

Preparation and characterization of heat-resistant interpenetrating polymer network (IPN)

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Abstract

Interpenetrating polymer network (IPN) is a novel type of polymer hybrids, which possess physicochemical properties suitable for high performance coatings. Heat-resistant IPN have been prepared from immiscible resins, epoxy and silicones using a cross-linking agent and a catalyst. The products were analyzed by GPC, FT-IR, TG, DTA and SEM studies. The heat resistance property and corrosion behaviour of the IPNs were also determined. It was different from those of the individual resins. Silicone microdomains could be seen uniformly distributed in epoxy regions. Corrosion resistance property of the IPNs was evaluated by salt spray and impedance measurements. The IPNs withstood longer durations in the salt spray chamber.

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1. Introduction

Commonly available coating systems are heat resistant up to 333 K. As the operating temperature increases, the deterioration becomes rapid. Inorganic binder-based formulations perform well at high temperatures and protect the structure even at 1273 K if suitably pigmented [1]. Interpenetrating polymer network (IPN) are a novel type of polymer blends. This is a combination of chemically dissimilar polymers in which the chain of one polymer is completely entangled with those of another. The entanglement is permanent due to the homo-cross-linking of the polymers [2]. Preparation of high-temperature IPN composition from vinyl/acrylic copolymer with polystyrene/styrene–butadiene is known [3].

The present work deals with IPN in which two resins (epoxy and silicone resins), which are immiscible with each other, were combined by using a cross-linking agent and a catalyst. The formation of the IPN was characterized by gel permeation chromatography (GPC) [4], Fourier transform infrared spectroscopy

(FT-IR), thermogravimetry (TG), differential thermal analysis (DTA) [5,6] and scanning electron microscopy (SEM) [7].

2. Experimental

Two types of IPNs were prepared by using 50% resin solution of an air-drying silicone resin, epoxy resin and polyamidoamine hardener. The IPNs were prepared from these resin solutions after refluxing the resin composition with dibutyltin laurate as a catalyst and butyl titanate as a cross-linking agent at 353 K for 1 h. A description of the IPNs as well as thickness and drying time are given in Table 1.

The resin and the IPN were coated on sand-blasted mild steel substrates and dried for 7 days. The baking type silicone resin-coated panels were baked in an air oven for 15 min at 453 K. After complete drying, the resin and IPN-coated panels were characterized by GPC, FT-IR, TG, DTA and SEM. The coated panels were also subjected to salt spray tests. Their heat-resistance properties and electrochemical impedance were also investigated.

The molecular weight and polydispersity of the IPN were determined by using a software-controlled GPC (JASCO, a chromatopac). FT-IR spectra of the resins and the IPN were recorded using a Paragon-500 FT-IR spectrometer. TG and DTA curves

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Table 1
Composition of IPN

| System | Description | Drying time (h) | Thickness (μm) |
|--|------------------|-----------------|-----------------------------|
| Silicone air-drying type | Si ₁ | 2.5 | 22 \pm 2 |
| Silicone baking type | Si ₂ | 0.25 (393 K) | 21 \pm 2 |
| Epoxy–polyamidoamine | Ep | 4.0 | 20 \pm 2 |
| Epoxy–silicone with air-drying type–polyamidoamine | IPN ₁ | 1.0 | 22 \pm 2 |
| Epoxy–silicone with baking type–polyamidoamine | IPN ₂ | 1.0 (453 K) | 22 \pm 2 |

were traced in air by a simultaneous thermal analysis STA-1500 Polymer Laboratory to understand the thermal behaviour of resins and the IPNs. The entire system was software controlled (V400) for data processing and analysis. SEM studies were carried out by using a Hitachi.3000H scanning electron microscope.

Heat-resistance properties were carried out as per ASTM specification D2485. Salt spray tests were conducted as per ASTM standard B117. The A.C. impedance measurements were carried out in 3% sodium chloride solution as the electrolyte using a PAR model 6310 systems between 10 kHz and 100 mHz at applied signal amplitude of 10 mV. The impedance measurements were done periodically after 1 h, 1 day, 7 days and 15 days duration.

3. Characterization of resins and IPNs

3.1. Gel permeation chromatograph

The molecular weight of the two IPN namely, IPN₁ and IPN₂, were found to be 18,128 and 22,189, respectively. The dispersity index for IPN₁ (1.1399) and IPN₂ (1.2177) are

greater than 1, suggesting that the formation of the IPNs from the resin is homogeneous.

