structure could not resist heat at 950°C for the 60 min duration due to absence of inorganic ingredient which can enhance the char resistance.

The expansion of IF2-BA is 3 times lower than the char expansions of all the other formulations. The temperature of substrate was 331°C after 30 minutes and it increased to 360°C after 60min, as shown in Figure 4.80. Figure 4.82(b) shows the char of IF2-BA, no cracks or holes are observed in the char. The IF2-BA contains 11.76% of boric acid and IF1-Mel contains 11.76 wt% of melamine; this composition is the possible reason for the less char expansion and low substrate temperature. IF2-BA formulation bonded well with the substrate. The bonding or adhesion is due to the reaction of boric acid with APP forming borophosphate and boron oxide, which form the final protective layers on the substrate.

The char of IF3-BA-Mel formulation showing holes and cracks can be seen in Figure 4.82(c); the appearance of holes and cracks is due to the lesser weight percentage of boric acid compared to that of melamine in the coating. The substrate temperature after 30 minutes was 385 °C and increased to 480°C after 60 minutes. This temperature is 10°C higher than IF1-Mel, and 80°C higher than IF2-BA. The char expansion of the IF3-BA-Mel is 7.5 times, and is 4.5 times higher than IF2-BA and 2.5 times lower than IF1-Mel as shown in Figure 4.81. The presence of melamine expands the char, and boric acid provides the resistance to heat with the formation of borophosphate and boron oxide protective layers on the steel substrate. The char could not protect the substrate due to less percentage of boric acid used, which is 5.5 wt% of the total coating composition.

Figure 4.82(d) shows the char photograph of IF4-BA-Mel formulation, the char expansion is 5.3 times which is 5.7 times lower than IF1-Mel, and 2.27 times lower than IF3-BA-Mel. However, the expansion is 2.37 times higher than IF2-BA due to the presence of blowing agent (Mel) as shown in Figure 4.81. The substrate temperature of the IF4-BA-Mel after 30 minutes was 342°C which is lower by 83°C compared to IF1-Mel, and 93°C compared to IF3-BA-Mel. The substrate temperature of IF4-BA-Mel after 60 minutes was 27°C higher to IF2-BA as shown in Figure 4.80. Increasing the wt% of boric acid shows a decrease in char expansion while the heat shielding effect of the formulation increased. Figure 4.82(d) shows cracks on the
surface of char but the char stick to the substrate. The substrate temperature gradually increased after 60 minutes due to the cracks in the char. Figure 4.82(e) shows the cross-sectional view of IF5-BA-Mel char. The char expansion was 4.6 times which decreased further as the wt% of boric acid was increased up to 11.11wt%. The substrate temperature of IF5-BA-Mel was 337°C after 30 minutes. The substrate temperature was 367°C after 60 minutes which is 103, 113, 20°C less than IF1-Mel, IF3-BA-Mel, and IF4-BA-Mel, respectively whereas 7°C higher than IF2-BA. Jimenez at al. [12] reported the substrate temperature 450°C after 60 minutes fire test, obtained from thermoset resin/APP/boric acid coating formulation.

Figure 4.80: Time and substrate temperature curve of boric acid and Mel ICF

Figure 4.81: Char expansion of boric acid and Mel ICF
Char photograph: (a) IF1-Mel cracks inside (b) IF2-BA thick char

(c) IF3-BA-Mel showing crack and holes due to the oxidation of the char (d) IF4-BA-Mel cracked surface

(e) IF5-BA-Mel small cracks on the surface (f) Cross sectional view of IF5-BA-Mel char

Figure 4.82: Char photograph (a,b,c,d, e and f): after fire test by Bunsen burner
4.6.2 Char morphology of boric acid and melamine ICFs

The SEM micrographs of char from the four coating formulations IF1-Mel, IF2-BA, IF4-BA-Mel and IF5-BA-Mel are given in Figures 4.83 to 4.85.

Figure 4.83(a, b) show the outer and inner surface of the IF1-Mel. The outer surface of char shows a smooth char layer without any cracks observed; while the inner surface of char shows some cracks and holes. From the results of heat shielding, the substrate temperature was increased to 470°C after 60 minutes; this is supported by the SEM results which shows the char morphology. The inner structure of char is cracked and could not stop the heat flow to the substrate. Figure 4.84(a) shows the morphology of IF2-BA; the inner surface of char is very thick and porous with holes which are produced due to dehydration of coating during the fire test. The inner structure of IF4-BA-Mel char formulation in Figure 4.84(b) also have the same structure as IF2-BA, but there are cracks on the inner surface of the IF4-BA-Mel which increased the substrate temperature 27°C more than IF2-BA formulation during the fire test. The char morphology of IF5-BA-Mel formulation is shown in the Figure 4.85 (a,b). The inner surface of char is thick, and porous with bubbles which formed due to the emission of CO₂ and NH₃ gases during the fire test. These bubbles expanded the char. The EDX analysis is indicates the presence of phosphate inside the char as shown in Figure 4.86. It explains the dehydration that took place during charring of APP, boric acid, EG and melamine with cured epoxy resin in the respective temperature range with the formation of borophosphate and boron oxide. The multiporous arrangement in the char can hinder heat transfer to the substrate. The heat transfer rate through the char layer depends on the resistance of substrate to fire. The expansion of char and char structure are very vital to common fire retardant properties of coating [84]. The charring layers of intumescent formulation with bubbles protect the steel substrate.
Figure 4.83: (a) IF1-Mel outer surface (b) IF1-Mel inner surface

Figure 4.84: (a) IF2-BA inner surface with thick porous char layers (b) IF4-BA-Mel inner surface with thick porous and crack surface

Figure 4.85: (a) IF5-BA-Mel multiporous cellular inner surface (b) IF5-BA-Mel showing agglomerates

Figure 4.86: Figure 4.87: EDX of IF5-BA-Mel char
4.6.3 Composition of boric acid and melamine ICFs char

At high temperature the char layer gradually oxidizes, only some amorphous carbon and inorganic materials remained. The inorganic materials become an important protecting shield at later stages of fire when the temperature is higher than 600°C [67]. The residual char of IF1-Mel, IF3-BA-Mel, IF4-BA-Mel and IF5-BA-Mel were analyzed by XRD and the results are presented in Figures 4.87 and 4.88.

Figure 4.87 shows a comparison of XRD spectra between IF1-Mel and IF3-BA-Mel in which IF1-Mel shows a peak at $2\theta = 26.5^\circ$ and $d$ spacing of 3.34 characteristic of carbon from graphite (JCPDS card no 12-0212). While IF3-BA-Mel char shows three peaks; the first peak at $2\theta = 25^\circ$, $d = 3.67$ is characteristic of borophosphate (JCPDS card no 34-0132), and the next peak is of carbon from graphite same as in IF1-Mel, and the last one at $2\theta = 40^\circ$ and $d = 2.25$ is characteristic of boron oxide (JCPDS card no 06-0297).

Figure 4.88 is the XRD analysis of IF4-BA-Mel and IF5-BA-Mel. Both formulations have almost the same peaks to their specific $2\theta$ and $d$ value. The first peak represents boron oxide at $2\theta = 15^\circ$ and $d = 4.56$, the next peak is borophosphate at $2\theta = 25^\circ$ and $d = 3.64$, graphite is identified at $2\theta = 26.5^\circ$, $d = 3.38$, sassolite (JCPDS card no 13-0570) at $2\theta = 27^\circ$ and $d = 3.15$, and the last peak is boron phosphate oxide (JCPDS card no 01-0519) at $2\theta = 40^\circ$ and $d$ value of 2.25.

The XRD results have shown that the products of reaction between boric acid, melamine, APP and $O_2$ can improve the anti-oxidation performance of the coating. So the formation of high temperature products such as boron oxide, borophosphate and graphite can protect the substrate from fire above 800°C.
4.6.4 Functional groups of boric acid and melamine ICFs char

FTIR was used to determine the functional groups of the compounds formed in the char during fire test. The FTIR spectra of IF1-Mel, IF4-BA-Mel and IF5-BA-Mel char...
are presented in Figures 4.89 to 4.91. The FTIR spectrum of IF1-Mel representing the phosphate and amide region is presented in Figure 4.89. In the region of phosphate, P-O-P in the range of 800--1400cm$^{-1}$ at 972cm$^{-1}$ shows the presence of P-O asymmetric vibration in the chain of P-O-P phosphate, and PO$_4^{3-}$ is present at 1140cm$^{-1}$. Carbonyl stretching of CH$_2$ or CH$_3$ stretching occurred at 1402cm$^{-1}$ and three weak bands of amino groups are observed namely C-N at 3162cm$^{-1}$, C=N at 2440cm$^{-1}$, C≡N at 1621cm$^{-1}$. In the region from 1380 cm$^{-1}$ to 1700cm$^{-1}$, the peaks at 1619, and 1521, are due to the amino groups (NH$_2$) and the peak at 1429cm$^{-1}$ belongs to ring(C N) [133].

Figures 4.90 and 4.91 have almost the same spectra as the ingredients in the formulations are the same and both were subjected to the same environment of fire test; the only difference is the amount of melamine and boric acid used in the formulations. In the region of P-O-P from 1400 to 800cm$^{-1}$, the peak at 936cm$^{-1}$ represents the presence of P-O asymmetric vibration in the P-O-P chain while the symmetric vibration is present at 1084cm$^{-1}$. The asymmetric vibration of P-O group occurred in the region of 890-950cm$^{-1}$ and the P-O symmetric vibration of P-O-P chain is in the 1400-1080cm$^{-1}$ region [121, 150].

In the 2$^{nd}$ region from 1380-1700cm$^{-1}$, there are two peaks at 1413 and 1615cm$^{-1}$ representing the stretching vibration of CH$_2$ or CH$_3$ deformation vibration, and polyaromatic compound, respectively. In the 3$^{rd}$ region above 2100cm$^{-1}$ there are two weak bending peaks at 2833, 3467cm$^{-1}$ which represent the bending vibrations of (-CH$_3$- CH$_2$-) and O-H groups. The results suggest that there are two main stages of thermal degradation, the first stage occurred between 400 and 500°C and the second stage occurred between 600 to 700°C. As shown in Figure 4-74, at the first stage the residues containing phosphorus, -CH$_3$, -CH$_2$ and aromatic compounds save some structure of cured epoxy resin with the interactions between EG, cured epoxy resin. As the burning continues, APP, boric acid, melamine, and residues from the first stage decomposed further (at the second stage) to form a compact char. When this happens, the concentration of cured epoxy resin decreases eventually leaving only polyaromatic and phosphorus compounds to react with boron and form boron phosphate and boron oxide and sassolite that are the main composing of the char at 950°C. These results agree with the analysis of X-ray diffraction.
Figure 4.89: FTIR spectrum of IF1-Mel char

Figure 4.90: FTIR spectrum of IF4-BA-Mel char

Figure 4.91: FTIR spectrum of IF5-BA-Mel char
4.6.5 Residual weight and DTGA of boric acid and melamine ICFs

The degradation of boric acid and melamine has been reported in the previous section of residual weight of intumescent coating based on two ingredients. The residual weight of the formulations IF1-Mel, IF2-BA, IF4-BA-Mel and IF5-BA-Mel from TGA is 22.64, 29.96, 25.85 and 28.58%, respectively as illustrated in Figure 4.92. TGA results show that the formulation IF1-Mel has a lower residual weight than the formulation IF2-BA. Since other ingredients in these both formulations are same, the higher residual weight percentage of the formulation IF1-BA could be contributed by boric acid.

The formulation IF4-BA-Mel has a lower residual weight percentage than formulation IF5-BA-Mel due to lesser concentration of boric acid in IF4-BA-Mel. These results seem to suggest that boric acid and/or its degradation/reaction products are the main components of the final protective structure that develops when the intumescent coating is exposed to fire.

The derivative of thermogravimetric analysis (DTGA) is used to determine the degradation temperature of ICF. DTGA curves of IF1-Mel, IF2-BA, IF4-BA-Mel and IF5-BA-Mel are illustrated in the Figures 4.93 to 4.96.

From Figure 4.93, there are two degradation temperatures of IF1-Mel i.e. 289 °C and 400°C which represent the decomposition of melamine and other intumescent ingredients such as APP, EG, epoxy and hardener. Melamine starts to decompose after 290°C and reacts with APP to form melamine phosphate [11, 131].

The DTGA curve of IF2-BA presents that the decomposition of IF2-BA occurred at three temperatures 129°C, 409 °C and 469°C as indicated in Figure 4.94. At 129°C, the degradation of boric acid starts. The 2nd degradation temperature shows the degradation of melamine and APP, and the next one is the degradation of melamine phosphate at 469°C due the chemical reaction product of the coating formulation [12].

Figure 4.95 shows the decomposition temperature of the respective component in the formulation IF4-BA-Mel: boric acid into boron oxide at 178°C, melamine at 284°C, melamine phosphate at 387°C, and boron phosphate to borophosphate at 456°C. The slight variation in temperature derivation especially at 387°C and 456°C,
compared to the results reported in Figures 4.93 and 4.94, is due to higher weight percentage of melamine than boric acid in ICF.

The DTG curve of IF5-BA-Mel is shown in Figure 4.95. As can be observed in the figure, at 130°C boric acid starts to decompose into metaboric acid which is further converted into boron oxide. The decomposition of melamine starts at 284°C, while the decomposition of melamine phosphate starts at 425°C and boron phosphate starts to decompose at 475°C. In these results, the decomposition temperatures change as the result of increasing the amount of boric acid in the formulation relative to melamine.

The results of TGA and DTGA show similar behaviour of thermal degradation for each of the coating as the coatings contain the same intumescent materials. However, the residual weight percentage is increased with increased amount of boric acid.

