char expansion and char morphology of intumescent fire retardant coating formulations. Four sets of intumescent coating formulations were prepared with each particle size of EG and each set of intumescent coating contained 9 formulations.

4.5.1 ICFs with EG particle size 63µm

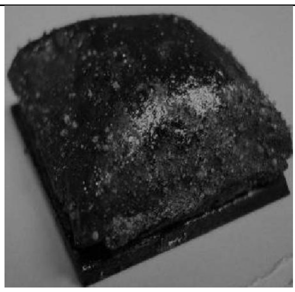
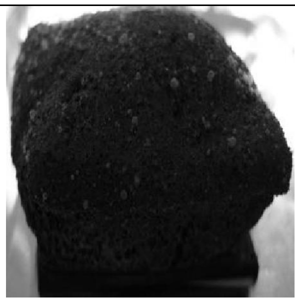
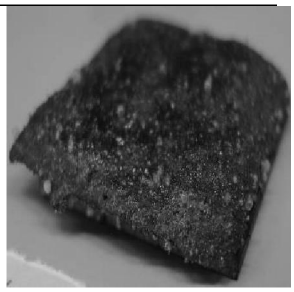
From Table 3.12 nine formulations were developed with 63µm particle size of EG. The physical appearance and observation of the 63µm EG coatings before and after fire are described below in the Table 4.10 and 4.11, respectively.

Table 4.10: Intumescent coating of 63µm EG before furnace test

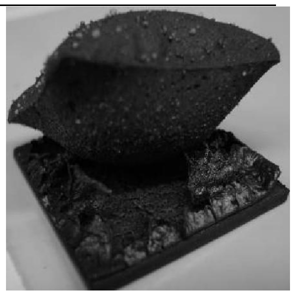
	Formulation IF4-1-63µm	**Formulation IF4-2-63µm**	**Formulation IF4-3-63µm**
Physical appearance			
Observation	– less viscous – Slightly black – Sticky surface – Touch dry after 8 days	– Less viscous – Slightly black – Sticky surface – Touch dry after 8 days	– Less viscous – Slightly black – Severe coagulation of solid particles after a while – Touch dry after 8 days
	Formulation IF4-4-63µm	**Formulation IF4-5-63µm**	**Formulation IF4-6-63µm**
Physical appearance			
Observation	– Less viscous – Severe coagulation of solid particles after a while – Touch dry after 7 days	– Less viscous – Severe coagulation of solid particles after a while – Touch dry after 6 days	– highly viscous – Severe coagulation of solid particles after a while – Touch dry after 6 days

	Formulation IF4-7-63µm	Formulation IF4-8-63µm	Formulation IF4-9-63µm
Physical appearance			
Observation	– highly viscous – Difficult to stir with mixer – Difficult to apply with brush – Black colour – Severe coagulation of solid particles after a while – Touch dry after 4 days	– highly viscous – Difficult to stir with mixer – Difficult to apply with brush – Black colour – Severe coagulation of solid particles after a while – Touch dry after 4 days	– highly viscous – Difficult to stir with mixer – Difficult to apply with brush – Black colour – Touch dry after 4 days

Table 4.11: Intumescent coating of 63µm EG after furnace test

	Formulation IF4-1-63µm	Formulation IF4-2-63µm	Formulation IF4-3-63µm
Physical appearance			
Observation	– Ave coating thickness: 2.5mm – Ave char thickness: 7.27mm – Expansion: 2.91 times	– Ave coating thickness: 2.35mm – Ave char thickness: 16.45mm – Expansion: 7.0 times	– Ave coating thickness: 2.0mm – Ave char thickness: 11.2mm – Expansion: 5.6 times
	– Rigid char – No void	– Weak char – void in middle	– Hard char – Small void in middle – Small bubbles on surface
	Formulation IF4-4-63µm	**Formulation IF4-5-63µm**	**Formulation IF4-6-63µm**
Physical appearance			
Observation	– Ave coating thickness: 2.2mm	– Ave coating thickness: 2.15mm	– Ave coating thickness: 1.8mm

	– Ave char thickness: 15.86mm – Expansion: 7.2times – Hard char – Small void in middle	– Ave char thickness: 18.27mm – Expansion: 8.5 times – Hard char – small void in middle	– Ave char thickness: 8.37mm – Expansion: 4.65 times – Weak char – large void in middle

	Formulation IF4-7-63µm	Formulation IF4-8-63µm	Formulation IF4-9-63µm
Physical appearance			
Observation	– Ave coating thickness: 2.0mm – Ave char thickness: 10.76mm – Expansion: 5.38 times – Hard char – Small void in middle – Bubbles on surface	– Ave coating thickness: 2.9mm – Ave char thickness: 19.22mm – Expansion: 6.63 times – Hard char – Week adhesion	– Ave coating thickness: 2.8mm – Ave char thickness: 11.5mm – Expansion: 4.12 times – Hard char – Week adhesion

4.5.1.1 Char expansion of 63µm EG ICFs

Figure 4.49 shows the char expansion of 63µm EG ICF, char expansion formed by each formulation is 2.91(IF4-1-63µm), 4.3 (IF4-2-63µm), 5.6 (IF4-3-63µm), 7.21 (IF4-4-63µm), 8.51 (IF4-5-63µm), 4.65 (IF4-6-63µm), 5.38 (IF4-7-63µm), 6.63(IF4-8-63µm) and 4.12 (IF4-9-63µm). The char expansion was increased due to increase in the wt% of expandable graphite 9.8% up to formulation IF4-5-63µm, further addition of EG, the expansion is decreased by increase the wt% of EG as shown in Figure 4.35. The IF4-5-63µm give 8.15 times expansion which showed 192, 97, 51, 15, 83, 57, 28, 107 percent higher char expansion compared to IF4-1-63µm, IF4-2-63µm, IF4-3-63µm, IF4-4-63µm, IF4-6-63µm, IF4-7-63µm, IF4-8-63µm and IF4-9-63µm, respectively.

The physical appearance of char expansion in Table 4.11 showed that the formulations IF4-7-63µm, IF4-8-63µm, IF4-9-63µm were detached from the substrate as weight percentage of EG was above to 10.8%. It is assumed that excess amount of

EG 63μm above than 10.8 wt%; char expanded abruptly with uniform network structure by affecting the char adhesion on the substrate.

From the studies reported earlier in this chapter (one, two and three ingredients on intumescent behaviour with epoxy and hardener) showed that EG expands uniformly during fire test at 350°C with the release of CO_2 and insulate the substrate. Melamine decompose into its derivatives after 250°C by releasing NH_3 gas which escape by the char as result the char will expand. APP is an acid source which also starts to decomposed at 290°C releasing NH_3 with the formation of poly phosphoric acid which further reacted with rich polyhydric carbon source to form the thick layer of the char to insulate the substrate. Boric acid used to increase the adhesion of char with substrate. The role of EG is to make the carboneous char and expand the char by release of CO_2 and H_2O. The CO_2 acts as fire extinguisher and reduce the flame temperature during the fire [129, 142].

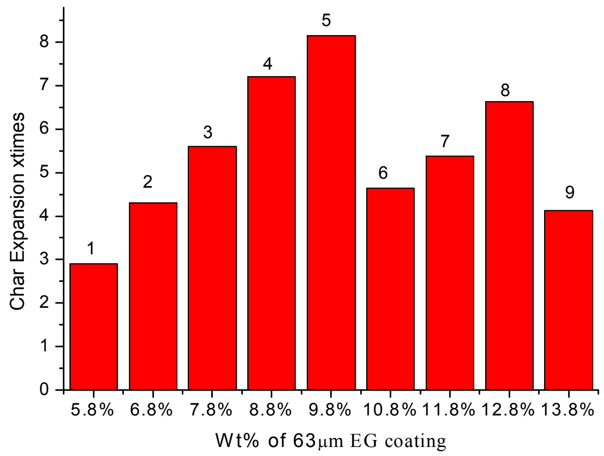


Figure 4.49: Char expansion of IF4-63μm EG formulations

4.5.1.2 Char morphology of IF4-63μm EG ICFs

The formation of charring layer protects the metal substrate from fire, and its heat shielding property depends on the physical and chemical structure of the charring layer [68]. The formation of chars and their morphological structures were studied by SEM. The selected samples were examined for physical appearance of intumescent coating after fire test.

