs by the AFM study.[24]

Electrochemical impedance measurements

Table III shows the resistance and capacitance values of IPN coated steel plates as derived from Bode plots in 0.5M NaCl solution for different durations. It is seen from the table that the resistance produced by these two IPN coating decreases with duration. The impedence spectra of IPN$_3$ and IPN$_7$ in 0.5M NaCl for 7 days are shown in Figures 8 and 9. An analysis of the Bode plots indicates that the IPN coatings are capacitive in nature. The nature of the impedance spectra is slightly inclined at an angle of 45° toward the frequency axis. With increasing duration of immersion, the curve starts to bend toward the frequency axis, suggesting that the resistance of the coating depends on the extend of penetration of water in the micro pores in the coating.[25] Pore resistance is a measure of the degradation of the coating. Further more, the pore resistance is related to the capillary channels in the IPN coating, which are perpendicular to the substrate surface through which the electrolyte can reach the coating substrate interface and initiate corrosion processes.[26] The impedance data shows a decrease in resistance for samples subjected to 7 days of immersion. From Table III, it is seen that the resistance exerted by the two IPN coatings are in the range of 10^6 to 10^7 Ω cm^2 in the initial stage, decreasing gradually to 10^4 Ω cm^2 after 7 days of immersion. This shows that the IPN coatings offer good protection to the steel in the initial stage, but after 7 days, the coatings exhibit resistance below the protective range (10^4 Ω cm^2). This is an indication of the electrolyte reaching the metal surface through the pores present in the IPNs. In this way Iron/IPN polymer interfacial wetting area is increased with a corresponding decrease in the charge transfer resistance.[27] This phenomenon is further supported by the capacitance values of the IPN coatings (Table III). It can be seen that the capacitance values increased from 10^{-11} F cm^2 to 10^{-7} F cm^2 during a period of 7 days for the IPN coatings. The C_{dl} values reach a steady state, suggesting that water penetration through the IPN coatings reach a saturation level. The capacitance and resistance values derived from the Bode plots of the IPN coatings are nearly the same. Thus, the corrosion behavior of these two IPN coatings is similar on steel substrate in saline solution.

CONCLUSIONS

Interpenetrating network polymers were prepared by using different molar ratios of silicone, pyrrole, thiophene, and initiators. IPNs with a molar ratio of silicone : PPy/PTh of 0.346 : 0.569 exhibited excellent heat resistance properties. FTIR results confirmed of siloxane moieties on the second and fifth positions of the PTh heterocyclic polymer. The thermal stability of silicone-PTh IPN was found to be significantly higher than that of the Silicone-PPy IPN. However, impedance results suggest similar corrosion resistance properties for the two IPNs. NMR spectral analysis indicates branching at the third or fourth position of the pyrrole ring with silicone polymer linkage, confirming IPN formation. Finally, AFM morphologies of the IPN coatings confirm the influence of PPy/PTh on silicone polymer to form smooth heterogeneous microstructures.

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