![Figure 4.92: TGA of IF1-MEL, IF2-BA, IF4-BA-Mel, and IF5-BA-Mel ICF](image)
Figure 4.93: DTGA of IF1-Mel coating showing two steps degradation

Figure 4.94: DTGA of IF2-BA coating showing three steps degradation

Figure 4.95: DTGA of IF4-BA-Mel coating showing five steps degradation
4.6.6 Conclusion of boric acid and melamine ICFs

The fire resistant time of boric acid and melamine based coating formulations were lowered the substrate temperature by various degrees. The coating IF2-BA and IF5-BA-Mel show better heat shielding as indicated by the lowered substrate temperature, 360 °C for IF2-BA and 367°C for IF5-BA-Mel after 60 minutes. The SEM results show that the cellular structure of char improves (formation of cellular structure) by increasing the wt% of boric acid relative to melamine. Results from XRD and FTIR show the presence of boron oxide, graphite and borophosphate in the residual char. TGA and DTGA show that boric acid can enhance the weight of residue more effectively than melamine. Boric acid forms boron oxide and sassolite layers on the surface of the substrate and act as the protective barrier during fire. Thus, the heat transfer can be reduced and this gives a better effect of intumescent to the coating formulations.

4.7 Effect of boric acid and APP on ICFs with 300µm EG

From Table 3.18, five formulations were prepared to study the effect of boric acid and APP on heat shielding and char expansion. The formulations were further characterized by XRD, FTIR, SEM and TGA.
4.7.1 Heat shielding and char expansion of boric acid and APP ICF

Five samples of coating with different compositions of intumescent ingredients were burned at 950°C; photographs of the resultant char are shown in Figure 4.99. Time versus substrate temperature curve for heat shielding/insulation is illustrated in Figure 4.97, and the char expansion results are shown in Figure 4.98. The char expansion results are as follows: 2 (IF1-BA), 9.6 (IF2-APP), 7.61 (IF3-BA-APP), 6.34 (IF4-BA-APP), and 5.27 (IF5-BA-APP) times, from their original coating thickness. The order of the char expansion is IF2-APP > IF3-BA-APP > IF4-BA-APP > IF5-BA-APP > IF1-BA. The formulation IF2-APP attained the highest char expansion of 9.6 times from its original coating thickness due to the presence of APP (acid source, initiated the chemical reaction and formed a carboneous char) which expands the char. Initially the formulation expanded uniformly, but with the progressing fire over time it was oxidized and could not protect the steel substrate.

The substrate temperature of IF1-BA and IF2-APP after 30 minutes is 374 and 416°C, and after 60 minutes they the temperature reached 503 and 470°C, respectively as reported in Figure 4-80. The IF1-BA contains EG, melamine, boric acid and epoxy resin with hardener; the char structure could not sustain at 950°C for 60min as there was no reaction product which can trim down the temperature. Figure 4.99(a, b) show the char photograph of IF-BA and IF2-APP with cracked char surface. The substrate temperature of IF3-BA-APP was 385 and 480°C after 30 and 60 minutes respectively. This temperature is 23°C less than IF1-BA and 10°C higher than IF2-APP. Figure 4.99(c) shows that the surface of IF3-BA-APP char is also cracked and oxidized.

The char expansion of IF4-BA-APP is 6.34 times which is 220 percent higher than that of IF1-BA, but 50 percent and 18.75 percent less than IF2-APP and IF3-BA-APP, respectively. Apparently, the decrease in the weight percentage of APP resulted in reducing the char expansion of ICF, as APP is an acid source which reacts with rich polyhydric carbon source to form carboneous char [12]. Figure 4.99(d) shows a better looking IF4-BA-APP char compared to the other chars. The substrate temperature of IF4-BA-APP formulation reached 339°C after 30 minutes and 385°C after 60 minutes. This substrate temperature is 118°C less than IF1-BA, 85°C than IF2-APP, and 95°C is, than IF3-BA-APP after 60 minutes. Figure 4.99(d) of char
photograph of burnt IF4-BA-APP formulation shows the existence of cracks on the surface. The cracks gradually increased the substrate temperature to 385°C after 60 minutes. The substrate temperature of IF5-BA-APP was 359°C after 30 minutes, and reached 421°C after 60 minutes. This substrate temperature is 82°C less than IF1-BA, 49 °C less than IF2-APP, 59°C less than IF3-BA-APP but 36°C higher than IF4-BA-APP. Figure 4.99(e) of char photograph of IF5-BA-APP shows wide cracks on the surface. In general, the addition of boric acid into xxx reduces char expansion but on the other hand increases adhesion of char to substrate. From the literature, it was reported that when APP and boric acid were combined into the resin; the temperature of steel substrate reached 400°C in 29.5min in contrast to 4min when epoxy resin was used alone, and the char remains well stuck on the substrate [12]. Increasing the wt% of boric acid in ICF decreases the expansion, is while heat shielding is increased up to 11.11wt% of boric acid.

Figure 4.97: Time and substrate temperature curve of boric acid and APP ICF

Figure 4.98: Char expansion of boric acid and APP ICF
Char morphology of boric acid and APP ICFs

The SEM micrographs of IF1-BA, F2-APP, IF3-BA-APP, IF4-BA-APP and IF5-BA-APP char are shown in Figure 4.100 (a, b, c, d and e). Figure 4.100 (a, b) shows cracked microstructure on the surfaces of IF1-BA and IF2-APP. Figure 4.100(c) shows char morphology of IF3-BA-APP, which is similar to the structure of inner layer of IF2-APP with cracked surface and gaps. The layers of flakes found inside of the char structure of IF4-AB-APP shown in Figure 4.100(d) are due to increased amount of boric acid relative to APP. The char morphology of IF5-BA-APP formulation in Figure 4.100(e) shows a thick and porous inner surface with the
bubbles formation which is formed due to emission of gaseous compounds during the fire test. These gaseous compounds are produced from the thermal degradation of ICF during the fire test.

(a) IF1-BA showing bubbles and cracks  
(b) IF2-APP showing rough and cracked surface  
(c) IF3-BA-APP cracked surface,  
(d) IF4-BA-APP thick char with flakes  
(e) IF5-BA-APP inner cellular surface with agglomerates

Figure 4.100: SEM images (a, b, c, d, e) showed the char morphology of boric acid and APP ICF
4.7.3 Char composition of boric acid and APP ICFs

The residual char of IF1-BA, IF2-APP, IF4-BA-APP and IF5-BA-APP were analyzed by XRD and are shown in Figures 4.101 and 4.102. The XRD analyses of IF1-BA and IF2-APP are compared in Figure 4.101. Both spectra have a peak at \(2\theta = 26.5^\circ\) and \(d\) value = 3.47 which belongs to graphite (carbon). These two formulations do not have any reaction products in the char. As for IF4-BA-APP and IF5-BA-APP, five peaks are observed as shown in Figure 4.102. The first peak at \(2\theta = 15^\circ\) and \(d\) value = 4.56 represents boron oxide. Borophosphate is observed at \(2\theta = 25^\circ\) and \(d\) value = 3.61, while graphite sassolite and boron phosphate oxide show their peaks at \(2\theta = 26.5^\circ\) and \(d\) value = 3.37. The last two peaks at \(2\theta = 27^\circ\) and \(40^\circ\), and \(d\) values of 3.17 and 2.25 represent sassolite and boron phosphate oxide, respectively.

The results of XRD confirms that the reaction between boric acid with APP, melamine, EG and \(O_2\) occurred to form the protective layer in the residual char consisting of borophosphate, sassolite, boron oxide.

Figure 4.101: XRD spectra of IF1-BA and IF2-APP ICF char
4.7.4 Functional groups of boric acid and APP ICFs char

The functional groups of boric acid and APP ICF char are determined using FTIR analysis. The FTIR spectra of IF1-BA, IF2-APP, IF3-BA-APP, IF4-BA-APP and IF5-BA-APP char are presented in Figures 4.103 to 4.107. The FTIR spectra of IF1-BA char in Figure 4.103 shows two regions of absorption. In the 1st region, the three bands at 743, 1029 and 1418 cm\(^{-1}\) are attributed to \(\nu(B-O-H)\) stretching mode, \(\delta(B-O-H)\) deformation bond, and \(\nu(B-O)\) stretching bond, respectively [134]. In the 2nd region above 2100 cm\(^{-1}\), three weak bending peaks occurred at 2921, 3219 cm\(^{-1}\) and 3394 cm\(^{-1}\) which represent the weak stretching vibrations of (-CH\(_3\)- CH\(_2\)-) and O-H groups.

The FTIR spectrum of IF2-APP char in Figure 4.104 shows three regions of absorption. In the low frequency side, at 494 cm\(^{-1}\) of the spectrum is attributed to \(\nu_4\) regions of PO\(_4\) [151]. The two broad bands centered on 1151 and 970 cm\(^{-1}\) are characteristic of phosphate anion [134, 140, 141]. In the region from 1380 – 1700 cm\(^{-1}\), the peaks at 1633 and 1402 cm\(^{-1}\) are due to amino groups (NH\(_2\)) and ring(C, N), respectively. In the 3rd region above 2100 cm\(^{-1}\), one stretching peak at 2627 cm\(^{-1}\) vibrations of (-CH\(_3\)- CH\(_2\)-) and two weak bending peaks at 3154 and 3450 cm\(^{-1}\) are
identified the O-H groups. The spectra of IF3-AB-APP, IF4-BA-APP and IF5-BA-APP are shown in Figures 4.105, 4.106 and 4.107, respectively. The spectra look almost similar as the ingredients and testing environment during fire test are the same. The difference in the formulations is in the amount between APP and boric acid.

In the Figures 4.105, 4.106 and 4.107, the B-O-P bending motions are observed at 613, 618, 644 cm\(^{-1}\) [25, 26] and O-P-O are observed at 548, 537 and 539 cm\(^{-1}\), respectively. The peak from 548-537 cm\(^{-1}\) in B\(_2\)O\(_3\) is assigned to \(\delta (O-B-O)\) mode. The two bands in the range of 975-824 cm\(^{-1}\) and 1089-1185 cm\(^{-1}\) are the stretching mode of \(\nu (B-O-P)\) [134]. The bending vibrations observed at 1412, 1436 and 1446 cm\(^{-1}\) of CH\(_2\) or CH\(_3\) are due to epoxy binder, while the C≡C stretching vibration at 1630 cm\(^{-1}\) is due to epoxy binder and APP derivative in the char. In the second region around 2257-2348 cm\(^{-1}\) a strong stretching vibration characteristic of C=N is due to polyamide hardener. In the region above 2400 cm\(^{-1}\), a single broad peak at 2495–2895 cm\(^{-1}\) is a weak bending peak due to the bending vibration of CH\(_3\)-CH\(_2\) and a double peak at 3213, 3405, 3467 cm\(^{-1}\) is identified as the weak bending peaks of O-H group. Both types of peak originate from the epoxy binder. The functional group of residual char compounds is identified by FTIR spectroscopy which revealed that the char contains functional groups of borophosphate, phosphate oxide, boron oxide, -CH\(_3\)-CH\(_2\) and aromatic compounds obtained from the reaction between EG, APP, boric acid, melamine and cured epoxy resin during the fire test. These results agree with the analysis of X-ray diffraction of Boric acid and APP formulations.

![Figure 4.103: Figure 4.114: FTIR spectrum of IF1-BA-APP char](image-url)
Figure 4.104: FTIR spectrum of IF2-BA-APP char

Figure 4.105: FTIR spectrum of IF3-BA-APP char

Figure 4.106: FTIR spectrum of IF4-BA-APP char
4.7.5 Residual weight and DTGA of APP and boric acid ICFs

The residual weights of boric acid and APP ICF are shown by the TG curves in Figure 4.108. The residual weight of each formulation at 800°C is: 22.6 wt% (IF1-BA), 19.3 wt% (IF2-APP), 18.19 wt% (IF3-BA-APP), 24 wt% (IF4-BA-APP) and 28.35 wt% (IF5-BA-APP).

The TGA results show that the formulation IF1-BA has 17 percent higher residual weight than formulation IF2-APP as the residual weight of boric acid and APP at 800°C is 54.14% and 4.14% respectively. The higher residual weight of boric acid contributed to an increase in the residual weight of IF1-BA. The TG curve shows that increasing the weight percentage of boric acid relative to APP increases the total residual weight. The residual weight of IF5-BA-APP formulation is 28.35%, which is 49 percent higher than that of IF3-BA-APP and 18 percent higher than the residual weight of IF4-BA-APP. Based on these results, it is possible that boric acid, APP and/or their degradation/reaction products are main components in the final protective layer developed in the char when the intumescent coating is exposed to fire.

The DTGA curves of IF1-BA, IF2-APP, IF3-BA-APP, IF4-BA-APP and IF5-BA-APP are shown in Figures 4.109 to 4.113. Four degradation curves of IF1-BA are observed at 84°C, 118°C, 288°C and 427°C as illustrated in Figure 4.109. The first curve represents the decomposition of epoxy, second curve - boric acid, third curve -
melamine, and the fourth curve - the other intumescent ingredients such as EG, epoxy and hardener. Melamine starts its decomposition after 280°C and cured epoxy binder decomposes around 427°C.

The DTGA curve of IF2-APP in Figure 4.110 shows five degradation curves at 104°C, 294°C, 356°C, 368°C and 476°C. At 104°C showed the dehydration of H₂O from epoxy and hardener. The 2nd degradation temperature shows the degradation of melamine. The 3rd and 4th degradation occurred at 358 and 368°C due to decomposition of APP, oxidation of EG. The 5th degradation occurred at 476°C due to the epoxy binder and the reaction products of APP and melamine. The formulation IF3-BA-APP, IF4-BA-APP and IF5-BA-APP contain EG, APP, melamine, boric acid, epoxy and hardener which show the degradation of all the intumescent ingredients at their respective degradation temperatures.