3.2. Fourier transform-infrared spectroscopy (FT-IR)

Figs. 1 and 2 depict the IR spectra for silicone resins Si₁ and Si₂, respectively. A broad absorption band between 1100 and 1020 cm^{-1} confirms the presence of Si–O bond in the resin. Sharp absorption peaks at 1450 and 1260 cm^{-1} indicate Si–CH₃ stretching in the molecules. The sharp peaks at 1593 cm^{-1} and 1495 cm^{-1} indicate the presence of aromatic C=C linkages in the silicone resin. The peaks in between 1660–2000 cm^{-1} show the presence of aromatic combination bonds. The broad peak in between 2700–3200 cm^{-1} indicates CH₂ stretches in the silicone resin and the peaks at 3500–3700 cm^{-1} show the presence free OH groups. Thus the silicone resin contain phenyl and methyl group and so it has the property of stability at high temperature application. Additional peaks appearing (Fig. 2) in the 840–800 cm^{-1} region indicate the presence of an excess amount of Si–CH₃ in this baking type silicone resin compared to that in the air-drying type silicone resin. This is inferred from the sharp peaks at 840–800 cm^{-1} upon drying the resin. Fig. 3 presents the IR spectra of the epoxy resin. Generally, the epoxy group shows three characteristic absorption bands at 1250, 916 and 830 cm^{-1} . These three characteristic peaks are observed in our spectrum and thus the presence of free epoxy terminal groups in the low-molecular weight epoxy resin is confirmed. Aliphatic secondary alcoholic groups are present in this molecule, which are indicated by the sharp peaks in the 1110–1107 cm^{-1} region.

Figs. 4 and 5 present the IR spectra of IPN₁ and IPN₂, respectively. The peaks of the epoxy and silicone resins are almost similar except for the absence of the peak at 1110–1107 cm^{-1} in the IPNs. This is probably due to the interlinking point of silicone

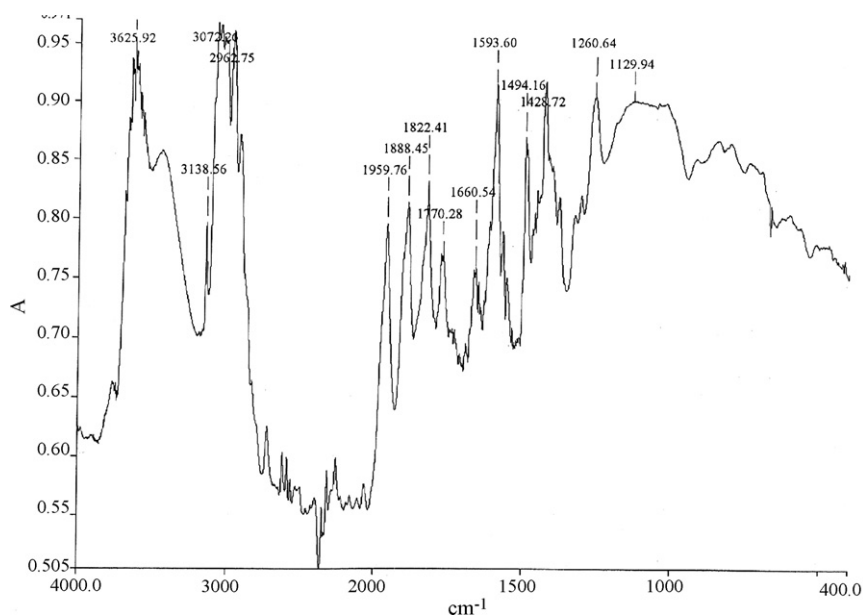


Fig. 1. IR spectrum for air-drying type silicone resin.