SEM micrographs of IF4-1-63μm, IF4-4-63μm, IF4-5-63μm and IF4-6-63μm char are shown in the Figures 4.50(a, b), 4.51 (a, b), 4.52(a, b) and 4.53 (a, b), respectively. The multicellular structure can hinder heat transferring to the substrate, and protect the substrate from fire. Transfer speed of heat through the char layer depends on the resistance of the coating to fire. The expansion of the char and structure are very important to common fire resistant properties of coating [84]. From Figure 4.50a, the upper surface microstructure char of IF4-1-63μm showed smooth surface and inner was thick char as exposed in Figure 4.50b.

Figure 4.51a showed the SEM images of IF4-4-63μm which is modified from IF4-1-63μm formulation by increasing the weight of EG upto 9.8%. The SEM image showed the smooth surface area with thick layer of upper surface of IF4-4-63μm illustrated in Figure 4.37a and the inner char structure is thick multicellular structure which hinders the heat to the substrate illustrated in Figure 4.51b. The different aperture surface tensions in the route of gas cavities led to the irregularity of swelling, the surface tension rely on the viscosity and regularity of the coating [68].

From Figure 4.52 (a, b) represented the microstructures of the IF4-5-63μm formulations, outer surface showed smooth top surface of the char. There are small cracks and holes observed on microstructure of IF4-5-63μm which represents the dehydration of water. Air in these holes can lower heat penetration to the substrate [119, 143]. The charring layers formation is thick and more uniform hindered the heat to penetrate the substrate, which gives better effect of flame retardancy. There are many irregular petite holes of the soft foam in the charring layer due the dehydration of APP, boric acid and melamine proceeds in the range of relatively suitable temperature [144].

The SEM images of IF4-6-63μm showed thick char and agglomerates in Figure 4.53 (a, b). The asymmetry of swelling, the different aperture surface tension is the cause and they depend on the thickness and regularity of the formulation. The intumescent char with tiny stoma contributes to heat wadding and shield the internal matrix substrate.

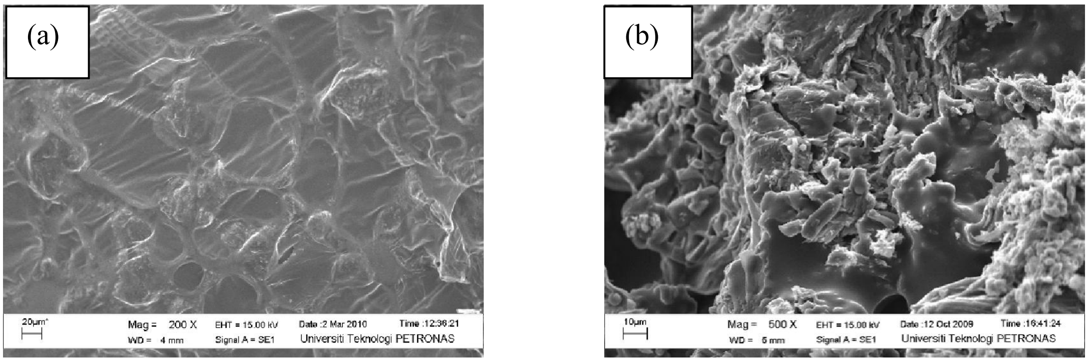


Figure 4.50: (a) IF4-1-63µm thin layer with smooth surface and b) inside thick char insulate the substrate

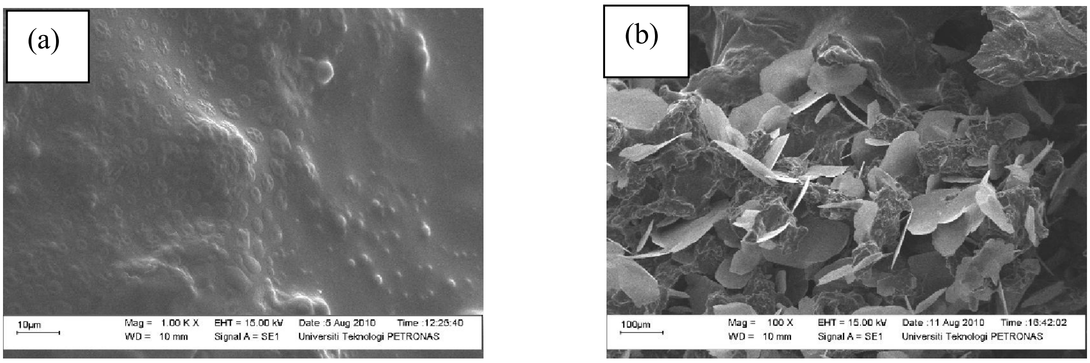


Figure 4.51: a) IF4-4-63µm thin layer with smooth surface. b) Inside char flakes prevent the fire to penetrate inside the substrate

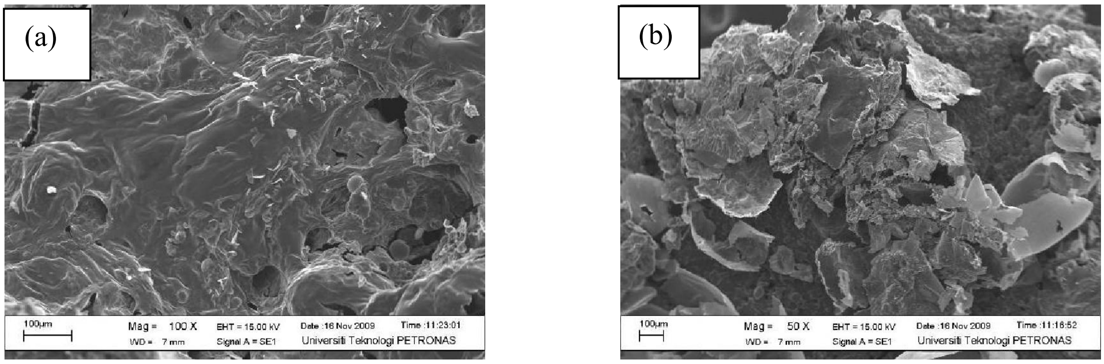


Figure 4.52: a) IF4-5-63µm smooth outer b) thick inner surface with flacks

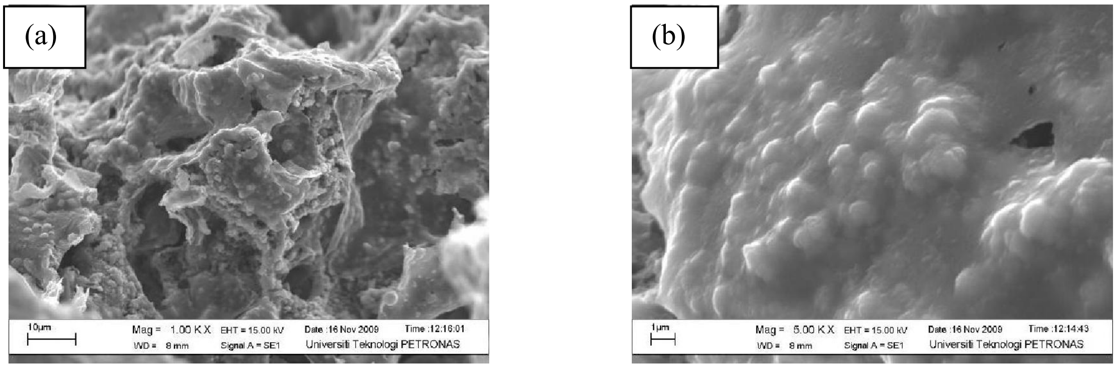
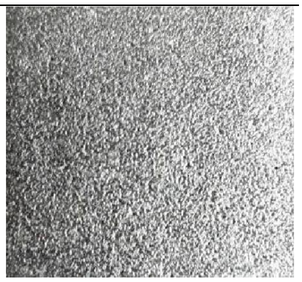
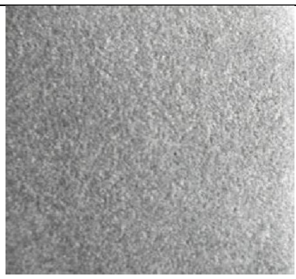
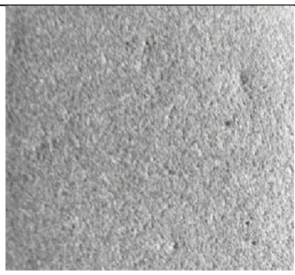
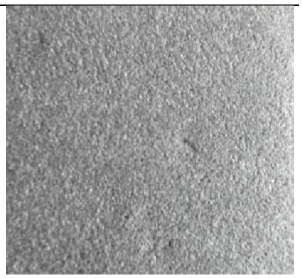


Figure 4.53: a) IF4-6-63µm inside char thick char b) Char agglomerates

4.5.2 ICFs with EG particle size 150µm

From table 3.13 nine formulations were prepared with 150µm particle size of EG. . The physical appearance and observation of the 150µm EG coatings before and after fire test are described below in the Table 4.12 and 4.13, respectively.