The degradation curves of ICF formulations incorporated with boric acid and APP namely IF3-BA-APP, IF4-BA-APP and IF5-BA-APP are presented in Figures 4.111 to 4.113. In these figure, it is observed that the decomposition of boric acid into meta boric acid occurred at 121°C, 124°C and 121.6°C. Further conversion of meta boric acid into boron oxide occurred at 153°C, 172°C and 167°C. The decomposition of melamine and APP occurred at 309°C, 302°C and 294°C. The decomposition of EG and epoxy is observed at 353°C, 379°C and 359°C. The maximum degradation occurred after 400°C; specifically at 462°C, 427°C and 424°C. At these temperatures, the degradation is of cured epoxy, decomposition of melamine derivatives and APP, and the reaction product such as melamine phosphate. In these results, the degradation temperature of the respective components in the formulations has been shifted due to increased amount of boric acid relative to the amount of APP.

The results of TGA and DTGA also show similar behaviour of thermal degradation for each of these formulations as they contain the same intumescent ingredients. However, the percentage of residual weight is slightly from one formulation to another the weight percentages of the two ingredients (boric acid and APP) in each formulation are different. Thus coating IF5-BA-APP that contains the highest amount (11.55wt %) of boric acid gives the highest residual weight compared to other formulations.
Figure 4.108: TGA of boric acid and APP ICF

Figure 4.109: DTGA curve of IF1-BA formulation showing four steps degradation

Figure 4.110: DTGA curve of IF2-APP formulation showing five steps degradation
Figure 4.111: DTGA curve of IF3-BA-APP showing five steps degradation

Figure 4.112: DTG of IF4-BA-APP showing six steps degradation

Figure 4.113: DTG of IF5-BA-APP formulation showing seven steps degradation
4.7.6 Conclusion of boric acid and APP ICFs

The incorporation of boric acid and APP into ICF, either singly or together, improves fire retardant properties of the ICF formulations. This is evident from the measurement of substrate temperature which shows that the substrate temperature has been lowered by various degrees. The formulations IF4-BA-APP and IF5- BA-APP have shown better results on the substrate temperature, 385°C and 421°C respectively after 60 minute fire test. SEM results show improvements in the structure of residue char flakes when the wt% of boric acid was increased relative to APP. XRD and FTIR results confirm the presence of boron oxide, graphite, borophosphate, sassolite and boron phosphate oxide in the residual char. TGA and DTGA results have shown that boric acid enhances the residual weight of char which contributes towards reducing penetration of heat to the substrate.

4.8 Effect of APP and EG on ICFs

From Table 3.19, five formulations IF-APP, IF2-EG, IF3-APP-EG, IF4-APP-EG and IF5-APP-EG were prepared to study the effect of APP and EG on heat shielding, char expansion, morphology, composition of char and residual weight. Their characterization was done using SEM, XRD, FTIR, and TGA.

4.8.1 Heat shielding and char expansion of APP and EG ICF

The time versus substrate temperature curve of APP and EG ICF is shown in Figure 4.114 and the expansion of char after fire test of each formulation is shown in Figure 4.115.

The substrate temperature of IF1-APP and IF2-EG after 30 minutes was 397°C and 374°C, and after 60 minutes it was 464 °C and 503°C, respectively as reported in Figure 4.114. The substrate temperature of IF3-BA-APP was 390 °C after 30 minutes and 489°C after 60 minutes, which is 14°C lower than IF2-EG but 25°C higher than IF1-APP. The IF3-APP-EG composition was modified by adding 11.76wt% of APP relative to 5.8wt% of EG.
The substrate temperature of IF-APP-EG after 30 min is 375 °C and after 60 min the temperature reached 461°C. The substrate temperature of IF5-APP-EG coating after 30 minutes and 60 minutes are 346°C and 389°C, respectively. The substrate temperature of IF5-APP-EG is 389°C after 60 minutes which is 75°C lower than IF1-APP, 114°C lower than IF2-EG, 100 °C lower than IF3-APP-EG, 72°C lower than IF4-APP-EG. The IF5-APP-EG provided good heat shielding to substrate as apparently a few cracks were observed on the char surface as shown by the photograph in Figure 4.116.

The char expansion of IF1-APP, IF2-EG, IF3-APP-EG, IF4-APP-EG, and IF5-APP-EG is 6.4, 2, 8.7, 7.5 and 6.2 times, respectively from original coating thickness; a comparison of their char expansion values is illustrated in Figure 4.115. The order of the char expansion is IF3-APP-EG > IF4-APP-EG > IF1-APP > IF5-BA-APP > IF2-EG. The formulation IF3-APP-EG has the best char expansion of 8.7 times, which is contributed by the amount of, APP (11.76 wt%) and EG (5.8 wt%).

![Time and substrate temperature curve of APP and EG ICF](image)

Figure 4.114: Time and substrate temperature curve of APP and EG ICF
4.8.2 Char morphology of APP and EG ICF

The SEM micrographs of char from the five coating formulations IF1-APP, IF2-EG, IF3-APP-EG, IF4-APP-EG and IF5-APP-EG are provided in Figure 4.117(a, b, c, d, e). Figure 4.117 (a, b) show the outer surfaces of IF1-APP and IF2-EG where cracks are observed. Figure 4.117 (c, d and e) show the char microstructures of IF3-BA-APP, IF4-BA-APP and IF5-BA-APP where layers of graphite flakes inside the char structures can be observed. The appearance of layers of graphite flakes is attributed to the increased weight percentage of EG in the formulations. Flakes layers increased with weight percent of EG (5.8, 8.33 and 11.11wt %). The formation of flakes itself hinder the heat flow to the underlying substrate.
Figure 4.117: SEM images (a, b, c, d, e) showed the char morphology of APP and EG ICF.

4.8.3 Char composition of APP and EG ICFs

The residual char sample of IF1-APP, IF2-EG, IF4-APP-EG and IF5-APP-EG formulations are analyzed by XRD analysis as shown in Figures 4.118 to 4.120. IF1-APP shows two peaks at $\theta = 25, 40^\circ$, and $d$ values = 3.61 and 2.25, assigned to borophosphate and boron phosphate oxide, respectively in Figure 4.118. IF2-EG
shows a peak at $\theta=3.37$ and $d$ value is 26.5° of graphite in Figure 4.118. As for IF4-APP-EG and IF5-APP-EG, five peaks are observed as shown in Figures 4.119 and Figure 4.120, respectively. In both spectra, the respective peaks appear at the same $\theta$. The peaks are identified as follows: at $(\theta=15^\circ, d=6.05)$ - boron oxide, $(\theta=25^\circ, d=3.65)$ - boron phosphate, $(\theta=26.5, d = 3.37)$ – graphite (carbon), $(\theta = 27^\circ, d = 3.17)$ - sassolite, and $(\theta = 40^\circ, d = 2.25)$ - boron phosphate oxide. Comparing the XRD spectra of IF4-APP-EG and IF5-APP-EG, the intensity of the borophosphate peak in Figure 4.19 (25 to 50 counts) is (25 to 30 counts) lower than that in Figure 4.120. This is due to decreased wt% of APP in IF5-APP-EG, and the intensity of graphite in Figure 4.120 is increased as contains 11.11wt% higher amount of EG. The reaction products in the char are determined from XRD results, which show that boric acid and APP react to form borophosphate and boron oxide in the residual char. The presence of APP and EG in the coating formulations impart a significant effect on the char composition.

Figure 4.118: XRD spectra of IF1-APP and IF2-EG char
4.8.4 Functional groups of APP and EG ICFs Char

Figures 4.121 to 4.123 present the FTIR spectra of IF1-APP, IF4-APP-EG and IF5-APP-EG. The FTIR spectrum of IF1-APP showing the phosphate and melamine region is shown in Figure 4.121. In the region of phosphate (P-O-P) from 1400-800 cm$^{-1}$, phosphate PO$_4^{3-}$ is present at 919 and 1087cm$^{-1}$. In the melamine region, carbonyl stretching of CH$_2$ or CH$_3$ stretching is observed at 1411cm$^{-1}$, two weak bands of band of amino groups: C=N -2440 cm$^{-1}$, and C≡N-1621cm$^{-1}$ and one weak
band of O-H at 3416 cm\(^{-1}\). The region 1380–1700 cm\(^{-1}\) is assigned to the amino groups (NH\(_2\)) and the absorption peak at 1624 cm\(^{-1}\) is assigned to ring (C, N) [133].

Figures 4.122 and 4.123 have the same spectra as the ingredients of coating and fire test environment are same. The difference is in the amount of APP and EG between IF4-APP-EG and IF5-APP-EG formulations. In region of P-O-P (1400-800 cm\(^{-1}\)), two peaks are observed; at 919 cm\(^{-1}\) represents the presence of P-O asymmetric vibration in the chain of P-O-P while the symmetric vibration is present at 1084 cm\(^{-1}\). This is in agreement with phosphate group where The asymmetric vibration of P-O group occurred in the region of 890-950 cm\(^{-1}\) and the P-O symmetric region of P-O-P chain is 1400-1080 cm\(^{-1}\) [140, 141].

The bending vibrations observed at 1412, 1436 and 1446 cm\(^{-1}\) of CH\(_2\) or CH\(_3\) are due to epoxy binder, while the C≡C stretching vibration at 1630 cm\(^{-1}\) is due to epoxy binder and APP derivative in the char.

In the 2\(^{nd}\) region between 1380-1700 cm\(^{-1}\), the two peaks at 1418 cm\(^{-1}\) belong to bending vibrations of CH\(_2\) or CH\(_3\) and 1622 cm\(^{-1}\) belongs stretching vibration of C≡C due to epoxy binder and APP derivative in the char in IF4-APP-EG char. The peak at 1449 cm\(^{-1}\) in IF5-APP-EG char represents the stretching vibration of CH\(_2\) or CH\(_3\) deformation vibration, due to polyaromatic compounds.

In the 3\(^{rd}\) region above 2100 cm\(^{-1}\), two weak bending peaks occurred at 2885, 3219 cm\(^{-1}\) represents the bending vibrations of (-CH\(_3\)-CH\(_2\)-) and O-H at 3413 cm\(^{-1}\) groups in spectrum of IF4-APP-EG Figure 4.122. In the spectrum of IF5-APP-EG char, the four stretching peaks observed at 2255, 2385, 2534 and 3219 cm\(^{-1}\) are characteristic of C=N stretching vibrations of (-CH\(_3\)- CH\(_2\)-) group. The functional groups of APP and EG formulations are almost the same as reported earlier for boric acid/melamine and boric acid/APP formulations.
Figure 4.121: FTIR spectrum of IF1-APP char

Figure 4.122: FTIR spectrum of IF4-APP-EG char

Figure 4.123: FTIR spectrum of IF5-APP-EG char
4.8.5 Residual weight and DTGA of APP and EG ICFs

TG curves showing the residual weight percentage of APP and EG formulations are illustrated in Figure 4.124. At 800°C, the residual weight retained by the coating formulations IF1-APP, IF2-EG, IF4-BA-APP and IF5-BA-APP is 21.3%, 19.66%, 27.3% and 28.25%, respectively. The order of residual weight percentage is IF5-APP-EG > IF4-EG-APP > IF1-APP > IF2-EG.

TGA results show that formulation IF1-APP has 8.6 percent higher residual weight than formulation IF2-EG. IF1-APP contained 11.76wt% of APP, 5.88 wt% of boric acid which formed stable borophosphate compound during thermal degradation of the coating and increased the residual weight of the char. While IF2-EG does not contain any reaction product due to the absence of APP as confirmed by the XRD spectrum shown in Figure 4.118. A comparison of residual weight among the four formulations show that IF5-APP-EG has the highest residual weight which is 33% more than IF1-APP, 44 % more than IF2-EG, and 4 % more than IF4-BA-APP. This observation is the result of increasing the concentration of EG in the formulations IF3-APP-EG, IF4-APP-EG and IF5-APP-EG relative to APP. This is supported by the TGA results in Figure 4.13 showing that EG retained 87.48 % of its weight at 800°C.

The derivative of thermo gravimetric analysis (DTGA) curves of IF1-APP, IF2-APP-EG, IF4-APP-EG and IF5-APP-EG are given in the Figures 4-125 to 4-128. Five degradation curves are shown at 147°C, 328°C, 371°C, 422°C and 464°C for IF1-APP as illustrated in Figure 4.125, representing the decomposition of boric acid, melamine, APP and cured epoxy. The DTGA curves of IF2-EG in Figure 4.126 show four degradation temperatures 121°C, 153°C, 311°C and 473°C. The degradation at 121°C and 151°C is characteristic of boric acid degradation into meta boric acid and boron oxide, and at 311°C and 473°C are the oxidation of EG and decomposition of melamine and cured epoxy binder.

The degradation curves of formulations IF4-APP-EG and IF5-APP-EG which are composed of EG, APP, melamine, boric acid, epoxy and hardener are shown in Figures 4.127 and 4.128. In Figure 4.127 and 4.128, the decomposition of boric acid into meta boric acid is observed at 121°C, but further conversion of meta boric acid into boron oxide is observed at 166°C in Figure 4.127, and at 144°C in Figure 4.128. While the decomposition of melamine, EG and APP occurred at 283°C in Figure
Degradation of melamine and APP derivatives, cured epoxy, and the reaction products such as melamine phosphate occurred after 400°C, specifically 420°C, 407°C and 476°C. In these results, the degradation temperature of the formulations has been shifted due increased weight percentage of EG relative to APP. The results of the TGA and DTGA show a similar behaviour of thermal degradation for each of the samples as the samples contain the same intumescent materials. However, the residual weight percentage has also increased as the result of increasing the wt% of EG. The coating IF5-APP-EG has the highest residual weight (28.25%) compared to other APP and EG formulations.