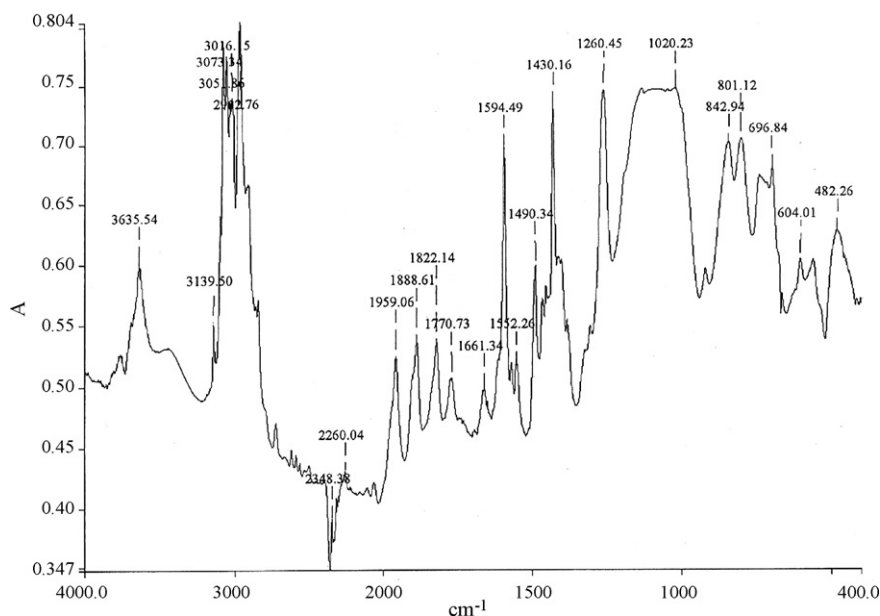


Fig. 2. IR spectrum for baking type silicone resin.

and the epoxy resin in the formation of IPNs. The presence of a broad band between 1035 and 1150 cm^{-1} confirms a Ti–O linkage followed by ester group, indicating an effective participation of the cross-linking agent during the formation of IPNs. The characteristic terminal epoxy group peaks remain unaltered in these IPNs. These epoxy groups further react with the polyamidoamine hardener and form hard-cured films over the surface.

3.3. Thermogravimetry/differential thermal analysis

TG for the air-drying type silicone resin, Si₁ (Fig. 6) shows an almost horizontal line along the temperature axis up to 548 K. This shows that there is no change in the physical and chemi-

cal properties of the resin up to 548 K. After 548 K this curve slowly falls up to 653 K. This may be due to a slow degradation of low-molecular weight resin fractions present in the coating. Beyond this temperature the thermogram shows a steady drop and reaches a residual value of 79% at 773 K. This is due to the decomposition of the resin into small molecules.

A broad exothermic curve is observed between 303 and 683 K with a maximum at 540 K. This indicates further polymerization reaction and formation of fused polymer coating on the surface, which protects the surface up to 540 K. Depolymerization followed by oxidation reaction takes place between 683 and 773 K. The appearance of a small exothermic peak suggests a further oxidation of the polymers in the coating.

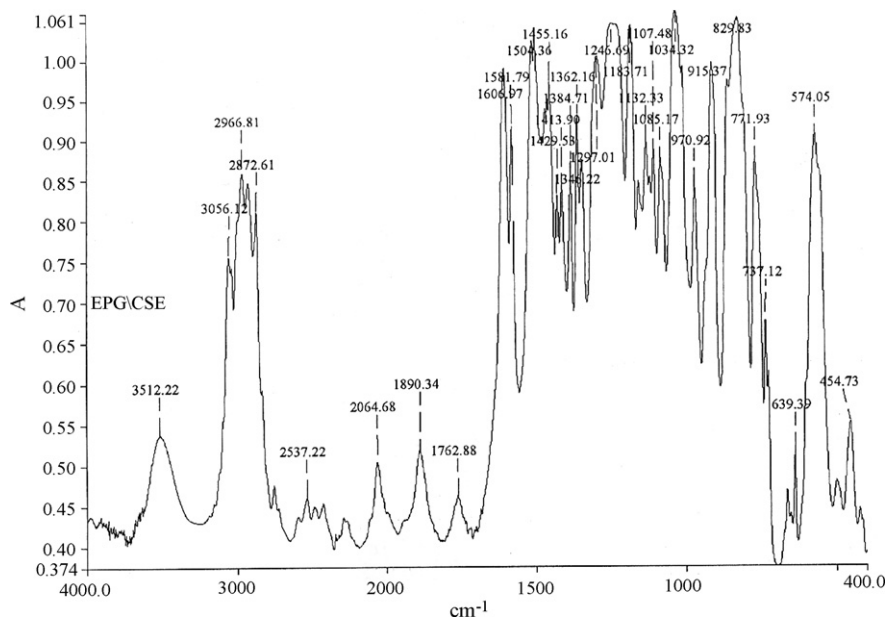
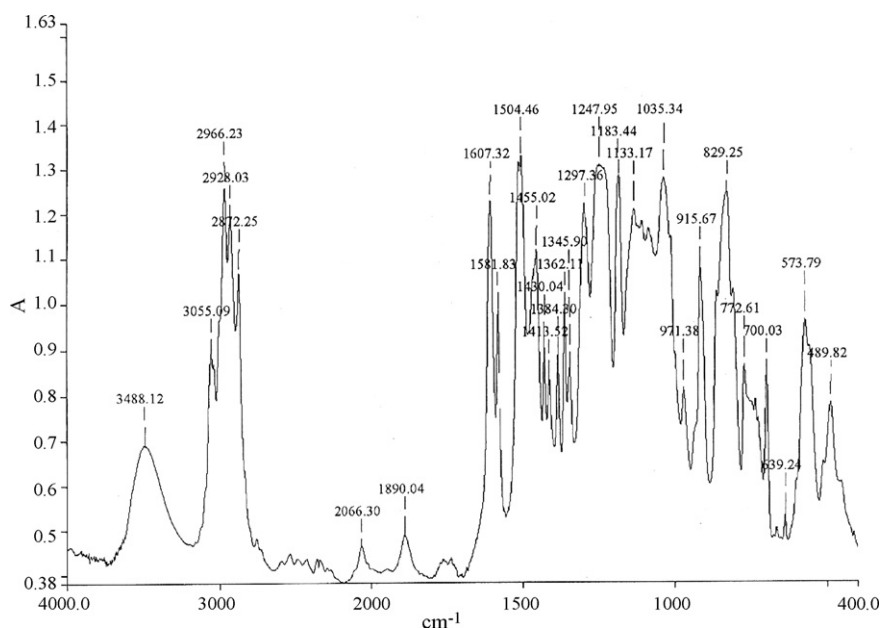