Table 4.12: Intumescent coating of 150µm EG before furnace test

	Formulation IF4-1-150µm	**Formulation IF4-2-150µm**	**Formulation IF4-3-150µm**
Physical appearance			
Observations	− Less viscous − Easy to stir with mixer − Easy to apply with brush − Touch dry after 8 day	− Less viscous − Easy to stir with mixer − Easy to apply with brush − Touch dry after 8 days	− Less viscous − Easy to stir with mixer − Easy to apply with brush − Touch dry after 8 days
	Formulation IF4-4-150µm	**Formulation IF4-5-150µm**	**Formulation IF4-6-150µm**
Physical appearance			
Observations	− Less viscous − Severe coagulation of solid particles after a while − Touch dry after 7 days	− Less viscous − Severe coagulation of solid particles after a while − Touch dry after 6 days	− High viscous − Severe coagulation of solid particles after a while − Touch dry after 6 days

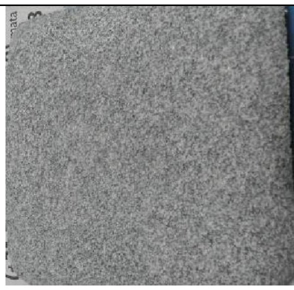
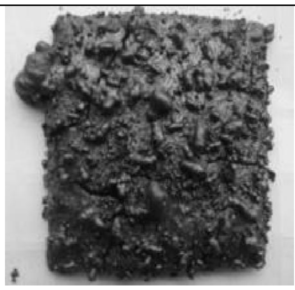
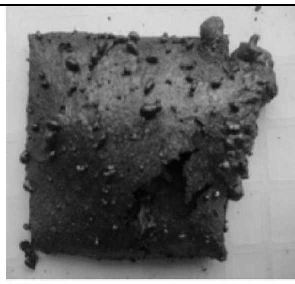
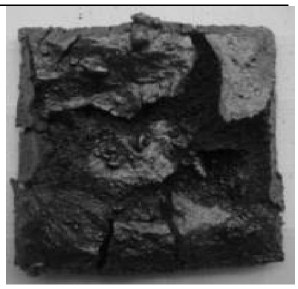
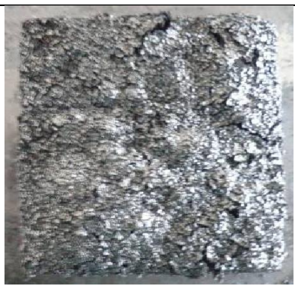
	Formulation IF4-7-150µm	Formulation IF4-8-150µm	Formulation IF4-9-150µm
Physical appearance			
Observations	– Black colour – High viscous – Severe coagulation of solid particles after a while – Touch dry after 4 days	– Black colour – High viscous – Severe coagulation of solid particles after a while – Touch dry after 4 days	– Black colour – High viscous – Severe coagulation of solid particles after a while Touch dry after 4 days

Table 4.13: Intumescent coating of 150µm EG after furnace test

	Formulation IF4-1-150µm	Formulation IF4-2-150µm	Formulation IF4-3-150µm
Physical appearance			
Observations	– Ave coating thickness: 1.5mm – Ave char thickness: 4.8mm – Expansion: 3.2 times – Soft char – No void – Small bubbles on surface	– Ave coating thickness: 1.2mm – Ave char thickness: 5.4mm – Expansion: 4.5 times – Hard char – Large void in middle – Small bubbles on surface	– Ave coating thickness: 1.5mm – Ave char thickness: 10.2mm – Expansion: 6.8 times – Hard char – Small void in middle
	Formulation IF4-4-150µm	**Formulation IF4-5-150µm**	**Formulation IF4-6-150µm**
Physical appearance			
Observations	– Ave coating thickness: 2.1mm – Ave char thickness: 23.73mm – Expansion: 11.3 times – Hard char	– Ave coating thickness: 2.25mm – Ave char thickness: 10.12mm – Expansion: 4.5 times – Hard char	– Ave coating thickness: 1.8mm – Ave char thickness: 12.42mm – Expansion: 6.9 times – Soft and weak char

	Formulation IF4-7-150µm	Formulation IF4-8-150µm	Formulation IF4-9-150µm
Physical appearance			
Observations	− Ave coating thickness: 1.7mm − Ave char thickness: 15.0mm − Expansion: 8.82 times − Weak char	− Ave coating thickness: 2.1mm − Ave char thickness: 9.24mm − Expansion: 4.4 times − Cracked and weak char	− Ave coating thickness: 1.9mm − Ave char thickness: 4.37mm − Expansion: 2.3 times − Cracked and weak char

4.5.2.1 Char expansion of IF4-150µm EG ICFs

Figure 4-40 represents the char expansion of formulation IF4-150µm after fire test. The char expansion by each formulation is 3.2 times (IF4-1-150µm),4.5 (IF4-2-150µm), 6.8 (IF4-3-150µm), 11.3 (IF4-4-150µm), 4.5 (IF4-5-150µm), 6.9 (IF4-6-150µm), 8.82 IF4-7-150µm, 4.4 times (IF4-8-150µm), 2.3 times (IF4-9-150µm) showed in Figure 4.54. The char expansion of IF4-1-150µm, IF4-2-150µm, IF4-3-150µm and IF4-4-150µm was increased 9.96, 4.65, 21, 30 percent compared to IF4-1-63µm, IF4-2-63um, IF4-3-63um, IF4-4-63um due to increased the particle size of EG from 63µm to 150µm. The maximum char expansion was obtained 9.38 time of IF4-4-150µm with 8.8wt of EG. Formulation IF4-5-150µm, IF4-6-150µm, IF4-7-150µm, IF4-8-150µm and IF4-9-150µm decreased the char expansion by increased the wt% of EG as illustrated in Figure 4-40. It is clear from the physical appearance of char described in Tabled 4.13 that the char expansion is decreased due to cracks on the surface of the char. These cracks are due to the rapid expansion of EG with excess wt% of certain limit. EG expand 100 or more times from original graphite [120].

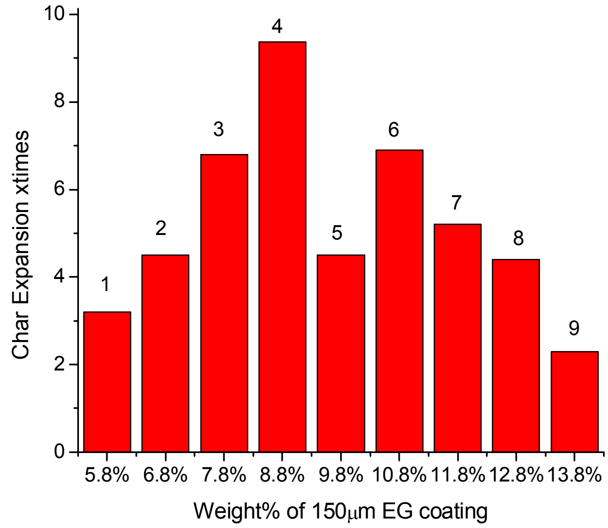


Figure 4.54: Char expansion of IF4-150μm EG formulations

4.5.2.2 Char morphology of IF4-150μm EG ICFs

Three char samples IF4-2-150μm, IF4-4-150μm and IF4-6-150μm were chosen based on the physical appearance and char expansion of intumescent coating after fire test.

Figure 4.55(a) represents the outer char surface of IF4-2-150μm which showed thick surface of the char with cracks. These cracks and holes with a diameter of 10–60μm in the char structure are presented in Figure 4-55(a). Air can lower the heat transfer in these holes; the speed of heat transfer increased if the diameter of these holes is larger than 40μm [75]. The inside char microstructure, bubbles were observed due to emission of non flammable gases as shown in Figure 4.55(b). These bubbles expanded the char due the emission of N_2, NH_3 and CO_2 [129]. It explains the dehydration of APP, boric Acid and frothing of melamine proceeds in the range of rather appropriate temperature. The intumescent charring layers with bubbles act as the effect of the flame retardant, heat insulation and protecting inner matrix substrate. Figure 4.56(a) showed the upper surface of the char IF4-4-150μm, it is smooth and no hole or bubbles observed on the surface of the char which showed the complete insulation on substrate and protected from fire. The inside micro images of IF-4-150μm in Figure 4.56 (b, c and d) showed the formation of bubbles and cracks respectively. The morphology of IF4-6-150μm presented in the Figure 4.57 (a, b), it has similar outer surface structure compared to IF4-2-150µm in Figure 4-41a, while holes and cracks are noted in Figure 4-43b.