Figure 4.124: TGA of APP and EG ICF

Figure 4.125: DTGA curve of IF1-APP showing five steps of degradation
Figure 4.126: DTGA curve-IF2-EG showing four steps of degradation

Figure 4.127: DTGA curve IF4-APP-EG showing four steps of degradation

Figure 4.128: DTGA curve of IF5-APP-EG showing five steps of degradation
4.8.6 Conclusion of APP and EG ICFs

Based on the above results, the formulation IF5-APP-EG has the best insulating property (heat shielding) as indicated by the substrate temperature after 60 minutes of fire test which is the lowest among all other formulations. The recorded temperature of 389°C is 75°C, 114°C, 100°C, and 72°C lower than IF1-APP, IF2-EG, IF3-APP-EG and IF4-APP-EG, respectively. SEM results show the formation of graphite flakes in the structure of residue char which increased as the wt% of EG in the formulation was increased. XRD and FTIR show the presence of boron oxide, graphite and borophosphate, sassolite in the residual char similar to the formulation (IF4-BA-Mel, IF5-BA-Mel, IF4-BA-APP and IF5-BA-APP) reported earlier. TGA and DTGA show that the effect of increasing the amount of EG also contributed to increasing the residual weight.

The best optimized formulation among these fifteen formulations of (Effect of boric acid/melamine, boric acid/APP and APP/EG) is IF5-BA-Mel. The characteristic of the formulation are exhibited by lower substrate temperature, cellular char structure, better char composition and high residual weight. The substrate temperature of IF5-BA-Mel was 367°C after 60 minutes is lowest among all fourteen formulations studied. The cellular char structure is better compared to other formulations. The XRD and FTIR analyses show that the char residue contains boron oxide, borophosphate, graphite, sassolite and borophosphate oxide. TGA result shows that it has the highest residual weight compared to IF4-BA-APP (19 percent), IF5-BA-APP (0.18 percent) and IF5-APP-EG (1.16 percent) formulations.

Based on these results, the formulation IF5-BA-Mel was selected for further improvement in terms of substrate temperature, char expansion, morphology and residual weight by incorporating inorganic fillers such as MWCNTs, kaolin clay and zirconium silicate.
4.9 Reinforcement of Multi-walled carbon nano tubes (MWCNTs) in optimized formulation IF5-BA-Mel

The optimized formulation IF5-BA-Mel is further reinforced by 0.2-0.4wt% of MWCNTs. Three formulations as listed in Table 3.20 were prepared to study the heat shielding effect, char expansion, char morphology, char residue composition and thermal degradation of MWCNTs formulations.

4.9.1 Heat shielding and char expansion of ICF reinforced with MWCNTs

The curves of time versus substrate temperature of ICF reinforced with MWCNTs are presented in Figure 4.129. The char expansion of IF5-BA-Mel, IF1-MWCNTs, IF2-MWCNTs and IF3-MWCNTs after furnace test at 800°C is presented in a bar chart as in Figure 4.130 and the char photograph of IF3-MWCNTs is shown in Figure 4-131.

Results of the substrate temperature reported in Figure 4.129 are as follows: IF1-MWCNTs -, 327°C (30 min), 354°C (60 min); IF2-MWCNTs -, 279°C (30 min), 318°C (60 min); IF3-MWCNTs -, 256°C (30 min), 273°C (60 min). Results after 30 minutes fire test show that the substrate temperature of MWCNTs reinforced ICFs is lower than the temperature recorded for the IF5-BA-Mel. The substrate temperature of IF5-BA-Mel is lowered by 13°C, 49°C and 94°C by the addition of 0.2, 0.3 and 0.4wt% of MWCNTs, respectively. However, results after 60 minutes fire test show that the temperature recorded for IF3-MWCNTs is the lowest, which is 273°C. The substrate temperature of IF3-MWCNTs formulation after 60 minutes fire test is 94°C lower than IF5-BA-Mel, 81°C lower than IF1-MWCNTs, and 45°C lower than IF2-MWCNTs.

The reinforcement of the MWCNTs enhances the char expansion of IF5-BA-Mel coating. The char expansions of IF1-MWCNTs, IF2-MWCNTs and IF3-MWCNTs formulations are 5.4, 6.2 and 7.5 times, respectively as illustrated in Figure 4-130. The char expansion is increases the weight percentage of MWCNTs is increased. The expansion of the char and structure are very important to common fire resistant
properties of coating [77]. The reason of char expansion is explained by char morphology section.

![Char Expansion Curve of MWCNTs ICF](image1)

**Figure 4.129:** Time and substrate temperature curve of MWCNTs ICF

![Char Expansion Chart of MWCNTs ICF](image2)

**Figure 4.130:** Char expansion of MWCNTs ICF

![Char Photograph of IF3-MWCNTs ICF after fire test at 800°C](image3)

**Figure 4.131:** Char photograph of IF3-MWCNTs ICF after fire test at 800°C
4.9.2 Char morphology of ICF reinforced with MWCNTs

The microstructure of IF1-MWCNTs, IF2-MWCNTs and IF3-MWCNTs are presented in Figure 4.132, 4.133 and 4.134, respectively.

The FESEM micrograph of IF1-MWCNTs and in Figure 4.132(a, b) show improved char structure with the formation of multicellular structure which hinders heat penetration to the substrate [84]. Further improvements observed in the chars of IF2-MWCNTs and IF3-MWCNTs can be observed in Figures 4.133 (a, b). Figures 4.134 (a, b, c, d, e, f,) show the presence of MWCNTs in IF3-MWCNTs char after fire test. MWCNTs act as an insulator and joined with the cracks, they increase char resistance during fire. The sealing or physically joining the cracks decreased the substrate temperature of IF3-MWCNTs by 94°C compared to IF5-BA-Mel formulation. This proves that the rate of heat transfer through the char layer depends on the resistance of coating to fire [84].

Figure 4.118 shows EDX spectrum of IF3-MWCNTs. The spectrum shows the presence of carbon, phosphorous and oxygen in the char residue. It is observed that the MWCNTs enhance the char resistance to protect the substrate from heat penetration during fire.

Figure 4.132: FESEM micrograph showed thick char with flakes of IF1-MWCNTs
Figure 4.133: (a) microstructure of char by adding 0.3 (b) 0.4 wt % of MWCNTs.

Presence of CNTs inside the char of IF3-MWCNTs

Figure 4.134: (a, b, c, d) Cracks are linked by MCNTs and (e, f) MCNTs strengthening the char in IF3-MWCNTs
Figure 4.135: EDX of IF3-MWCNTs correspond to the presence of carbon and phosphorous and oxygen in char residue at 800°C furnace test.

4.9.3 Char composition of ICF reinforced with MWCNTs

The XRD of residual char sample of IF3-MWCNTs is shown in Figure 4.136. Five peaks are observed: 2θ=15°, d value = 6.16 is boron oxide; 2θ=25°, d value = 3.64 is borophosphate; 2θ=25, 26.5°, d values = 3.37 is graphite; 2θ=27°, d value = 3.18 is sassolite and 2θ=40°, d value = 2.25 is boron phosphate oxide. The results of XRD show that the components in the residual char are formed by the reactions between the fire retardant additives in the coating. The results also show that anti-oxidation performance of the intumescent fire retardant coating has been enhanced by (0.4wt%) MWCNTs as these are present in the protective char layer.

Figure 4.136: shows the XRD spectrum of IF3-MWCNTs char
4.9.4 Functional groups of ICF char reinforced with MWCNTs

The ingredients in IF3-MWCNTs are same as in IF5-BA-Mel, except for the addition of 0.4% MCNTs in IF3-MWCNTs. The environment of fire test is the same as for IF5-BA-Mel. The spectrum of IF3-MWCNTs is shown in Figure 4.137. In the P-O-P region (1400-800 cm\(^{-1}\)) the symmetric vibration at 936 cm\(^{-1}\) is identified as due to PO\(_4\)\(^{-1}\) and at 1103 cm\(^{-1}\) due to APP [140, 141]. In the 2\(^{\text{nd}}\) region, two weak bands of amino groups at 1437 cm\(^{-1}\) -1622 cm\(^{-1}\) due to gaseous product of APP and cured epoxy resin are noted, as cured epoxy contains polyamide hardener. In the 3\(^{\text{rd}}\) region above 2100 cm\(^{-1}\), a strong bending peak occurred at 2346 cm\(^{-1}\) which represents the bending vibrations of (-CH\(_3\)-CH\(_2\)-) groups in the cured epoxy. The peaks observed at 3312 cm\(^{-1}\) corresponds to boric acid in char residue[151]. These results of functional groups recommend two major phases of thermal degradation of IF3-MWCNTs. In the first stage (400-500\(^{\circ}\)C) degradation, char residues containing phosphorus, -CH\(_3\)-CH\(_2\) and aromatic compounds save some structure of cured epoxy resin with the interactions between, EG, APP, boric acid and melamine. The residues decomposed further in the second stage (600-700\(^{\circ}\)C) to form a compact char with the absorption of cured epoxy resin decreasing, leaving the absorption of polyaromatic and phosphorous compounds with boron oxide, boron phosphate, graphite, sassolite and boron phosphate oxide that are the main component of the char. As illustrated in Figure 4.137, the second stage lead to form a compact char with the absorption of polyaromatic and phosphorous compounds with borophosphate that are the main component of the char at 800\(^{\circ}\)C. These results point to the same conclusion as the XRD analysis of IF3-MWCNTs presented in Figure 4.136.

![Figure 4.137: FTIR spectrum of IF3-MCNTs ICF char](image)
4.9.5 Residual weight and DTGA of ICF reinforced with MWCNTs

The residual weight of MWCNTs ICFs is shown in Figure 4.138: IF1-MWCNTs - 28.65 wt%, IF2-MWCNTs - 28.86 wt% and IF3-MWCNTs - , 29.36 wt%. From the Figure 4.138, it can be observed that increasing the residual weight of MWCNTs ICFs increases with the wt% of MWCNTs. The residual weight of IF3-MWCNTs is 29.36 %, which is 2.87, 2.4, and 1.76 percent higher than IF5-BA-Mel, IF1-MWCNTs and IF2-MWCNTs, respectively.

The DTGA curve of IF3-MWCNTs is presented in Figure 4.139. It is observed that the degradation temperatures of IF3-MWCNTs have been changed from those of IF5-BA-Mel by the addition of 0.4wt% MWCNTs. The DTGA curve of IF3-MWCNTs shows three degradation temperatures at 138°C, 416°C and 667°C. The degradation of boric acid at 138°C, degradation of epoxy, EG and APP observed at 416°C and the degradation of APP and melamine reaction product decomposing into phosphate oxide at 667°C. The presence of phosphate in the char at 800°C has been confirmed from EDX results. The results of the DTGA show different thermal degradation behaviour of IF3-MWCNTs compared to the behaviour of IF5-BA-Mel. The residual weight of IF3-MWCNTs has also been increased by 2.87% is as the result of adding 0.4 wt% MWCNTs in IF5-BA-Mel formulations.

4.9.6 DTA of ICF reinforced with MWCNTs

The DTA results of IF5-BA-Mel and IF3-MWCNTs are shown in Figure 4.140. Five endothermic peaks are noted for IF5-BA-Mel formulation in Figure 4-140. The first two endothermic peaks in the range of 100-200°C also confirms the decomposition of boric acid into meta boric acid which typically occurs at 100-140°C, and then later converted to boron oxide in the range 140-200°C. The 3rd and 4th peaks show the melting point of melamine, APP and EG epoxy mixture in the range of 300-400°C. The last endothermic peak at 483°C indicates the melting point of reaction product such as melamine phosphate and its derivatives.

The DTA results of IF3-MWCNTs reported in Figure 4.141 show four endothermic peaks in range of 100-200 °C, 300-400 °C and 500-600°C. These three
temperature ranges also confirm the melting points of boric acid, melamine, APP, EG and epoxy, and hardener with their reaction products.

Figure 4.138: TGA results with the residual weight% of the MWCNTs ICF

Figure 4.139: DTGA curve of IF3-MWCNs
4.9.7 Conclusion of ICF reinforced with MWCNTs

The substrate temperature is lowered by 94°C (from 367-273°C) by the addition of 0.4wt % of MWCNTs in IF5-BA-Mel and the char expansion is increased by 63%. The FESEM result shows that the structure of residue char has also been improved as the
cracks are linked by MWCNTs. The results from XRD and FTIR show the presence of boron oxide, borophosphate, graphite and sassolite in the residual char. TGA and DTGA show that MWCNTs can enhance the residual weight by 2.87 percent than that of IF5-BA-Mel coating. MWCNTs as an additive contribute to improved heat insulation property by sealing or physically joining the cracked char layers together. Thus, the heat transfer rate can be reduced by using MWCNTs, and this will give a better effect of intumescent to the coating formulations.

4.10 Reinforcement of the optimized formulation IF5-BA-Mel by Kaolin Clay (KC)

The effect of Kaolin Clay as the reinforcing material has also been studied. A total of five formulations, each containing various amount of Kaolin ranging from 1 to 5wt% were prepared as listed in Table 3.21 to study the heat shielding property, char expansion, char morphology, char residue composition and thermal degradation properties.

4.10.1 Heat shielding and char expansion of ICF reinforced with kaolin clay

The time versus substrate temperature curves are shown in Figure 4.142, expansion of char is presented in Figure 4.143, and the char photographs of IF4-KC and IF5-KC after fire test are shown in Figure 4.144.

The substrate temperatures of the formulations after the fire test as reported in Figure 4.142 are as follows: IF1-KC – 336°C (30 min), 360°C (60 min); IF2-KC – 311°C (30 min), 334°C (60 min), IF3-KC – 270°C (30 min), 306°C (60 min), IF4-KC – 241°C (30 min), 286°C (60 min) and IF5-KC – 226°C (30 min), 257°C (60 min). From the measurement of substrate temperature, it is apparent that Kaolin contributes to heat shielding effectively as indicated by the lowered substrate temperature for all Kaolin reinforced formulations. Relative to IF5-BA-Mel, the substrate temperature of the formulations are lowered by: 7°C (IF1-KC - 1 wt%), 33°C (IF2-KC - 2 wt%), 61°C (IF3-KC - 3 wt%), 81°C (IF3-KC - 4 wt%) and 110°C (IF5-KC - 5 wt%). Li et
al. [84] reported the substrate temperature 400°C after 60 minutes fire test obtained from 5wt% of EG and 9 wt% of MoSi₂ coating formulation.