Fig. 3. IR spectrum for epoxy resin.

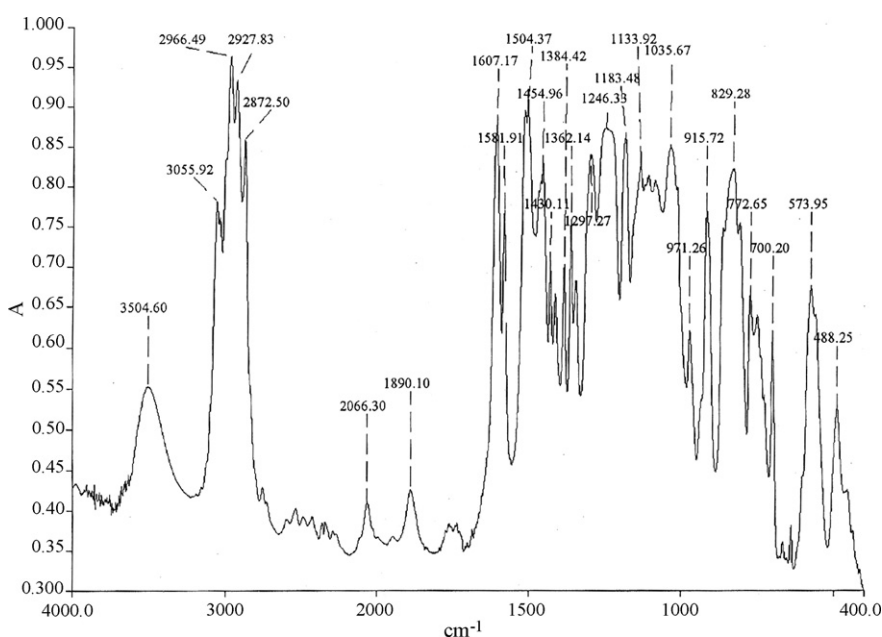
Fig. 4. IR spectrum for IPN₁.

The TG of the baking type silicone resin Si₂ (Fig. 7) shows a rising trend up to 533 K, beyond which it falls. This behaviour of the silicone resin is similar to that of the air-drying type except that the residue of the coating is 90% at 773 K. The DTA for the resin is also similar to that for the air-drying type with a continuous exothermic profile or a hump from 323 to 773 K with a maximum at 533 K. Unlike in the Si₁ system, the small exothermic reaction peak between 723 and 773 K is not seen in this coating suggesting that after an initial region of stability up to 473 K, there is a continuous degradation of the coating.