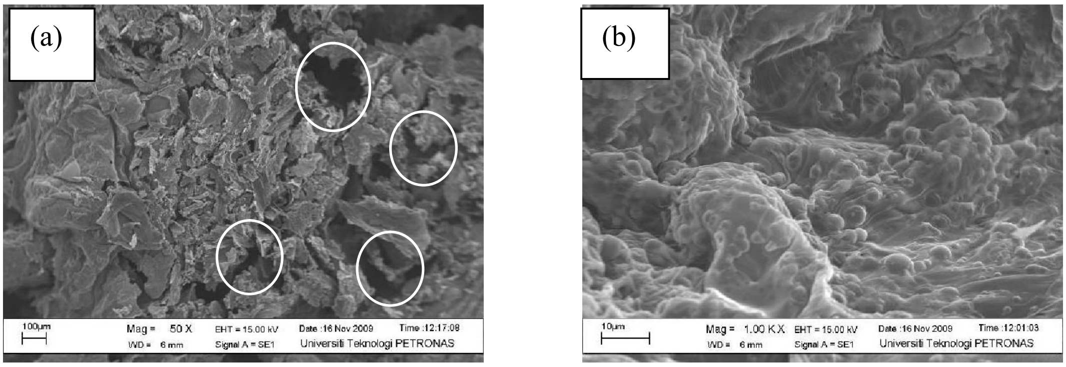


Figure 4.55: (a) The IF4-2-150µm outer surface of the char with rough surface and cracks, (b) inside the charring layers contained bubbles.

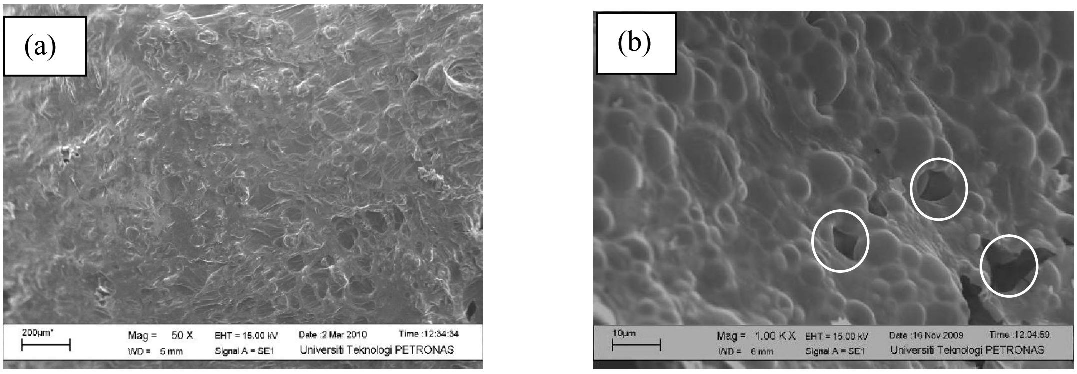
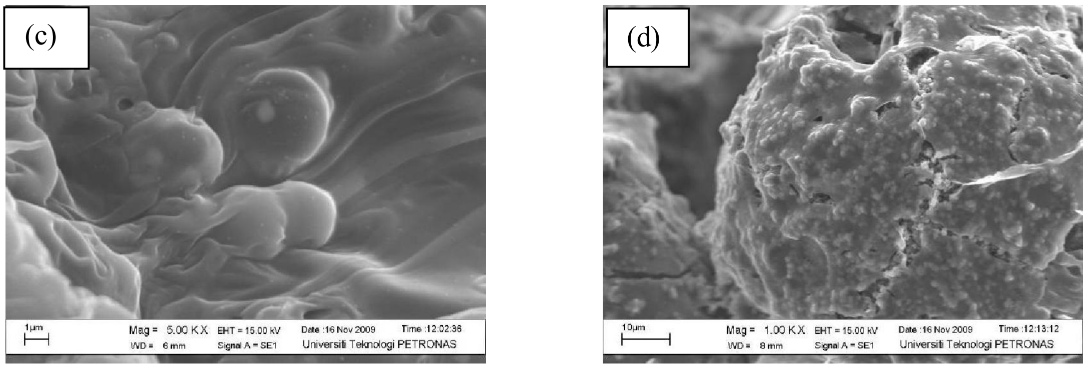


Figure 4.56: (a) IF4-4-150µm with smooth surface area on the upper surface, (b) with small bubbles on inside the char



(c) Inside bubbles with thick char of IF4-4-150µm, (d) Cracks in side of the char

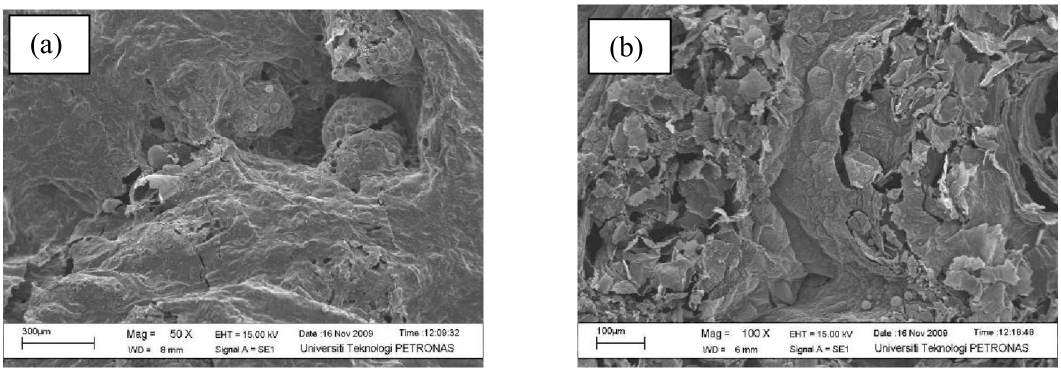
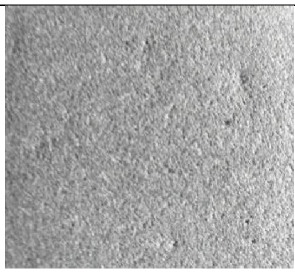
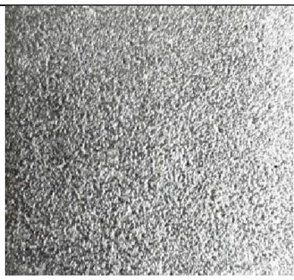
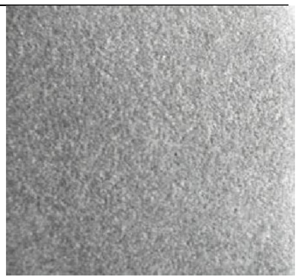


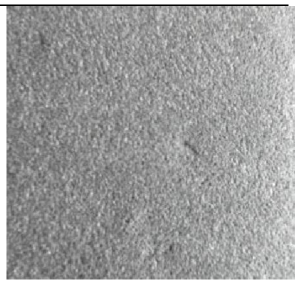
Figure 4.57: (a) rough outer surface of IF4-6-150µm (b) holes and cracks in side of the char

4.5.3 ICFs with EG particle size 212µm

From table 3.14 nine formulations were prepared with 212µm particle size of EG. The weight percentages of 212µm EG were varied from 5.8-13.8% in the formulations studied. The weight percentage of all other ingredients were fixed to study the effect of 212µm EG on char expansion and char morphology. The physical appearance of the 212µm EG based coatings and corresponding char after fire are given below in the Table 4.14 and 4.15, respectively.