The reinforcement of the kaolin clay enhances char expansion; better char expansion is achieved with each increasing weight percentage of kaolin clay in the formulations. The char expansion of IF5-BA-MEL is 4.7, while for the Kaolin reinforced formulations the char expansion is: 6.1 (IF1-KC), 8.3 (IF2-KC), 12.57 (IF3-KC), 13.83 (IF4-KC) and 15.42 (IF5-KC) times from their original thickness. These results are presented in Figure 4.143. In terms of percentage, the char expansion has been increased by 29.78% (IF1-KC), 76.59% (IF2-KC), 167.44% (IF3-KC), 194% (IF4-KC) and 228% (IF5-KC).

Figure 4.142: Time vs substrate temperature curve of kaolin clay ICF

Figure 4.143: Char expansion of kaolin clay ICF
This proves that 5wt% kaolin clay show the best intumescent effect in the case of substrate temperature and char expansion. The kaolin clay created a ceramic like protective barrier on the surface of the insulating char.

4.10.2 Char morphology of ICF reinforced with kaolin clay

In order to explore how the micro structure of intumescent char determines fire-resistant properties, the residue chars of coatings burnt at 800°C are examined by SEM. Figures 4.145(a, b), 4.145 (c, d) and 4.146(a, b, c, d) present the SEM micrographs of intumescent chars obtained from IF3-KC, IF4-KC, and IF5-KC, respectively. The rapid formation of protective char layer is highly dependent upon factors such as fire temperature and viscosity of the melting coating [68].

As for IF3-KC in Figure 4-145 (a, b), porous char structure is observed due to the good interaction of boric acid, EG, APP, MEL, epoxy, hardener and kaolin clay. It is also contributed by the right viscosity of the melting mixture. In Figure 4.145 (c, d), improved porous char structure from IF4-KC is observed. This is because of the increased weight percentage of kaolin clay which results in synergistic effect between fire retardant additive (boric acid) and inorganic filler (kaolin clay), that leads to the formation of a strong char structure. In Figure 4.146 (a, b, c, d), the char structure is further improved (flake structure) as the weight percent of kaolin clay was increased.
from 4 to 5%. The char structure obtained from IF5-KC is more compact than that obtained from IF3-KC and IF4-KC.

Figure 4.145: SEM images of (a, b) IF3-KC and (c, d) IF4-KC

(a): IF5-KC outer surface smooth char  
(b): IF5-KC flakes helped to reduce the substrate temperature
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(c) Char agglomerates in IF5-KC

(d) char agglomerates in IF5-KC

Figure 4.146: SEM micrographs of intumescent char obtained from (a, b, c, d) IF5-KC.

The kaolin clay forms a network with flame retardant additives at high temperature. This refers to the network to enhance the char structure, and reduce cracks and shrinkage. Fire resistant properties of fire retardant coatings are directly connected with the formation of char structure. The SEM analysis has shown that kaolin clay could improve char structure and fire resistant properties of the IF5-BA-Mel coating.

4.10.3 Char composition of ICF reinforced with kaolin clay

The XRD spectrum of kaolin clay is presented in Figure 4.147. It shows high intensity peak with 20 = 26° and d value = 3.38 which is identified as kaolinite (JCPDS card no 12-0447). As shown in Figures 4.148, 4.49 of IF4-KC and IF5-KC, respectively have five peaks at the same interfaces; the first peak at 20=15°, d=6.09 is boron oxide, the second peak at 20=25°, d=3.66 is borophosphate, and the third peak at 20= 26.5°, d= 3.38 is graphite (carbon). The last three peaks show the composition of kaolinite, sassolite and boron phosphate oxide at 20= 26, 27, 40°, and d= 3.38, 3.19, 2.25, respectively. Kaolinite is a clay mineral; its structure is composed of silicate sheets (Si₂O₅) bonded to aluminium oxide/hydroxide layers (Al₂(OH)₄) which enhances the fire retardant properties of the char. The rest of the peaks are the same as shown in Figure 4.147 which shows that the composition of kaolin clay remained the same at 800°C. XRD results show that interactions between fire retardant additives enhance the anti-oxidation performance of the intumescent fire retardant.
coating as indicated by presence of kaolin clay to protective char layered on steel substrate.

Figure 4.147: XRD spectrum of powdered kaolin clay

Figure 4.148: XRD spectrum of IF4-KC char
4.10.4 Functional groups of ICF char reinforced with kaolin clay

From Figure 4.150 and Figure 4.151, it can be observed that IF4-KC and IF5-KC have almost the same spectra.

The spectrum of IF4-KC formulation in Figure 4.150 shows peaks at 3787, 3706, 3275, 3119, 2496, 2352, 1619, 1436, 1189, 1100, 924, 622 cm\(^{-1}\). B-O-P bending motions is observed at 624 cm\(^{-1}\) and two bands assigned to \(\nu(B-O-P)\) stretching mood due to borophosphate are observed at 924, 1089 cm\(^{-1}\). The peak at 1100 cm\(^{-1}\) is assigned to \(\nu_{as}(Si-O-Si)\) stretching mode of kaolin clay [152]. In the P-O-P region (1400-800 cm\(^{-1}\)), symmetric vibration is present at 1189 cm\(^{-1}\). Two bands at 1436, 1622 cm\(^{-1}\) are assigned to the amino groups NH\(_2\) of APP. In the region above 2100 cm\(^{-1}\), one strong bending peak is observed at 2346 cm\(^{-1}\) which represents the bending vibrations of (-CH\(_3\)-CH\(_2\)-) groups of cured epoxy resin. The weak bands at 3275 and 3119 cm\(^{-1}\) correspond to the presence of boric acid (sassolite) in the char residue [151]. The peaks 3706 and 3787 cm\(^{-1}\) are assigned to the hydroxyls of kaolin clay [152].
In Figure 4.151, the spectrum of IF5-KC formulation shows peaks at 3849, 3787, 3336, 3212, 2406, 2270, 1629, 1446, 1100, 933, 614, 531 cm$^{-1}$. In the first region (500-1400 cm$^{-1}$), a stretching peak at 531 cm$^{-1}$ is assigned to Al-O-Si [152]. It also shows B-O-P bending motions at 614 cm$^{-1}$ and (Al-O-H) stretching mood at 933 cm$^{-1}$ [153]. The peak at 1100 cm$^{-1}$ is assigned to vas(Si-O-Si) stretching mode[152]. In the 2$^{nd}$ region (1400-2100 cm$^{-1}$), two bands at 1446, 1629 cm$^{-1}$ are assigned to the amino groups NH$_2$ of APP. In the 3$^{rd}$ region above 2100 cm$^{-1}$, two strong bending peaks occurred at 2270, 2403 cm$^{-1}$ which represent the bending vibrations of (-CH$_3$-CH$_2$-) groups of cured epoxy resin. The weak bands at 3212 and 3336 cm$^{-1}$ correspond to the presence of boric acid (sassolite) in the char residue. The peaks at 3787 and 3849 cm$^{-1}$ are assigned to the hydroxyls of kaolin clay.

The results of FTIR show that the respective functional groups of the inorganic additives are present in the char residues; these functional groups have shown good fire resistance at 800$^\circ$C and enhanced the performance of the intumescent fire retardant coating. These results agree with the XRD results of IF4-KC and IF5-KC residual char.

![Figure 4.150: Figure 4.159: FTIR spectrum of IF4-KC char](image-url)
4.10.5 Residual weight and DTGA of ICF reinforced with kaolin clay

The residual weight obtained for the Kaolin Clay based formulations is: 35.16% (IF3-KC), 39.34% (IF4-KC) and 42.5% (IF5-KC). A graphical presentation of these results is given in Figure 4.152. With respect to IF5-BA-Mel formulation, this is an increase of 23% for IF3-KC, 37% for IF4-KC and 49% for IF5-KC. The results show that the residual weight is increased with each increasing weight% of kaolin clay in the formulation.

DTGA curve of IF3-KC is presented in Figure 4.153; there are six degradation temperature curves 132, 178, 328, 385, 468 and 486°C. From this curve, it is observed that the addition of kaolin clay by 3wt% has reduced the decomposition of IF5-BA-Mel coating. The degradation of boric acid occurred at 132°C, and the meta boric acid at 178°C while the decomposition of epoxy and EG, and APP are observed at 328 and 385°C, respectively. The decomposition of melamine phosphate into phosphate oxide, and boron, poly phosphoric acid into borophosphate respectively occurred at 468°C and 486°C. Compared to IF3-KC, the DTGA curve of IF4-KC has been improved as shown by the reduction in degradation points; four degradation peaks are observed at 184, 320, 385 and 485°C as illustrated in Figure 4.154. This is believed to be the effect of adding kaolin clay (about 3 to 4%). Boric acid decomposed into boron oxide.
at 184°C, melamine and APP decomposed at 320°C into its derivatives such as melamine phosphate, and poly phosphoric acid. EG oxidizes at 385°C, and at 485°C cure epoxy decomposed. Further improvement is obvious in IF5-KC by the addition of 4 to 5% kaolin clay as shown by the DTG curve in Figure 4.155 which shows four degradation temperatures at 194, 341, 402 and 508°C. In the earlier formulations, boric acid decomposed at 178 and 184°C but in this formulation it decomposed around 194°C. However, both melamine and APP decomposed at 341°C whereby normally they decomposed after 280°C. EG decomposed at 402°C, and the reaction products at 508°C.

The DTGA results have shown that increasing the weight percentage of kaolin clay by 3 to 5% increases the degradation temperature. The residual weight increased by 49% when 5 wt% of kaolin clay was added in IF5-BA-Mel coating. Thus the formulation IF5-KC shows the most improved residual weight of char.

![Figure 4.152: TGA curves of formulations IF3-KC3, IF4-KC4 and IF5-KC6](image-url)
Figure 4.153: DTGA curves of IF3-KC showing six steps of degradation

Figure 4.154: DTGA curves of IF4-KC four steps of degradation

Figure 4.155: DTG curves of IF5-KC four steps of degradation
4.10.6 DTA of ICF reinforced with kaolin clay

The DTA results of IF5-KCs are shown in Figure 4.156 revealing four endothermic peaks which are the melting points of IF5-KC formulation. The first two endothermic peaks in the range of 100-200°C confirms the decomposition of boric acid into meta boric acid at 100-168°C, and then converted into boron oxide. The 3rd and 4th peaks in the range of 200-550°C show the melting points of melamine, APP and EG epoxy mixture at 342°C. The last endothermic peak at 510°C indicates the melting point of the reaction product such as melamine phosphate and its derivatives. The DTA analysis also confirmed the melting point of intumescent ingredients used in IF5-KC ICF.

4.10.7 Elemental composition of ICF char reinforced with kaolin clay

XPS is used to determine the elemental composition of the residual char. The XPS spectra and elemental composition of residue chars obtained from IF4-KC and IF5-KC after thermal oxidation at 800°C are shown in Figures 4.157 to 4.163 and Table 4.18.

The ratio of carbon content in the residual char obtained from IF5-KC to that obtained from IF4-KC (41.83%/21.8%) is 1.91:1, and the ratio of oxygen content in
the residual char obtained from IF5-KC to that obtained from IF4-KC (66.88%/44.51) is 1.5:1. In addition, the intensity of C1s peak of the residue char obtained from IF5-KC is higher than that obtained from IF4-KC, whereas the intensity of O1s peak of the residue char obtained from IF4-KC is higher than that obtained from IF5-KC, these are shown in Figures 4.157 and 4.158. These results strongly suggest that the char accumulating degree and anti-oxidation of IF5-KC are better than those of IF4-KC. Carbon content in residual char indicates char accumulation degree, while oxygen content in residual char designates the oxidation degree of char at high temperature. High carbon content and low oxygen content in residue char is favorable for char accumulation and anti-oxidation of char layer [84, 118, 154].

Figures 4.159 to 4.163 show the P2p, N1s, B1s, Al2p and Si2p XPS spectra of the char obtained from IF4-KC and IF5-KC. Phosphorus is also an important element in the char that contributes to fire resistance at high temperature. The phosphorus content in the residual char of IF5-KC is 12.18% higher than that of IF4-KC (10.31%). So increase the wt% (4 to 5) kaolin clay can secure phosphorous compound and increase phosphorus content in condensed phase.