The TG of the cured epoxy resin (Fig. 8) shows an initial rise up to 353 K and a constant plateau near 393 K. Thereafter a sharp drop is observed at 473 K. This indicates that the coating

system is stable up to the glass transition temperature (393 K) and then thereafter decomposition reaction takes place with the formation of water and carbon dioxide leaving 92% in residual mass. The DTA shows a constancy in the energy absorbed up to 353 K, followed by region of no change up to 473 K.

Fig. 9 shows the thermal behaviour of IPN₁. The TG curve indicates a horizontal line up to 423 K followed by slow degradation (473 K), suggesting the absence of any significant thermal event in this region. A slow degradation trend can be observed up to 653 K, the corresponding weight loss being 29%. This suggests that the stability of the resin is ascertained up to 473 K, beyond which decomposition takes place with fragmentation into small molecules by chemical reaction between reactive

Fig. 5. IR spectrum for IPN₂.

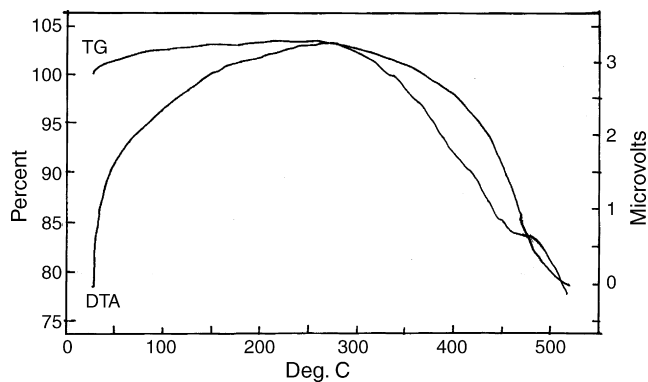


Fig. 6. Thermal behaviour of air-drying type silicone resin.

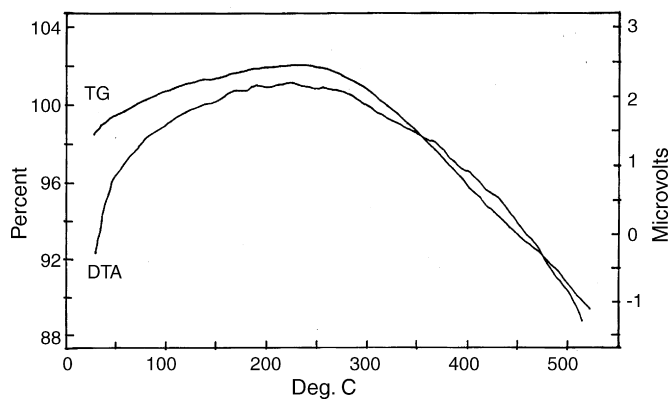


Fig. 7. Thermal behaviour of baking type silicone resin.

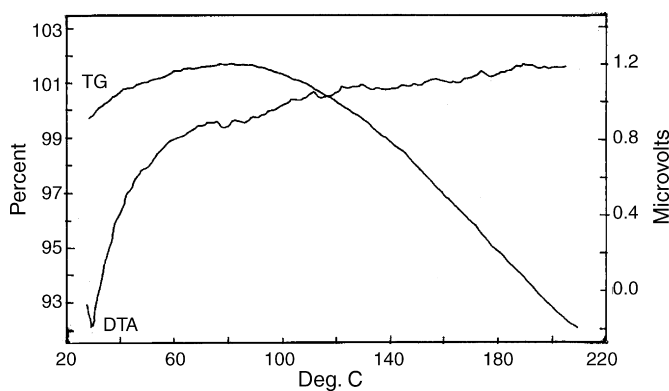
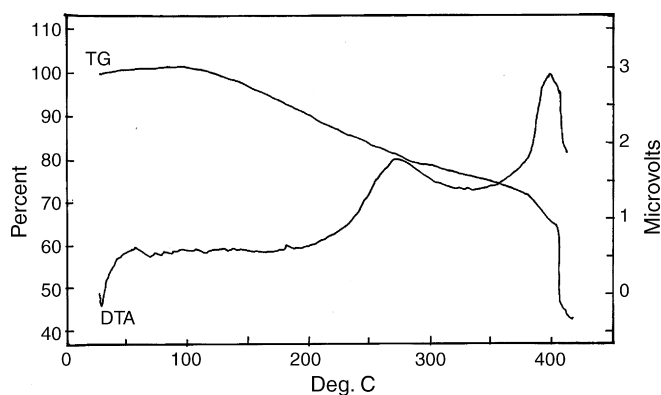
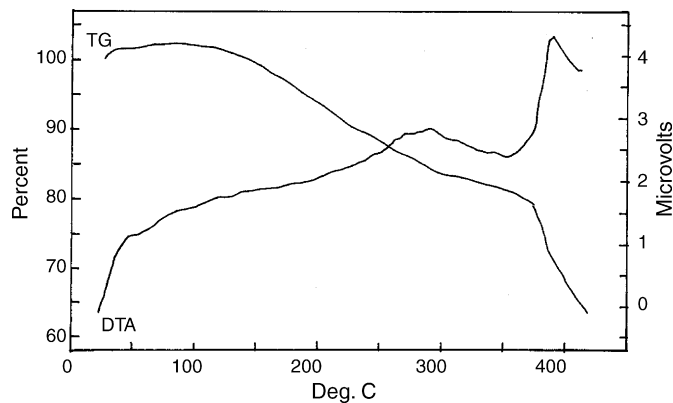