Table 4.14: Intumescent coating of 212µm EG before furnace test

	Formulation IF4-1-212µm	**Formulation IF4-2-212µm**	**Formulation IF4-3-212µm**
Physical appearance			
Observations	– Highly viscous – Easy to stir with mixer – Easy to apply with brush – Touch dry after 8 day	– Less viscous – Easy to stir with mixer – Easy to apply with brush – Touch dry after8 days	– Less viscous – Easy to stir with mixer – Easy to apply with brush – Touch dry after 8 days

	Formulation IF4-4-212µm	Formulation IF4-5-212µm	Formulation IF4-6-212µm
Physical appearance			
Observations	– Less viscous – Touch dry after 7 days	– Less viscous – Touch dry after 7 days	– Less viscous – Touch dry after 6 days

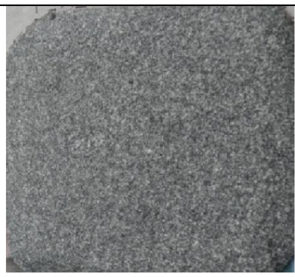
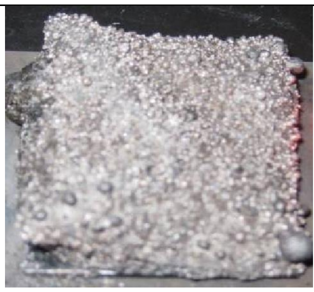
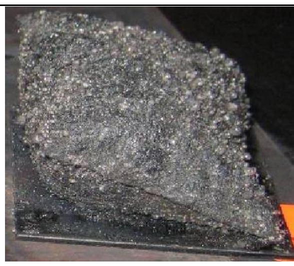
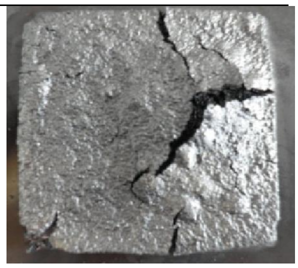
	Formulation IF4-7-212µm	Formulation IF4-8-212µm	Formulation IF4-9-212µm
Physical appearance			
Observations	– High viscous – Touch dry after 5 days	– High viscous – Touch dry after 5 days	– High Viscous – Touch dry after 5 days

Table 4.15: Intumescent coating of 212µm EG after furnace test

	Formulation IF4-1-212µm	Formulation IF4-2-212µm	Formulation IF4-3-212µm
Physical appearance			
Observations	– Ave. coating thickness: 1.5mm – Ave char thickness: 6.8mm – Expansion: 4.54 times – Hard char – Cracked char	– Ave. coating thickness: 1.7mm – Ave char thickness: 8.3mm – Expansion: 4.9 times – Hard char – Small bubbles on surface	– Ave. coating thickness: 1.2mm – Ave char thickness: 9.1mm – Expansion: 7.6 times – Hard char

	Formulation IF4-4-212µm	Formulation IF4-5-212µm	Formulation IF4-6-212µm
Physical appearance			
Observations	– Ave. coating thickness: 2.3mm – Ave char thickness: 25.3mm – Expansion: 11 times – Hard char	– Ave. coating thickness: 1.1mm – Ave char thickness: 9.27mm – Expansion: 8.4 times – Hard char	– Ave.coating thickness: 1.9mm – Ave char thickness: 5.60mm – Expansion: 2.95 times – Hard char

	Formulation IF4-7-212µm	Formulation IF4-8-212µm	Formulation IF4-9-212µm
Physical appearance			
Observations	– Ave. coating thickness: 1.3mm – Ave char thickness: 9.6mm – Expansion: 7.4 times – Detached from substrate	– Ave. coating thickness: 2.2mm – Ave char thickness:14.96 mm – Expansion: 6.8 times – Cracked char	– Ave. coating thickness: 1.9mm – Ave char thickness: 8.9mm – Expansion: 4.7 times – Cracked char

4.5.3.1 Char expansion of 212µm EG ICFs

Figure 4-44 represents the char expansion of formulations IF4-212µm after fire test. Formulation IF4-1-212µm, IF4-2-212µm IF4-3-212µm, IF4-4-212µm, IF4-5-212µm, IF4-6-212µm, IF4-7-212µm, IF4-8-212µm, IF4-9-212µm showed the char expansion 4.54, 4.90, 7.6, 11.0, 8.4, 2.95, 7.4, 6.8 and 4.7 times, respectively in Figure 4.58. Formulation IF4-1-212µm, IF4-2-212µm, IF4-3-212µm, IF4-4-212µm showed that increasing the weight percent 5.8 to 8.8 wt% of EG, the char expansion was increased 4.54, 4.90, 7.6, 11.0 times, respectively. The maximum char expansion 11.0 times was obtained from formulation IF4-4-212µm with 8.8wt% of EG. In formulation IF4-5-212µm char expansion is 8.4 times with 9.8wt% of EG; char expansion of IF4-5-212µm is decreased 32 percent compared to the IF4-4-212µm. The char expansion was decreased as wt% of EG was increased in the formulation IF4-5-212µm, IF4-6-212µm, IF4-7-212µm, IF4-8-212µm and IF4-9-212µm respectively, as shown in the Figure 4-44. As earlier it is discussed in IF-63µm, that above 8.8 wt% EG expand the char with release of CO_2 and char could not maintain its integrity in the case of expansion and adhesion. The formulation showed the weak char adhesion with substrate in Table 4.15 of IF4-5-212µm and IF4-7-212µm, the cracked char surface of IF4-8-212µm and IF4-9-212µm depicted in physical appearance Table 4.15. The formulation IF4-9-212µm showed the expansion 4.9 times. It is clear from Table 4.15 that the expansion is decreased due to cracks on the surface of the char. The phenomena of this reason is that these cracks helps to evacuate the evolved gases outside from the char resulted less expansion instead to trap these gases inside the char for higher expansion of the char. IF4-4-212µm showed excellent result in char expansion 11.62 times among all the pervious formulations.

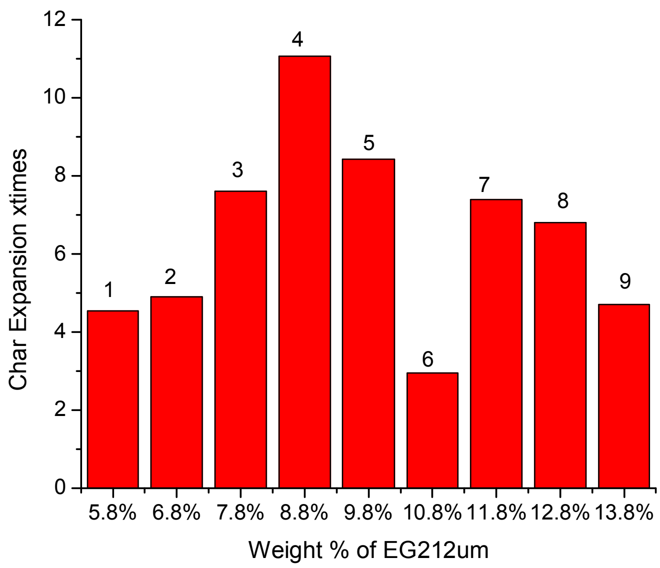


Figure 4.58: Char expansion of 212µm EG formulations

4.5.3.2 Char morphology of IF4-212µm EG ICFs

The char morphology was studied by optimizing the EG 212um based formulation with good expansion. Figure 4.59(a, b) represented the inner char surface of formulation IF4-3-212µm which showed the smooth surface which protected the substrate from fire, some bubbles and cracks are observed inside char micrograph. Figure 4-60(a) showed the outer surface of IF4-4-212µm char, it is smooth, no hole or bubbles were observed on the surface of the char which showed the effective insulation of the substrate, SEM image showed the thick surface inside the char which protected the substrate from fire shown in 4-60(b). The micrograph of IF4-5-212µm char showed the rough and cracked outer surface in Figure 4-61(a), micrograph showed the tiny bubbles inside char which are formed by removal of gases with formation of ridge uniform cellular structure are shown in Figure 4.61(b). The microstructure showed rough outer surface and flakes inside of the IF4-7-212µm char in Figure 4.62 (a, b). So IF4-4-212µm formulation showed better results in terms of char expansion and char morphology with 8.8wt% of EG.

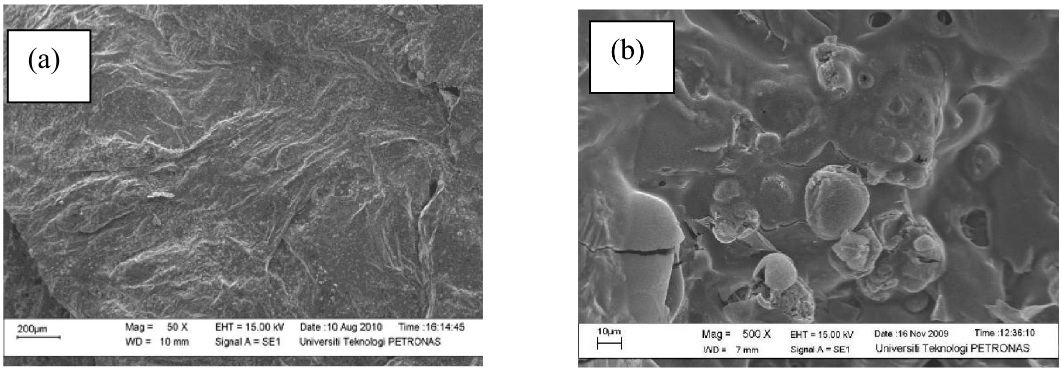


Figure 4.59: (a) IF4-3-212µm showing smooth outer surface, (b) Small bubbles inside the char