Silicon (0.69%) in the residue char obtained from IF5-KC shows the presence of SiO₂ network in the char structure which further enhanced the fire resistant properties of the char. Therefore, the intumescent char layer of IF5-KC provides good resistance to fire.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>C%</th>
<th>O%</th>
<th>P%</th>
<th>N%</th>
<th>B</th>
<th>Al</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>Char residue of IF4-KC</td>
<td>21.8</td>
<td>66.88</td>
<td>10.31</td>
<td>0.11</td>
<td>0.31</td>
<td>0.12</td>
<td>0.47</td>
</tr>
<tr>
<td>Char residue of IF5-KC</td>
<td>41.83</td>
<td>44.51</td>
<td>12.18</td>
<td>0.17</td>
<td>0.45</td>
<td>0.17</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Figure 4.157: XPS curves of C1s of IF4-KC and IF5-KC

Figure 4.158: XPS curves of O1s of IF4-KC and IF5-KC

Figure 4.159: XPS curves of P2p of IF4-KC and IF5-KC
Figure 4.160: XPS curves of N1s of IF4-KC and IF5-KC

Figure 4.161: XPS curves of B1s of IF4-KC and IF5-KC

Figure 4.162: XPS curves of Al2p of IF4-KC and IF5-KC
4.10.8 Conclusion of ICF reinforced with kaolin clay

Based on the above results, it can be concluded that char expansion increases by increasing the weight % of kaolin clay. The formulation IF5-KC shows char expansion of 15.42 times, which is 228 percent higher than IF5-BA-Mel. SEM results show that the structure of residual char is improved by increasing the wt% of kaolin clay. XRD and FTIR show the presence of boron oxide, borophosphate, sassolite, borophosphate oxide and kaolinite in the residual char which are the elements that enhance fire retardant properties of IF5-KC. TGA shows that the residual weight of IF5-KC formulation reinforced with 5wt% kaolin clay is 49% higher than that of IF5-BA-Mel formulation. DTA analysis confirmed the decomposition of fire retardant additives of IF5-KC. XPS shows the elemental composition of char residue from kaolin clay formulations and IF5-KC gave better carbon content in the residual char compared to IF4-KC. Kaolin clay is a reinforcement material that creates a ceramic like protective barrier on the surface of the insulating materials which reduces the heat transfer to the substrate. Consequently, gives a better effect of intumescent to the coating formulations.
4.11 Reinforcement of the optimized formulation IF5-BA-Mel by Zirconium Silicate (ZS)

Zirconium silicate is another reinforcement material used in the optimized formulation IF5-BA-Mel. Five formulations, as listed in Table 3.22, consisting of zirconium silicate ranging from 1 to 5wt% from were prepared to study the heat shielding, char expansion, char morphology, char residue composition, residual weight and thermal degradation.

4.11.1 Heat shielding and char expansion of ICF reinforced with zirconium silicate

In this study, five formulations were developed by adding zirconium silicate from 1 to 5wt% in IF5-BA-Mel coating to investigate the effect of zirconium silicate on char expansion, morphology, heat shielding and residual weight of the char.

The time vs substrate temperature curves are shown in Figure 4.164, and the expansion of char after fire test is presented in Figure 4.165. The char photographs of IF4-ZS and IF5-ZS after fire test are shown in Figure 4-166.

The substrate temperatures of the formulations after the fire test as reported in Figure 4.164 are as follows: IF1-ZS – 336°C (30 min), 359°C (60 min), IF2-ZS – 292°C (30 min), 330°C (60 min), IF3-ZS – 266°C (30 min), 292°C (60 min), IF4-ZS – 204°C (30 min), 249°C (60 min) and IF5-ZS – 190°C (30 min), 213°C (60 min). For each formulation of zirconium silicate reinforced IF5-BA-Mel, the substrate temperature was reduced by: 8°C (1 wt% ZS), 37°C (2 wt% ZS), 75°C (3 wt% ZS), 118°C (4 wt % ZS) and 154°C (5 wt% ZS). The addition of zirconium silicate to IF5-BA-Mel enhances the char expansion compared to unreinforced IF5-BA-Mel. The results of char expansion are: 4.7times (IF5-BA-MEL), 5.4times (IF1-ZS), 7.32times (IF2-ZS), 10.43times (IF3-ZS), 18.76times (IF4-ZS) and 24.05times (IF5-ZS) from their original coating thickness on the substrate; these results are illustrated in Figure 4.165. The best char expansion in this research work is 24.05 times obtained from IF5-ZS coating and it is 334 percent higher compared to IF5-BA-Mel coating. Wang et al. [67] recorded the substrate temperature 320°C after 60 minutes fire test with
char expansion 14.2 times from EG/APP/PER/Mel coating formulation. IF5-ZS shows excellent results in char expansion and it was able to retain the substrate temperature at 213°C after 60 minutes. Char photographs of IF4-ZS and IF5-ZS are shown in Figure 4.166.

Figure 4.164: Time vs substrate temperature curves of zirconium silicate ICF

Figure 4.165: Char expansion of zirconium silicate ICF after fire test at 800°C
4.11.2 Char morphology of ICF reinforced with zirconium silicate

In order to explore the structure of intumescent char that determines fire-resistant properties, the residual chars obtained after the coatings have been heated at 800°C are examined by FESEM analysis. Figure 4.167 (a, b, c, d), present the FESEM micrographs of the intumescent chars obtained from IF3-ZS, IF4-ZS and Figure 4.168 (a, b, c, d, e, f) illustrated FESEM images of IF5-ZS char, respectively. The micrograph of IF3-ZS is illustrated in Figure 4-167 (a, b), it shows a porous and flaky char structure. Figures 4-167 (c, d) show an improved (no cracks) flake char structure in IF4-ZS compared to IF3-ZS. The improved structure is due to increased weight% of zirconium silicate from 3% to 4% compared to IF3-ZS where the improved char structure is the result of synergistic effect between fire retardant additive and inorganic filler. This flaky structure leads to the formation of a strong char structure. The multicellular char structure can block heat transfer to the substrate and protects the substrate from fire [84, 154]. In Figures 4.168 (a, b, c, d, e, f) the char flak structure is further improved by increasing the weight% of zirconium silicate from 4 to 5%. The char structure of IF5-ZS is more compact due to the formation of more flakes than that obtained in IF3-ZS and IF4-ZS. The zirconium silicate forms a multicellular flake network like a honeycomb network with flame retardant additives at high temperature and enhances the char structure, and reduces crack and shrinkage. Fire resistant properties of fire retardant coatings are directly related to the formation of char structure. FESEM analysis shows that zirconium silicate improves char structure and fire resistance of the IF5-BA-Mel coating.

Figure 4.166: Char photograph of IF4-ZS and IF5-ZS fully insulated the substrate
Figure 4.167: FESEM micrographs of IF3-ZS (a, b) and IF4-ZS (c, d)

(a) IF3-ZS porous char
(b) Cellular and cracked structure
(c) Thick and porous char of IF4-ZS
(d) porous char

(a) IF5-ZS thick char with flakes
(b) char flakes hindered the heat to the substrate

(c) Porous structure of the char
(d) Thick char without any craks
4.11.3 Char composition of reinforced ICF with zirconium silicate

The XRD spectrum of ICF reinforced with zirconium silicate is presented in Figure 4.169. Three main peaks are shown, at $2\theta=20^\circ$, d spacing =4.42, $2\theta = 27^\circ$, d spacing =3.31 and $2\theta =36^\circ$, d spacing =2.52. All three peaks are identified as zirconium silicate (JCPDS card no 03-0456). The XRD spectra of IF4-ZS and IF5-ZS in Figures 4.170 and 4.171 show seven major peaks at the same interfaces: $2\theta = 15^\circ$, d spacing = 4.56 - boron oxide, $2\theta = 20^\circ$, d spacing = 3.66 - zirconium silicate, $2\theta = 25^\circ$, d spacing = 3.61 - borophosphate and $2\theta = 26.5^\circ$, d spacing = 3.47 – graphite, $2\theta = 27^\circ$, d spacing = 3.19 – sassolite, $2\theta = 40^\circ$, d spacing = 2.25 – boron phosphate oxide. The rest of the peaks are the same as shown in Figure 4.169 of zirconium silicate which shows that the composition of zirconium silicate remained the same at 800°C.

The results of XRD show that the reactions between fire retardant additives enhanced the anti-oxidation performance of the intumescent fire retardant coating due to the presence of zirconium silicate in the protective char layer.
Figure 4.169: XRD spectrum of powdered Zirconium Silicate

Figure 4.170: XRD spectrum of IF4-ZS char
4.11.4 Functional groups of ICF char reinforced with zirconium silicate

The ingredients used to prepare the zirconium silicate coatings (IF4-ZS and IF5-ZS) are the same as those used to prepare IF1-BA-Mel, except for the addition of 4wt% and 5wt% of zirconium silicate in IF4-ZS and IF5-ZS, respectively. The fire test environment is same as for IF1-BA-Mel. Both spectra of IF4-ZS and IF5-ZS are illustrated in Figures 4.172 and 4.173.

The spectrum of IF4-ZS char in Figure 4.172 shows peaks at 3869, 3770, 3220, 2822, 2516, 2389, 2360, 1465, 1189, 1080, 927, 623 and 539 cm\(^{-1}\) which are identified. In the first region (500-1400 cm\(^{-1}\)) a stretching peak at 539 cm\(^{-1}\) assigned to Zr-O-Si. The B-O-P bending motions at 623 cm\(^{-1}\) and a band at 924 cm\(^{-1}\) show (B–O–P) stretching mood due to borophosphate. The band at 1080 cm\(^{-1}\) is due to internal asymmetric stretching mode of SiO\(_4\) skeleton [155], while the symmetric vibration is present at 1189 cm\(^{-1}\) of SiO\(_4\). In the 2\(^{nd}\) region, two bands at 1465 cm\(^{-1}\), 1601 cm\(^{-1}\) assigned to the amino groups NH\(_2\) are due to (melamine and APP) and C=C of cured epoxy, respectively. In the 3\(^{rd}\) region above 2100 cm\(^{-1}\), a strong bending peak that occurs at 2280 cm\(^{-1}\) represents the bending vibrations of (-CH\(_3\)-CH\(_2\)-) groups of cured
epoxy. The weak bands at 3275, 3119 cm\(^{-1}\) correspond to the presence of boric acid (sassolite) in the char residue.

The spectrum of IF5-KC formulation in Figure 4.173 shows peaks at 3838, 3350, 3204, 3202, 2910, 2689, 2316, 2260, 1619, 1454, 1189, 1088, 924, 623, 548 and 487 cm\(^{-1}\). A (B-O-P) bending motion is observed at 623 cm\(^{-1}\) and O-P-O in borophosphate appears at around 588-545 cm\(^{-1}\) [133, 136]. The peak in the region 910-960 cm\(^{-1}\) is generally considered as the proof of the incorporation of heteroatoms such as P-O or PO\(_4\)\(^{-1}\) into the framework [92]. The band at 1088 cm\(^{-1}\) in the region 1055-1090 cm\(^{-1}\) is due to internal asymmetric stretching mode of SiO\(_4\) skeleton [155]. In the 2\(^{nd}\) region, two band at 1454 cm\(^{-1}\) and 1619 cm\(^{-1}\) are assigned to the amino groups NH\(_2\) of APP and C=C of cured epoxy. In the 3\(^{rd}\) region above 2100 cm\(^{-1}\), there is one strong bending peak at 2280 cm\(^{-1}\) which represents the bending vibrations of (-CH\(_3\)-CH\(_2\)-) groups of epoxy resin. A strong band at 1189 cm\(^{-1}\) and two weak bands at 3202, 3284 cm\(^{-1}\) show the presence of boric acid (sassolite) in the char residue [134].

The results of FTIR show that the respective functional groups of the fire additives are present in the char residues, which have shown good fire resistance behaviour at 950°C. Thus the addition of zirconium silicate has enhanced the performance of the intumescent coatings. The FTIR results agree with the results of XRD analyses of IF4-ZS and IF5-ZS residual chars.

![Figure 4.172: FTIR spectrum of IF4-ZS char](image-url)
4.11.5 Residual weight and DTGA of ICF reinforced with zirconium silicate

The residual weights of IF1-ZS, IF2-ZS, IF3-ZS, IF4-ZS and IF5-ZS are 30.92, 31.9, 34.5, 36.6 and 38.2%, respectively. It is apparent that the residual weight of char increases as the weight% of zirconium silicate is increased as shown in Figure 4.174.

The DTGA curve of IF3-ZS is presented in Figure 4.175. The DTGA curve of IF3-KC shows that the degradation occurred at six temperature curves, 139 °C, 183 °C, 282 °C, 371 °C, 408 °C and 457°C. The degradation of boric acid and meta boric acid occurred at 139°C and 183°C respectively, while the decomposition of epoxy and EG, and APP are observed at 381 °C and 408°C, respectively. The decomposition involving the conversion of melamine phosphate and phosphate reaction products into phosphate oxide, and borophosphate respectively, occurred at 457°C.

The DTG curve of IF4-ZS shows an improvement from IF3-ZS by the addition of 3 to 4% of zirconium silicate. Three decomposition curves at 164 °C, 367 °C, and 485°C are observed as illustrated in Figure 4.176. Boric acid decomposed to boron oxide at 165°C; melamine, APP and EG decomposed at 367°C into its derivatives such as melamine phosphate, poly phosphoric acid; at 485°C derivatives are further decomposed into borophosphate, borophosphate oxide with cured epoxy.
The DTG curve of IF5-KC is shown in Figure 4.177; four degradation temperature curves are observed: 169°C, 324°C, 383°C and 455°C. Boric acid decomposed at 169°C, melamine and APP decomposed at 324 the decomposition temperature is increased normally both are decomposed after 280°C, EG decomposed at 383°C and reaction product at 455°C.

The results of the DTGA show that increasing the weight percentage of zirconium silicate (3% to 5%) causes the degradation temperature to increase. The residual weight was increased by 38% when 5 wt% of zirconium silicate was added to IF5-BA-Mel coating. This shows that the residual weight of IF5-BA-Mel char is improved when 5wt% is added (formulation IF5-KC) which helps to reduce heat penetration to the substrate.
Figure 4.176: DTGA curve of IF4-ZS formulation showing three steps of degradation

Figure 4.177: DTGA curve of DTGA of IF5-ZS showing four steps of degradation

4.11.6 DTA of ICF reinforced with zirconium silicate

The DTA analysis of IF5-ZS is shown in Figure 4.178. Five endothermic peaks show the melting points of IF5-ZS formulation. The first two endothermic peaks in the range of 100-200°C confirms the decomposition of boric acid into meta boric acid at 100-169°C and then into boron oxide. The 3rd and 4th peaks show the melting point of melamine, APP and EG epoxy mixture in the range from 281 to 334°C. The last endothermic peak at 522.9°C is the melting point of reaction products such as melamine phosphate and its derivatives. The DTA analysis also confirmed the
decomposition of fire retardant additives. The DTA and DTG confirm the decomposition of intumescent ingredients and their reaction products at their respective temperature zone.