Fig. 8. Thermal behaviour of epoxy-polyamidoamine resin.

Fig. 9. Thermal behaviour of IPN₁.Fig. 10. Thermal behaviour of IPN₂.

functionalities of the resin and the hardener. Above 653–677 K, a sudden weight loss of 55% is noticed. In this temperature range an oxidation reaction followed by some bond breakage may be expected.

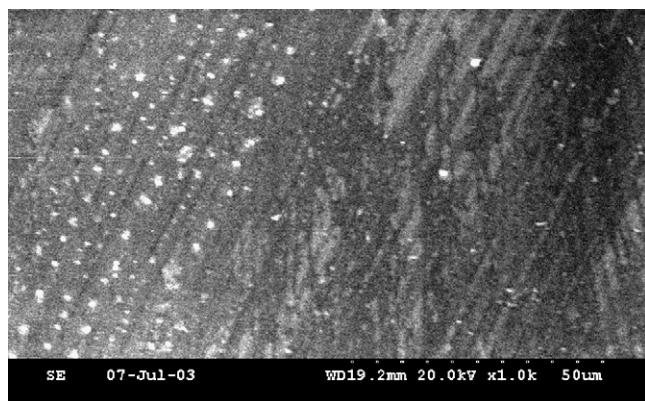
The DTA results indicate that initially an exothermic reaction takes place between 303 and 333 K. Hence the inter-linking bond is further strengthened in the IPNs. In the temperature range 333–523 K, there is no discernible effect on the IPN, but some rearrangements may be expected because of consumption of energy by the system. Above 523–623 K, a broad band due to some exothermic process is observed, which suggests the formation of higher cross-linked polymers in the IPN. In the temperature range 623–673 K an exothermic reaction with a narrow band is observed. Dissociation of the polymeric IPNs into smaller molecules (amorphous powder products) is inferred.

The TG and DTA curves of IPN₂ (Fig. 10) show a trend similar to that of IPN₁. The only differences between the two IPNs are the steep breakdown between 653 and 677 K and a weight loss of 35% for IPN₂. This lower weight loss may be due to a better cross-linking of the baking-type silicone resin with the epoxy resin.

3.4. Surface morphology of IPNs

SEM images of IPN₁ and IPN₂ are shown in Figs. 11 and 12, respectively. The silicone microdomains are distributed all over

Fig. 11. SEM photograph of IPN₁.

Fig. 12. SEM photograph of IPN₂.

the epoxy region of IPN₁ and IPN₂. But it is very clearly seen from these figures that the degree of entanglement is more in IPN₂ than in IPN₁, since the microdomains are more uniformly distributed in the former.

4. Heat-resistance property of the resins and the IPNs

The failure of the coating was observed visually by colour change, chalking, blistering, cracking and loss of adhesion (Table 2). The silicone resins withstood up to 533 K, whereas the epoxy-polyamidoamine coating performed well up to 423 K. But both the IPNs remained stable up to 478 K in terms of colour and gloss retention. The heat resistance property of the epoxy resin was improved by the silicone resin through the formation of the IPN. The gloss of the IPN did not change at that temperature. The gloss was changed at 533 K although no cracking or chalking failure was noticed on the surface. This suggests that the IPNs are stable at 533 K. This enhancement in heat resistance property of the epoxy resin is due to an extensive entanglement of the silicone resin with the epoxy polymer. This permanently entangled homopolymer has good heat resistance and corrosion resistance properties.