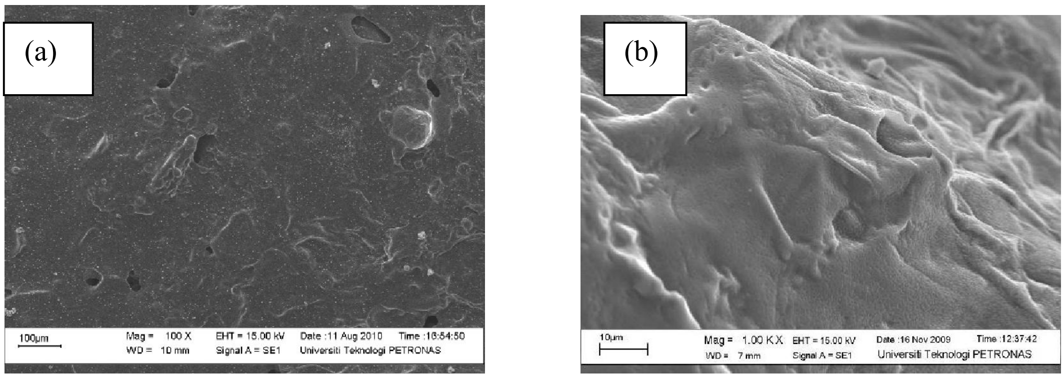


Figure 4.60: (a) IF4-4-212µm with smooth upper surface, (b) Inside thick char

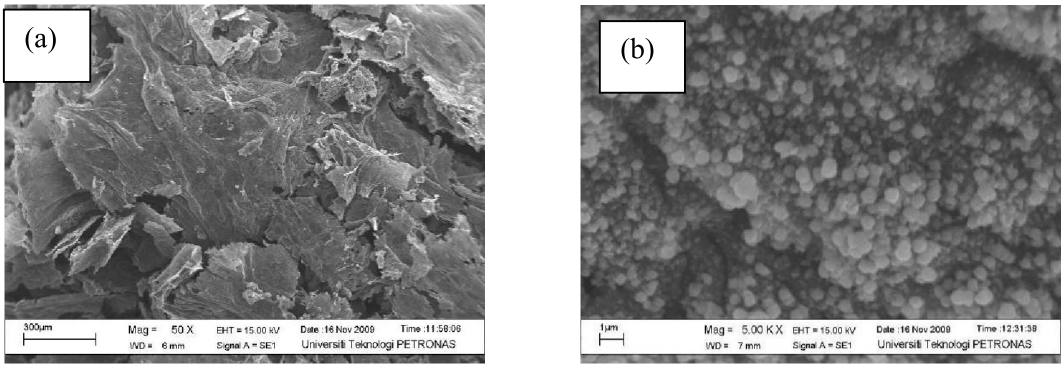


Figure 4.61: (a) IF4-5-212μm showes rough surface, (b) Representing the small buuble inside the char

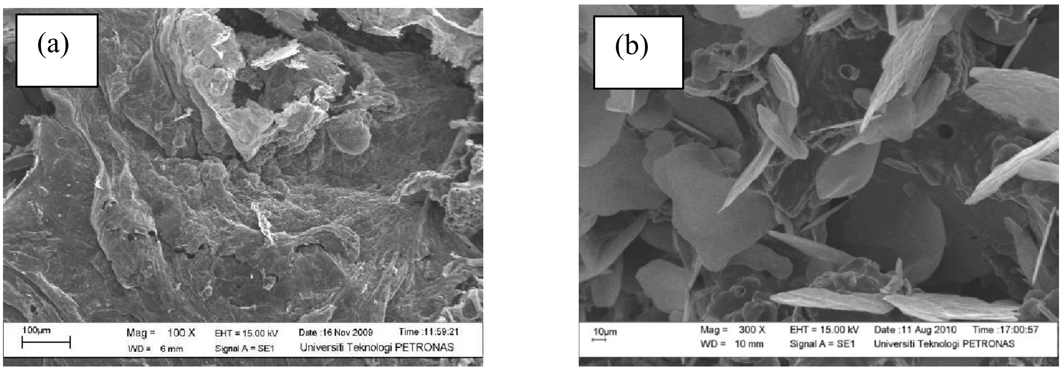


Figure 4.62: (a) IF4-7-212μm shows rough outer surface (b) Flakes inside the char

4.5.4 ICFs with EG particle size 300μm

From Table 3.15, nine formulations were prepared with 300μm particle size of EG. The weight percentages of 300μm EG were varied from 5.8-13.8% in the formulations. All the ingredients were fixed to study the effect of 300μm EG on char expansion and char morphology. The physical appearance and observation of the 300μm EG based coatings before fire test and resulting char after fire test are described below in the Table 4.16 and 4.17, respectively.

Table 4.16: Intumescent coating of 300µm EG before furnace test

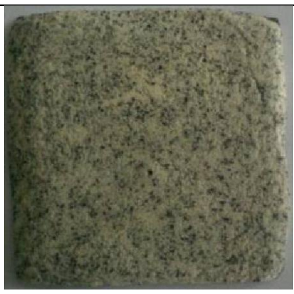
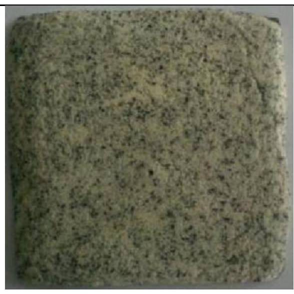
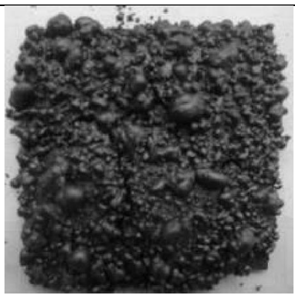
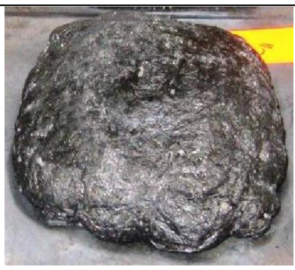
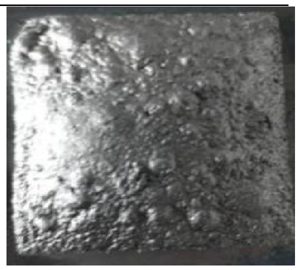
	Formulation IF4-1-300µm	**Formulation IF4-2-300µm**	**Formulation IF4-3-300µm**
Physical appearance			
Observations	– Less viscous – Easy to stir with mixer – Touch dry after 8 day	– Less viscous – Easy to stir with mixer – Touch dry after 8 days	– Less viscous – Easy to stir with mixer – Touch dry after 8 days
	Formulation IF4-4-300µm	**Formulation IF4-5-300µm**	**Formulation IF4-6-300µm**
Physical appearance			
Observations	– Less viscous – Easily mix – Touch dry after 7 days	– Less viscous – Easily mix – Touch dry after 7 days	– Less viscous – Easily mix – Touch dry after 7 days
	Formulation IF4-7-300µm	**Formulation IF4-8-300µm**	**Formulation IF4-9-300µm**
Physical appearance			
Observations	– Light black colour – Hard to mix – Touch dry after 5 days	– Highly viscous – Hard to mix – Touch dry after 5 days	– Highly viscous – Hard to mix – Touch dry after 5 days

Table 4.17: Intumescent coating of 300µm EG after furnace test

	Formulation IF4-1-300µm	**Formulation IF4-2-300µm**	**Formulation IF4-3-300µm**
Physical appearance			
Observations	– Ave. coating thickness: 1.5mm – Ave char thickness: 7.14mm – Expansion: 4.76 times – Hard char – Bubbles on the char	– Ave. coating thickness: 1.9mm – Ave char thickness: 10mm – Expansion: 5.3 times – Soft char – Large void in middle	– Ave. coating thickness: 2.3mm – Ave char thickness: 19.09mm – Expansion: 8.3 times – Hard char – Small void in middle – Small bubbles on surface
	Formulation IF4-4-300µm	**Formulation IF4-5-300µm**	**Formulation IF4-6-300µm**
Physical appearance			
Observations	– Ave. coating thickness: 1.7mm – Ave char thickness: 22.8mm – Expansion: 13.4 times – Hard char	– Ave. coating thickness: 2.1mm – Ave char thickness: 26.04mm – Expansion: 12.4 times – Hard char	– Ave. coating thickness: 1.4mm – Ave char thickness: 10.3mm – Expansion: 7.39 times – Hard char
	Formulation IF4-7-300µm	**Formulation IF4-8-300µm**	**Formulation IF4-9-300µm**
Physical appearance			
Observations	– Ave. coating thickness: 1.5mm – Ave char thickness: 10mm – Expansion: 6.7 times – strong char – Bubbles on surface	– Ave. coating thickness: 1.9mm – Ave char thickness: 10.4mm – Expansion: 5.48 times – Cracked Char	– Ave. coating thickness: 2.6mm – Ave char thickness: 7.28mm – Expansion: 2.8 times – Cracked char