Figure 4.178: DTA curve of IF5-ZS formulation

4.11.7 XPS of ICF reinforced with zirconium silicate

The C1s, O1s, P2p, N1s, B1s, Si2p and Zr3d XPS spectra and elemental composition of residue chars obtained from IF3-ZS, IF4-ZS and IF5-ZS after thermal oxidation for 60 min at 800°C are shown in Table 4.19 and Figures 4.179 to 4.185, respectively. The ratio of carbon content in the residue char obtained from IF3-ZS to that obtained from IF4-ZS and IF5-ZS is 1:1.21:2.29 respectively, and the ratio of oxygen content in the residue char of IF3-ZS to that obtained from IF4-ZS and IF5-ZS is 2.22:2.03:1. In addition, the intensity of C1s peak of the residue char obtained from IF5-ZS is stronger than that obtained from IF4-ZS and IF3-ZS as shown in Figure 4.179, whereas the intensity of O1s peak of the residue char obtained from IF3-ZS is also higher than that obtained from IF4-ZS and IF5-ZS as shown in Figure 4.180. These results state that the char accumulating degree and anti-oxidation of IF5-ZS are better than those of IF3-ZS and IF4-ZS [154]. Figures 4.181 to 4.185 show the P2p, N1s, B1s, Si2p and Zr3d, XPS spectra of the char obtained from IF3-ZS, IF4-ZS
and IF5-ZS. Phosphorus content in the residual char of IF3-ZS, IF4-ZS and IF5-ZS are 5.74%, 3.63% and 3.05%, respectively given in Table 4.19. As APP is an acid source to initiate the chemical reaction with carbon source to make carbonaceous char. So it is confirmed that increasing the char expansion lowers the phosphorus contents. Increasing the weight percent 3, 4 and 5 of zirconium silicate in the IF3-ZS, IF4-ZS and IF5ZS silicon content are also increased 0.31, 0.45 and 0.67%, respectively in the residual char structure. Silicon content in the residual char of IF3-ZS, IF4-ZS and IF5ZS increases accordingly with the amount of zirconium silicate in these formulations. IF3-ZS (3 wt% ZS), IF4-ZS (4 wt% ZS) and IF5ZS (5 wt% ZS) recorded an increase in silicon content by 0.31%, 0.45% and 0.67%, respectively. The presence of silicon in the char layer of IF5-ZS provides a good resistance to fire.

Table 4.19: Element composition of char residue of IF3-ZS, IF4-ZS and IF5-ZS

<table>
<thead>
<tr>
<th>Formulation</th>
<th>C%</th>
<th>O%</th>
<th>P%</th>
<th>N%</th>
<th>B</th>
<th>Zr</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char residue of IF3-ZS</td>
<td>26.48</td>
<td>62.40</td>
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<td>0.29</td>
<td>0.28</td>
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<tr>
<td>Char residue of IF4-ZS</td>
<td>32.09</td>
<td>57.20</td>
<td>3.63</td>
<td>5.84</td>
<td>0.37</td>
<td>0.33</td>
<td>0.45</td>
</tr>
<tr>
<td>Char residue of IF5-ZS</td>
<td>60.87</td>
<td>28.09</td>
<td>3.05</td>
<td>6.7</td>
<td>0.43</td>
<td>0.19</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Figure 4.179: XPS curves of C1s of IF3-ZS, IF4-ZS and IF5-ZS char residue
Figure 4.180: XPS curves of O1s of IF3-ZS, IF4-ZS and IF5-ZS char residue

Figure 4.181: XPS curves of P2p of IF3-ZS, IF4-ZS and IF5-ZS char residue

Figure 4.182: XPS curves of N1s of IF3-ZS, IF4-ZS and IF5-ZS char residue
Figure 4.183: XPS curves of B1s of IF3-ZS, IF4-ZS and IF5-ZS char residue

Figure 4.184: XPS curves of Si2p of IF3-ZS, IF4-ZS and IF5-ZS char residue

Figure 4.185: XPS curves of Zr3d of IF3-ZS, IF4-ZS and IF5-ZS char residue
4.11.8 Conclusion of ICF reinforced with zirconium silicate

Based on the above results, the incorporation of 5 wt% ZS has reduced side temperature of the IF5-ZS coating substrate up to 213°C after 60 min of fire test using Bunsen burner; the flame temperature of the Bunsen burner was 950°C. Char expansion is increased by increasing the weight % of zirconium silicate; IF5-KC gave better char expansion by 24.05 times the original coating thickness. This value is 345% higher than the expansion of IF5-BA-Mel char. SEM results show that the structure of residual char continues to improve with each increasing amount of zirconium silicate, the maximum amount used in this work is 5wt%.

XRD and FTIR show the presence of boron oxide, borophosphate, graphite and zirconium silicate, sassolite and boron phosphate oxide in the residual char. TGA, DTGA and DTA show that zirconium silicate enhanced the residual weight by 34% higher than that obtained from IF5-BA-Mel formulation. XPS results show the composition of char; IF5-ZS have high carbon content (60.87%) and low oxygen content (29.08%) in the residual char which is favorable to char accumulation and anti-oxidation of char layer. Zirconium silicate is a reinforcement material that created a silicate protective barrier on the surface of the insulating materials.

4.12 Analysis of gaseous products of ICF

The gaseous decomposition products from the pyrolysed samples of intumescent coating were identified with Gas Chromatograph-Mass Spectroscopy (GC-MS). Two formulations IF5-BA-Mel (as a controlled formulation) and IF5-ZS (as the best fire protection performance) were selected for the pyrolysis analysis. The study show that for the IF5-BA-Mel and IF5-ZS, only partial degradation was achieved at 800°C. The decomposition products formed at 800°C contain several carbon, oxygen, nitrogen, and phosphorous bearing compounds. The chromatograms of IF5-BA-Mel and IF5-ZS are plotted in Figure 4.186 and Figure 4.187.

The pyrolysis products of IF5-BA-Mel and IF5-ZS are reported in Tables 4.20 and 4.21. The major pyrolysis product of IF5-BA-Mel and IF5-ZS is cyclopropane in the gas phase. According to the TGA analysis of IF5-BA-Mel, the decomposition of
Boric acid into meta boric acid (HBO\textsubscript{2}) occurs at 100-140°C, and in the second step from 140-200°C is the dehydration of metaboric acid into boron oxide (B\textsubscript{2}O\textsubscript{3}) [149].

Melamine starts its decomposition after 290°C which further reacted with APP, and as a result, melamine phosphate is formed [148]. At higher temperatures, APP eliminated ammonia upon heating, forming polyphosphoric acid, a well-known highly reactive condensing agent or acid catalyst for organic reactions[156].

Polyphosphoric acid cross-links with itself. Also, it could possibly react with boron oxide and melamine to form melamine phosphate and borophosphate. At the same time, a portion of epoxy resin decomposed, most likely by a carbonium ion mechanism [157]. The formation of carbonium ions occurs from protonation of the phosphoric group followed by a skeletal rearrangement to give the more stable carbonium ion. In the next step, an olefin is generated by the cis-elimination mechanism followed by deprotonation to form a diene. At once, the dienes or olefins formed in this way are involved in exothermic polymerization producing new aliphatic bonds [131]. Simultaneously, a foamed char is produced. These reactions promote the formation of gaseous products to generate compact charred layers in the condensed phase during burning of intumescent coating. These compact charred layers slow down heat transfer and prevent the underlying substrate from further attack by the fire. The produced gaseous products trapped inside the char helps to expand the char during burning of the intumescent coating [12, 71, 158, 159].

IF5-ZS containing 5wt% of zirconium silicate gave better char expansion by 24.05 times and gave off less gaseous products compared to IF5-BA-Mel. Pyrolysis analysis confirms that IF5-ZS is an environmental friendly intumescent coating formulation as it releases less gaseous products in terms of type and concentration compared to IF5-BA-Mel coating.
Figure 4.186: Py-GC chromatogram of gaseous products obtained from IF5-BA-Mel at 800°C

Table 4.20: Gaseous products of IF5-BA-Mel obtained at 800°C

<table>
<thead>
<tr>
<th>IF5-BA-Mel at 800°C</th>
<th>Retention Time (minute)</th>
<th>% of gaseous product</th>
<th>Suspected compound name</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of Peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.52</td>
<td>21.517</td>
<td>Cyclopropane</td>
</tr>
<tr>
<td>2</td>
<td>2.60</td>
<td>1.06</td>
<td>1,4-Cyclohexadiene</td>
</tr>
<tr>
<td>3</td>
<td>2.89</td>
<td>3.43</td>
<td>Benzene</td>
</tr>
<tr>
<td>4</td>
<td>4.18</td>
<td>0.46</td>
<td>1-Hexene-3-yne</td>
</tr>
<tr>
<td>5</td>
<td>4.50</td>
<td>0.45</td>
<td>Pyrrole</td>
</tr>
<tr>
<td>6</td>
<td>4.90</td>
<td>3.21</td>
<td>Toluene</td>
</tr>
<tr>
<td>7</td>
<td>8.20</td>
<td>0.36</td>
<td>Ethyl benzene</td>
</tr>
<tr>
<td>8</td>
<td>8.67</td>
<td>0.96</td>
<td>Benzene, 1,3-dimethyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>-----</td>
<td>------------------------------</td>
</tr>
<tr>
<td>9</td>
<td>9.80</td>
<td>1.58</td>
<td>Styrene</td>
</tr>
<tr>
<td>10</td>
<td>16.01</td>
<td>2.71</td>
<td>Phosphonic acid</td>
</tr>
<tr>
<td>11</td>
<td>16.83</td>
<td>8.68</td>
<td>Phenol</td>
</tr>
<tr>
<td>12</td>
<td>20.99</td>
<td>2.65</td>
<td>Phenol 2-methyl</td>
</tr>
<tr>
<td>13</td>
<td>32.96</td>
<td>0.78</td>
<td>Benenamine, 2, 5-dimethyl-</td>
</tr>
<tr>
<td>14</td>
<td>33.20</td>
<td>0.84</td>
<td>Benzofurran, 2, 3-dihydroxy</td>
</tr>
<tr>
<td>15</td>
<td>38.46</td>
<td>1.32</td>
<td>Naphtalene, 1-methoxy</td>
</tr>
<tr>
<td>16</td>
<td>39.14</td>
<td>8.64</td>
<td>p-Isopropenyl phenol</td>
</tr>
<tr>
<td>17</td>
<td>45.86</td>
<td>1.09</td>
<td>I-Naphthol, 5,7-dimethyl-</td>
</tr>
<tr>
<td>18</td>
<td>63.36</td>
<td>0.94</td>
<td>P-Hydroxybiphenyl</td>
</tr>
<tr>
<td>19</td>
<td>69.72</td>
<td>1.07</td>
<td>Phenol 4-(2-phenoylethylene1)</td>
</tr>
<tr>
<td>20</td>
<td>76.21</td>
<td>3.56</td>
<td>n-hexadecanoic acid</td>
</tr>
<tr>
<td>21</td>
<td>85.02</td>
<td>1.77</td>
<td>Cis-vaccenic acid</td>
</tr>
<tr>
<td>22</td>
<td>85.25</td>
<td>1.44</td>
<td>octadecanoic acid</td>
</tr>
<tr>
<td>23</td>
<td>86.99</td>
<td>11.08</td>
<td>Naphthalene, 6-methoxy-2-(1- buten-3-yl)</td>
</tr>
<tr>
<td>24</td>
<td>92.47</td>
<td>3.38</td>
<td>6,7,8,9-Tetrahydro-1, 2, 3 trimethoxy-9-methyl-5H-benzocycloheptene</td>
</tr>
<tr>
<td>25</td>
<td>132.96</td>
<td>1.62</td>
<td>2,5,8,11,14-Pentaoxyapentadecane</td>
</tr>
</tbody>
</table>
Figure 4.187: Py-GC chromatogram of gaseous products obtained from IF5-BA-Mel at 800°C

Table 4.21: Gaseous products of IF5-ZS obtained at 800°C

<table>
<thead>
<tr>
<th>IF5-ZS at 800°C</th>
<th>Retention Time (minute)</th>
<th>% of gaseous product</th>
<th>Suspected compound name</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of Peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.547</td>
<td>42.097</td>
<td>Cyclopropane</td>
</tr>
<tr>
<td>2</td>
<td>1.761</td>
<td>5.76</td>
<td>Cyclobutane, methylene-</td>
</tr>
<tr>
<td>3</td>
<td>2.625</td>
<td>1.84</td>
<td>1,4-Cyclohexadiene</td>
</tr>
<tr>
<td>4</td>
<td>2.900</td>
<td>6.31</td>
<td>Benzene</td>
</tr>
<tr>
<td>5</td>
<td>3.159</td>
<td>0.62</td>
<td>1-Heptene</td>
</tr>
<tr>
<td>6</td>
<td>4.551</td>
<td>0.60</td>
<td>Pyridine</td>
</tr>
<tr>
<td>7</td>
<td>4.922</td>
<td>5.09</td>
<td>Toluene</td>
</tr>
<tr>
<td>8</td>
<td>9.835</td>
<td>1.61</td>
<td>Styrene</td>
</tr>
</tbody>
</table>
4.13 Effect of weathering on selected ICFs

The optimized formulations were selected for weathering test. From chapter 3 section no 3.12, weathering test is conducted to observe the physical changes in char expansion and microstructure of char. The physical appearance, char expansion and char morphology after weathering test are discussed below.