Table 2
Heat-resistance properties of the resin and IPNs

| System | Temperature (K) | Observation |
|-----------------------|-----------------|---|
| Silicone (air drying) | 433 | Colour—no change; gloss—slightly reduced |
| Silicone (baking) | 433 | Colour—no change; gloss—slightly reduced |
| Epoxy-polyamide | 423 | Colour—changes into brown; gloss—slightly reduced |
| IPN ₁ | 478 | Colour—change into brown; gloss—no change |
| IPN ₂ | 478 | Colour—changes into brown; gloss—no change |

Table 3
Results of salt spray tests

| System | Period of exposure (h) | Observation |
|-----------------------------|------------------------|------------------------------|
| Silicone resin (air drying) | 30 | Formation of red rust |
| Silicone resin (baking) | 30 | Formation of minute rust |
| Epoxy resin polyamidoamine | 80 | Formation of minute blisters |
| IPN ₁ | 90 | Formation of minute blisters |
| IPN ₂ | 95 | Formation of minute blisters |

5. Accelerated salt spray test

Silicone resin-coated panels failed within 30 h of exposure. This is due to the poor corrosion resistance property of this resin (Table 3). The epoxy resin-coated panels withstood for 80 h in the salt spray experiment, which proves the corrosion resistance of this resin in neutral medium. The IPN-coated panels performed better in the neutral environment suggesting that there is hardly any interaction of the functionality with the corrosive chloride ions.

6. Electrochemical impedance measurements

From the Bode plots the charge transfer resistance (R_t) was measured (Table 4.). The values of the charge transfer resistance obtained with the silicone resins are in the 10³ Ω cm² range which decreased to about 10² Ω cm². This is due to a thin film formed by the silicone resin, which easily allows penetration of the corrosive sodium chloride into it. The epoxy resin-coated panels exerted high resistance in the order 10⁷ to 10⁶ Ω cm² even after 15 days. This is due to the stable ether linkage between the resin and the hardener aiding good adhesion with the substrate, which makes the resin highly resistant in the sodium chloride environment [8]. The resistance produced by the IPN-coated panels are in the protective range, that is in the order of 10⁷ to 10⁵ Ω cm². The R_t value for IPN₂ is higher than that for IPN₁, suggesting a stronger interpenetrating network in IPN₂ than in IPN₁. This is due to the large number of reactive polar groups present in the baking type silicone resin formulation. The protective films formed by these IPNs do not allow permeation of the corrosive ion to the substrate and protects the substrate from corrosion.

Table 4
Effect of time on the charge transfer resistance of resin coating on steel

| System | Charge transfer resistance, R _t (Ω cm ²) | | | |
|-----------------------------|---|---------------------|---------------------|---------------------|
| | 1 h | 1 day | 7 days | 15 days |
| Silicone resin (air drying) | 4 × 10 ³ | 7 × 10 ³ | 1 × 10 ³ | 5 × 10 ² |
| Silicone resin (baking) | 3 × 10 ⁴ | 5 × 10 ³ | 8 × 10 ² | 8 × 10 ² |
| Epoxy-polyamidoamine | 2 × 10 ⁷ | 1 × 10 ⁷ | 5 × 10 ⁶ | 2 × 10 ⁶ |
| IPN ₁ | 2 × 10 ⁶ | 9 × 10 ⁵ | 5 × 10 ⁵ | 2 × 10 ⁵ |
| IPN ₂ | 4 × 10 ⁷ | 5 × 10 ⁶ | 5 × 10 ⁶ | 2 × 10 ⁶ |

7. Conclusions

Heat-resistant interpenetrating polymer networks (IPN) were prepared from epoxy and silicone resins with polyamidoamine as hardener. The formation of IPNs is confirmed by GPC, FT-IR, TG, DTA and SEM analysis. The GPC data indicate that the formed IPNs are homogeneous in nature. The FT-IR spectra show the presence of Ti–O linkage in the IPN molecules. The TG/DTA and heat resistance studies confirm the superior heat resistance properties of the IPNs as compared to the individual resins. SEM images suggest that the silicone grains are uniformly distributed throughout the epoxy resin confirming the formation of IPNs. Salt spray tests reveal improved chemical resistance of the IPNs. The IPN made with the baking type silicone resin was superior than the ones produced with epoxy resin and the air-drying type silicone resin. This is due to the excess

reactive polar groups present in the baking type silicone resin, which form strong IPN with the epoxy resin.

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