4.5.4.1 Char expansion of 300μm EG ICFs

Figure 4.63 represents the expansion of the coating formulation after fire test. IF4-1-300μm, IF4-2-300μm IF4-3-300μm, IF4-4-300μm, IF4-5-300μm, IF4-6-300μm, IF4-7-300μm, IF4-8-300μm, IF4-9-300μm showed the char expansion 4.76, 5.3, 8.3, 13.4, 12.4, 7.39, 6.7, 5.48 and 2.8 times, respectively compared to the coating thickness. Formulation IF4-1-300μm, IF4-2-300μm IF4-3-300μm, IF4-4-300μm, IF4-5-300μm showed 4.8, 8.16, 9.2, 21.8, 47 percent higher expansion compared to formulation IF4-1-212μm, IF4-2-212μm IF4-3-212μm, IF4-4-212μm and IF4-5-212μm, respectively due to increase in particle size from 212μm to 300μm of EG. The maximum char expansion 13.41 times was obtained from formulation IF4-4-300μm with 8.8wt% of EG. The first four formulations showed that increase in weight percent of EG the char expansion is increased, further on the expansion of char is decreased by increasing the wt% of EG as shown in Figure 4-49. The formulation IF4-5-300μm has char expansion 12.4 and fully insulated to the substrate as illustrated in physical appearance Table 4.17. Table 4.17 showed cracks on the top surface of the formulation IF4-8-300μm and IF4-9-300μm char due to high weight percentage of EG above than 10.8wt. It is assumed that excess amount of EG above than 10.8 wt% expand the char abruptly with uniform network structure and it effected the outer surface of the char.

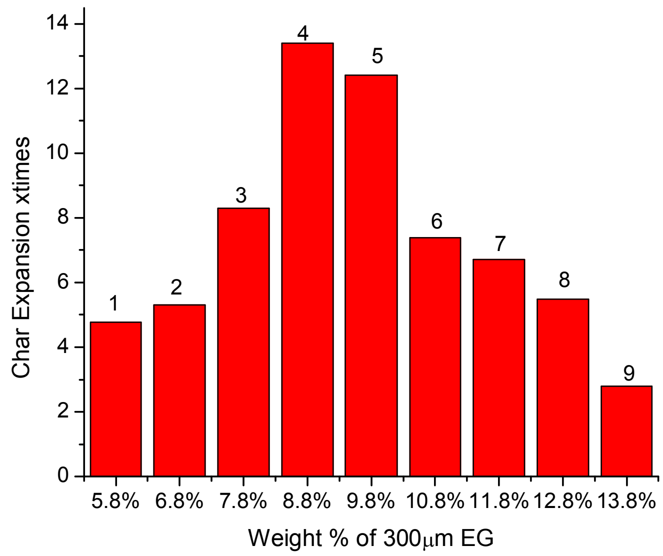


Figure 4.63: Char expansion of 300μm EG formulations

4.5.4.2 Char morphology of IF4-300μm EG ICFs

The char samples were selected based on the physical appearance of intumescent coating after fire test. The continuous and compact charred residue increases the ‘‘trap- ping’’ of the decomposed products, and consequently reduces the evolved, small, flammable molecules and decreases the toxicity of the combustion products [145, 146]. The interaction mechanism may be that the APP can produce the phosphorous acid and polyphosphoric acid and release the gaseous products, such as water (H_2O) and ammonia (NH_3). The polyphosphoric acid can react with carbonific compounds to yield the carbonaceous and phosphocarbonaceous residues, which act as a physical protective barrier via condensed- phase fire retardant mechanism. And the phosphorous acid during heating can also release the PO^o, which can capture H^o and HO^o via gas phase flame retardant mechanism and further restrain the flame spread. The detailed reactions are listed as following:

$$H_3PO_4 \rightarrow HPO_2 + PO^o$$

$$PO^o + H^o \rightarrow HPO$$

$$HPO + H^o \rightarrow H_2 + PO^o$$

$$PO^o + HO^o \rightarrow HPO + O^o$$

The EG loading also plays a positive role for the improved thermal stability and fire properties. The APP reacts with the EG, which is in favor of the formation of a phosphocarbonaceous residue structure. Meanwhile, the EG itself after heat treatment has high thermal stability and the function of heat insulation. The above-mentioned two aspects contribute to the improved thermal stability and flammability properties. So, there is a synergistic effect between the EG and APP, contributing to the improved thermal stability and decreased fire risk properties.

It can be seen in figure 4-64(a) of IF4-3-300μm coating the outer surface of the char residue has the agglomerates of swollen particles, Figure 4.64(b, c) showed some closed bubbles, holes respectively due to dehydration of epoxy resin, boric acid and the evolved of N_2, CO_2 and NH_3 gases from decomposition of melamine, EG and APP, respectively. In figure 4.64(d) showed the spherical shaped ball which is a mixture of carbon, oxygen and phosphorous. The char structure are very important to common fire resistant properties of coating [84].

Figure 4.65(a, b) illustrated the outer smooth char surface of formulation IF4-4-300μm. Small cavities on inner surface represents the dehydration of water illustrated in Figure 4.65(b). Figure 4.65(c, d) showed the inner surface of char which represents the bubbles due to release of gases products during fire test. The SEM images also indicate that the compact and homogeneous charred residue contributed to improve flame retardant properties of IF4-4-300μm. Figure 4.66(a) of IF4-5-300μm showed the outer surface of the char, smooth, no hole or bubbles observed on the surface which shows excellent insulation on the substrate to protect it from fire. Fig 4.66(b) of IF4-5-300μm shows inner surface of char bubbles observed which are formed by removal of gaseous products with formation of ridge uniform cellular structure. Figure 4.67(a) IF4-7-300μm shows the SEM image of outer surface of the char similar to Figure 4.66(a) of IF4-5-300μm. Figure 4.67 (b, c, d) of IF4-7-300μm shows inner surface of charred layers insulate the substrate, swellon char layered inside surface structure of the char.

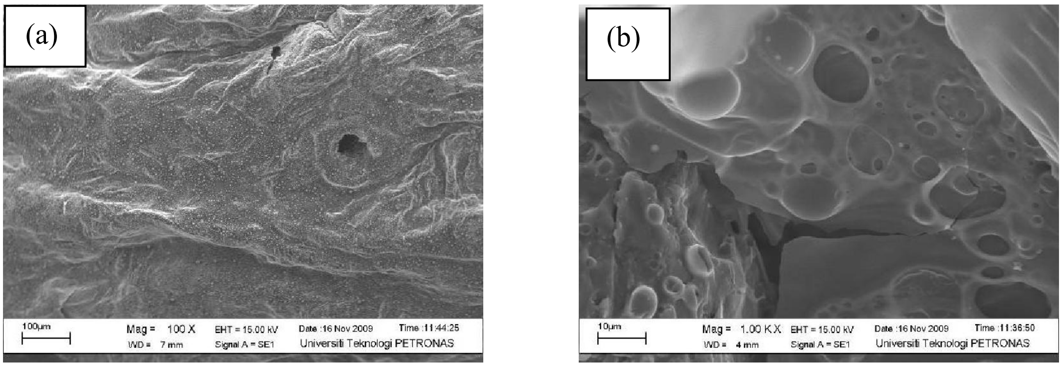
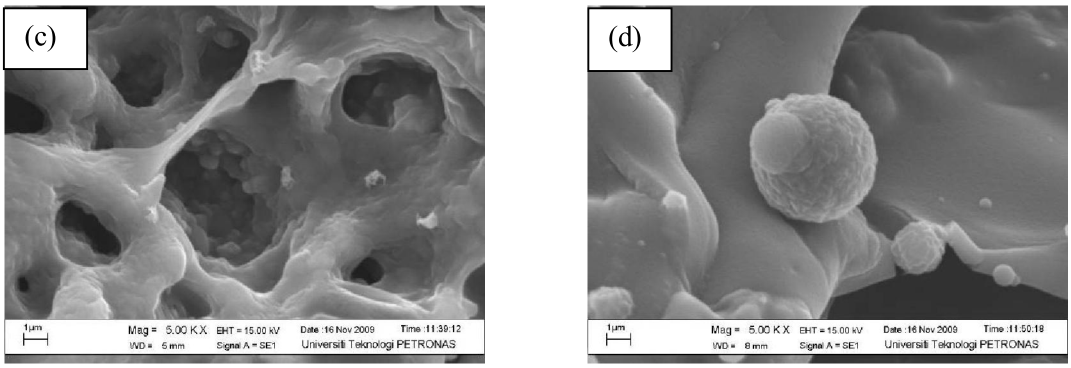


Figure 4.64: (a) IF4-3-300μm showing smooth surface (b) holes and bubbles due to release of gases



(c) IF4-3-300μm showing inner surface of char with holes due to dehydartion and release of gases, (d) a spherical bubble which might be consists of carbon, oxygen and phosphours.