4.13.1 Physical appearance and char morphology of selected ICFs after weathering

The physical appearance of the all the selected formulations (IF1-MWCNTs, IF2-MWCNTs, IF3-MWCNTs, IF3-KC, IF4-KC, IF5-KC, IF3-ZS, IF4-ZS and IF5-ZS) changed from light black colour to light yellow due to ultra violet light after weathering test. The physical appearance of the coated substrate before and after weathering test is reported in Table 4.20 to 4.22. There was no hole or cracks observed on the entire coating surface by physical inspection. The physical appearance of all the selected coatings is described in the Figures 4.188 to 4-190. The comparison of char expansion of the selected ICF before and after weathering test is illustrated in bar graph Figure 4.191. FTIR results are reported in the appendix A before and after weathering test of the selected ICFs, there is no considerable change observed in the functional groups.
The char expansion of IF1-MWCNTs, IF2-MWCNTs, IF3-MWCNTs, IF3-KC, IF4-KC, IF5-KC, IF3-ZS, IF4-ZS and IF5-ZS decreased to 2, 0.4, 1.1, 3.17, 2.53, 0.92, 1.25, 3 and 1.79 times, respectively as shown in Figure 4.191, from the original coating thickness after weathering test due to the penetration of ultraviolet rays on the surface of the coating [104, 106]. Fire spread is a surface dependent phenomenon and any changes in the surface will be reflected in the fire or heat release. Scission of macromolecules on the surface leads to formation of monomers and to chains with lower molecular weight leading to a decrease in char expansion [106]. In this study, 95% humidity was used in the weathering experiment. Due to high humidity environment, no surface water condensation was observed, but it is possible to have limited water vapour uptake by the coating which reduced the char expansion during burning of the coating. During low humidity and high temperature environment, water evaporates by diffusing through the coating [109].

Figures 4.192 to 4.194 show the morphology of IF3-MWCNTs char after burning at 800°C in a carbolite furnace. From Figure 4.192 (a, b) showing microstructures of the char, the substrate is covered with a layer of char. The microstructure of IF3-MWCNTs is similar to the microstructure of IF3-MWCNTs char before weathering reported in Figure 4.143. Figure 4.193 (a, b, c, d, e, f) show that the microstructures of IF4-KC and IF5-KC are also the same as reported in Figures 4.145 and 4.146; the char microstructure is thick and compact layers. The microstructure of zirconium silicate reinforced coatings IF3-ZS, IF4-ZS and IF5-ZS also show a thick and solid char layer structure after weathering test as shown in Figure 4.194. For IF3-MWCNTs, IF4-KC, IF5-KC, IF3-ZS, IF4-ZS and IF5-ZS coatings, flakes can be seen inside the char indicating that the higher melting point of the fillers used in these coating formulations. These flakes can withstand higher temperature and restrains the expansion of IF5-BA-Mel coating.

In Figures 4.193 (a, b), 193 (c, d, e, f), 4.194 (a, b), 4.194(c, d, e, f) and 4.194 (g, h, i, j) showing the microstructures of IF4-KC, IF5-KC, IF3-ZS, IF4-ZS and IF5-ZS, respectively, some voids can be observed in the micrograph. Voids are produced by trapped gas evolved from the blowing agent when the coating is exposed to fire. These voids act as thermal insulative barrier, which not only prevents heat transmission to the underlying substrate, but also prevents diffusion of gaseous
degradation products to the combustion zone, as well as oxygen diffusion to the surface of polymer [160].

The use of fillers such as MWCNTs, Kaolin clay and zirconium silicate contributes to develop a ceramic like protective layer on the surface of char which produced cellular structure that is helpful in reducing fire penetration to the substrate. It is believed that the addition of inorganic fillers into the coating formulations as flame retardants improves the efficiency of intumescent behaviour in ICF [81, 161, 162]. The fillers might have an effect on the cell structure of char foam [162]. Thus, it can be concluded that cellular structure is important for fire retardant effectiveness [77, 78].

Table 4.22: MWCNTs based intumescent coating before and after weathering

<table>
<thead>
<tr>
<th>Before IF1-MWCNTs</th>
<th>After IF1- MWCNTs</th>
<th>Before IF2- MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical appearance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Observation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– Less viscous</td>
<td>– Change in Colour Slightly yellowish</td>
<td>– Slightly high viscous</td>
</tr>
<tr>
<td>– Black</td>
<td></td>
<td>– Black</td>
</tr>
<tr>
<td>– Easy to stir with mixer</td>
<td></td>
<td>– Easy to stir with mixer</td>
</tr>
<tr>
<td>– Easy to apply with brush</td>
<td></td>
<td>– Easy to apply with brush</td>
</tr>
<tr>
<td>– Touch dry after 7 day</td>
<td></td>
<td>– Touch dry after 8 days</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After IF2- MWCNTs</th>
<th>Before IF3- MWCNTs</th>
<th>After IF3- MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical appearance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Observation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– Change in Colour</td>
<td>– High viscous</td>
<td>– Change in colour</td>
</tr>
<tr>
<td>– Slightly yellowish</td>
<td>– Black</td>
<td>– Slightly yellowish</td>
</tr>
<tr>
<td>– Hard to stir with mixer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– Hard to apply with brush</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– Touch dry after 6 days</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

238
(a) Physical appearance of IF1-MWCNTs char and coating after weathering test

(b) Physical appearance of IF2-MWCNTs char and coating after weathering test

(c) Physical appearance of IF3-MWCNTs char and coating after weathering test

Figure 4.188: (a, b, c, d) showing physical appearance of MWCNTs char and coating after weathering

Table 4.23: Kaolin clay based intumescent coating before and after weathering

<table>
<thead>
<tr>
<th></th>
<th>Before IF3-KC</th>
<th>After IF3-KC</th>
<th>Before IF4-KC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical appearance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before IF3-KC</td>
<td>After IF3-KC</td>
<td>Before IF4-KC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– Less viscous</td>
<td>– Change in Colour</td>
<td>– Less viscous</td>
<td>– Severe coagulation of solid particles after a while</td>
</tr>
<tr>
<td>– Slightly black</td>
<td>– Slightly yellowish</td>
<td>– Slightly Black</td>
<td>– Touch dry after 8 days</td>
</tr>
<tr>
<td>– Easy to stir with mixer</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>– Easy to apply with brush</td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>– Touch dry after 7 day</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
After IF4-KC | Before IF5-KC | After IF5-KC
--- | --- | ---
**Physical appearance** | | |
**Observation** | – Slightly yellow | – High viscous | – Slightly yellowish
| – Touch dry after 6 days |

(a) Physical appearance of IF3-KC char and coating after weathering test

(b) Physical appearance of IF4-KC char and coating after weathering test

(c) Physical appearance of IF5-KC char and coating after weathering test

Figure 4.189: (a, b, c, d) showing physical appearance of KC char and coatings after weathering
Table 4.24: Zirconium silicate based intumescent coating before and after weathering

<table>
<thead>
<tr>
<th>Physical appearance</th>
<th>Before IF3-ZS</th>
<th>After IF3-ZS</th>
<th>Before IF4-ZS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>− Less viscous</td>
<td>− Slightly yellowish</td>
<td>− Slightly high viscous</td>
<td></td>
</tr>
<tr>
<td>− Slightly black</td>
<td>− Slightly black</td>
<td>− Easy to stir with mixer</td>
<td></td>
</tr>
<tr>
<td>− Easy to stir with mixer</td>
<td>− Easy to apply with brush</td>
<td>− Touch dry after 8 days</td>
<td></td>
</tr>
<tr>
<td>− Easy to apply with brush</td>
<td>− Touch dry after 7 day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>− Touch dry after 7 day</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical appearance</th>
<th>After IF4-ZS</th>
<th>Before IF5-ZS</th>
<th>After IF5-ZS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>− Slightly yellowish</td>
<td>− High viscous</td>
<td>− Slightly yellowish</td>
<td></td>
</tr>
<tr>
<td>− Slightly yellowish</td>
<td>− Slightly black</td>
<td>− Easy to stir with mixer</td>
<td></td>
</tr>
<tr>
<td>− High viscous</td>
<td>− Slightly black</td>
<td>− Hard to stir with mixer</td>
<td></td>
</tr>
<tr>
<td>− Slightly yellowish</td>
<td>− Easy to apply with brush</td>
<td>− Touch dry after 6 days</td>
<td></td>
</tr>
<tr>
<td>− Hard to stir with mixer</td>
<td>− Touch dry after 8 days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>− Touch dry after 6 days</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Physical appearance of IF3-ZS char and coating after weathering test
(b) Physical appearance of IF4-ZS char and coating after weathering test

(c) Physical appearance of IF5-ZS char and coating after weathering test

Figure 4.190: (a, b, c, d) showing physical appearance of ZS char and coatings after weathering

Figure 4.191: Char expansion at 800°C of the selected coatings after weathering test
Figure 4.192: (a) FESEM micrograph of IF3-MWCNTs (b) MWCNTs linked char cracks

Figure 4.193: SEM micrograph of (a, b) IF4-KC and (c, d, e, f) IF5-KC
(a) Upper smooth char structure of IF3-ZS

(b) thick and cracks on the inner char structure of IF3-ZS

(c) Upper smooth surface of IF4-ZS

(d) Compact char structure of IF4-ZS

(e) Cracks inside of char

(f) Agglomerates of IF4-ZS

(g) Smooth upper char surface of IF5-ZS

(h) Compact char of IF5-ZS
4.13.2 Conclusion

From the above results, the formulation IF5-ZS has shown the better results in char expansion and char morphology after the weathering test. Of all the selected coatings, its char expansion was decreased the most after the weathering test. The char expansion of IF5-ZS is 22.26 times with respect to the original coating thickness on the substrate after the weathering test. SEM results show that the residual char retains its microstructure after the weathering test. The reinforcement of MWCNTs, kaolin clay and zirconium silicate created protective barrier layer on the surface of the insulating substrate which helps to minimize heat flow to the substrate.

Table 4.25: Summary of char expansion, substrate temperature and residual weight of ICFs

<table>
<thead>
<tr>
<th>Coating</th>
<th>Expansion</th>
<th>Substrate temp after 60min</th>
<th>Composition</th>
<th>Residual wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF1-Mel</td>
<td>11</td>
<td>470</td>
<td>Graphite</td>
<td>22.64</td>
</tr>
<tr>
<td>IF2-BA</td>
<td>3</td>
<td>360</td>
<td>------------</td>
<td>29.6</td>
</tr>
<tr>
<td>IF3-BA-Mel</td>
<td>7.5</td>
<td>480</td>
<td>Borophosphate, Graphite, boron oxide</td>
<td>-------</td>
</tr>
<tr>
<td>IF4-BA-Mel</td>
<td>5.3</td>
<td>387</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>25.58</td>
</tr>
<tr>
<td>IF5-BA-Mel</td>
<td>4.6</td>
<td>367°C</td>
<td>Boron oxide, borophosphate, graphite,</td>
<td>28.54%</td>
</tr>
<tr>
<td>Coating</td>
<td>Expansion</td>
<td>Substrate temp after 1 h</td>
<td>Composition</td>
<td>Residual wt%</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>--------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>IF1-BAP</td>
<td>2</td>
<td>503</td>
<td>Graphite (Carbon)</td>
<td>22.6</td>
</tr>
<tr>
<td>IF2-APP</td>
<td>9.6</td>
<td>470</td>
<td>Graphite (Carbon)</td>
<td>19.3</td>
</tr>
<tr>
<td>IF3-BA-APP</td>
<td>7.61</td>
<td>480</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>18.19</td>
</tr>
<tr>
<td>IF4-BA-APP</td>
<td>6.34</td>
<td>385</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>24</td>
</tr>
<tr>
<td>IF5-BA-APP</td>
<td>5.27</td>
<td>421</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>28.35</td>
</tr>
<tr>
<td>IF1-APP</td>
<td>6.4</td>
<td>464</td>
<td>Boron phosphate, boron phosphate oxide</td>
<td>21.3</td>
</tr>
<tr>
<td>IF2-EG</td>
<td>2</td>
<td>503</td>
<td>Graphite</td>
<td>19.66</td>
</tr>
<tr>
<td>IF3-APP-EG</td>
<td>8.7</td>
<td>489</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>----</td>
</tr>
<tr>
<td>IF4-APP-EG</td>
<td>7.5</td>
<td>461</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>27.3</td>
</tr>
<tr>
<td>IF5-APP-EG</td>
<td>6.2</td>
<td>389</td>
<td>Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Table 4.26: Summary of char expansion, substrate temperature, char composition and residual weight of MWCNTs, kaolin clay and zirconium silicate reinforced ICF
| IF3-MWCNTs | 7.5 | 273 | Boron oxide, borophosphate, graphite, sassolite boron phosphate oxide | 29.36 |
| IF1-KC     | 6.1 | 360 | Boron oxide, borophosphate, kaolinite graphite, sassolite boron phosphate oxide | ----- |
| IF2-KC     | 8.3 | 334 | Boron oxide, borophosphate, kaolinite graphite, sassolite boron phosphate oxide | ----- |
| IF3-KC     | 12.57 | 306 | Boron oxide, borophosphate, kaolinite graphite, sassolite boron phosphate oxide | 35.6 |
| IF4-KC     | 13.83 | 286 | Boron oxide, borophosphate, kaolinite graphite, sassolite boron phosphate oxide | 39.43 |
| IF5-KC     | 15   | 257 | Boron oxide, borophosphate, kaolinite graphite, sassolite boron phosphate oxide | 42.5 |
| IF1-ZS     | 5.4  | 359 | Boron oxide, borophosphate, zirconium silicate, graphite, sassolite boron phosphate oxide | 30.92 |
| IF2-ZS     | 7.32 | 330 | Boron oxide, borophosphate, zirconium silicate, graphite, sassolite boron phosphate oxide | 31.90 |
| IF3-ZS     | 10.43 | 292 | Boron oxide, borophosphate, zirconium silicate, graphite, sassolite boron phosphate oxide | 34.50 |
| IF4-ZS     | 18.76 | 249 | Boron oxide, borophosphate, zirconium silicate, graphite, sassolite boron phosphate oxide | 36.60 |
| IF5-ZS     | 24.05 | 213 | Boron oxide, borophosphate, zirconium silicate, graphite, sassolite boron phosphate oxide | 38.20 |