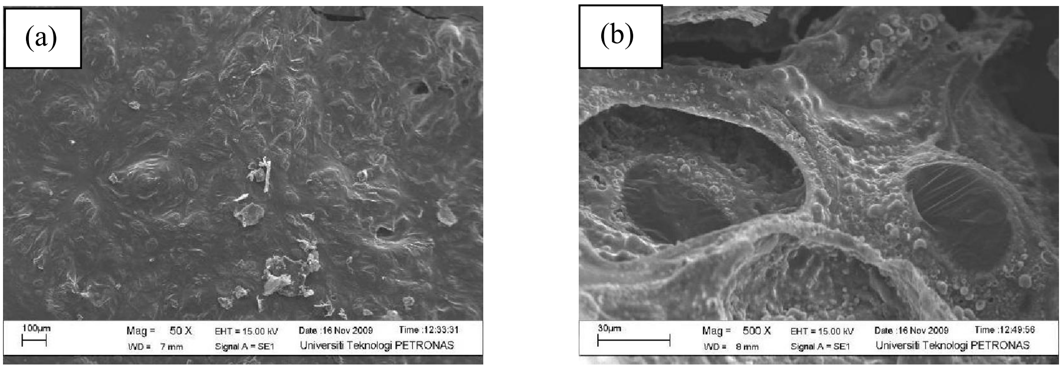
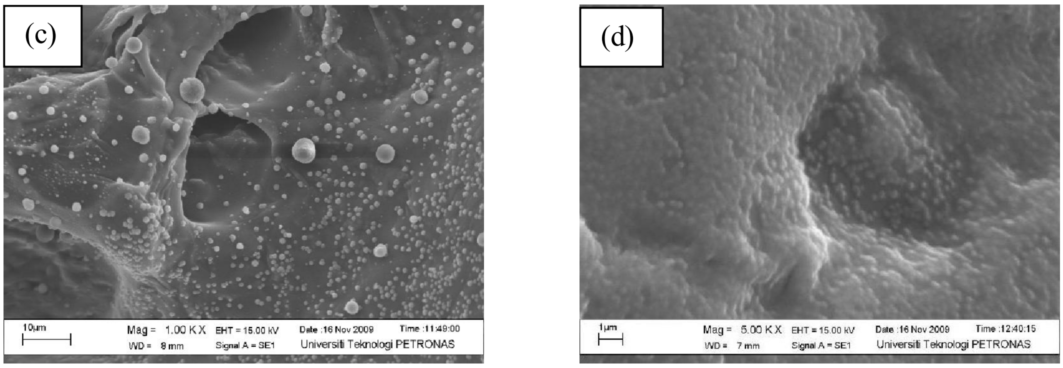


Figure 4.65: (a) IF4-4-300µm showing smooth surface (b) holes and bubbles due to release of gases such as N_2, NH_3 and CO_2



(c) inside the char showing bubbles due to gases products released (d) showing bubbles inside the char

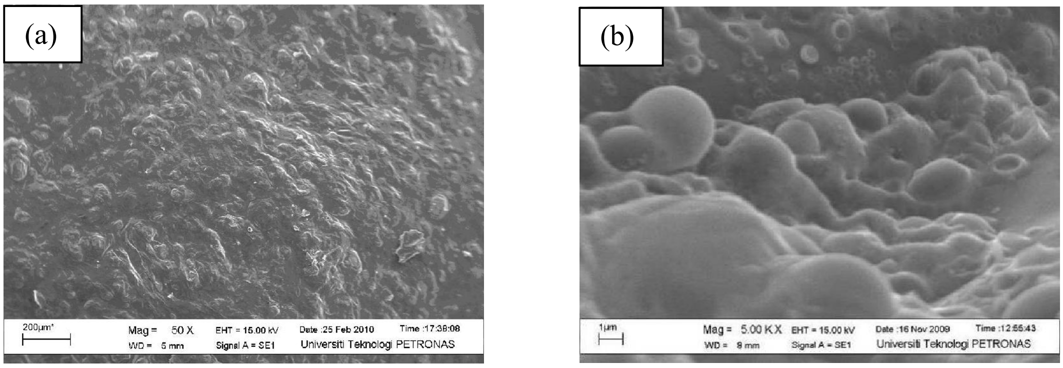


Figure 4.66: (a) IF4-5-300µm showed smooth outer surface (b) a range of small bubbles due to release of gaseous products which are useful in expansion of char

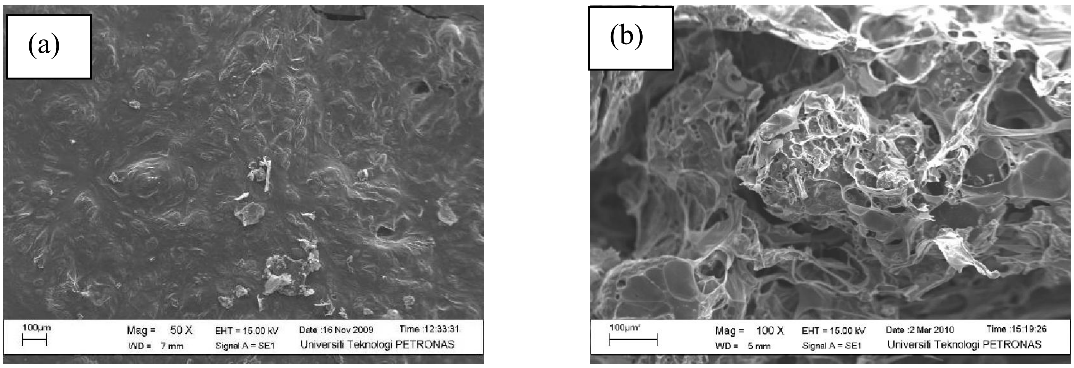
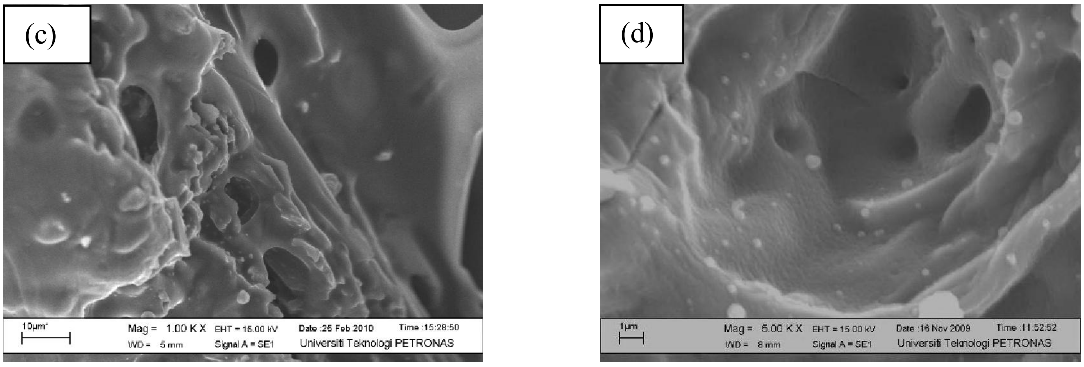


Figure 4.67: (a) IF4-7-300µm showed smooth outer surface (b) inner surface of the char



c) Swellon char layered inside surface structure of the char d) inner surface of the char

4.5.4.3 Comparison of char expansion of EG particle sizes

From the above results it is clear that increasing the particle size of EG the expansion is increased shown in Figure 4.68 and increased wt% of EG in coating formulation char expansion is increased upto 8.8wt% EG. Smaller particle size of EG have higher surface area than the bigger particle size of EG due to this reason the bigger particle size showed high char expansion compared to smaller particle size. The highest char expansion 13.41 times obtained from IF4-4-300µm. The comparison of char expansion of four different particle sizes of EG shows the overall char expansion odder is 300µm >212µm >150µm >63µm.

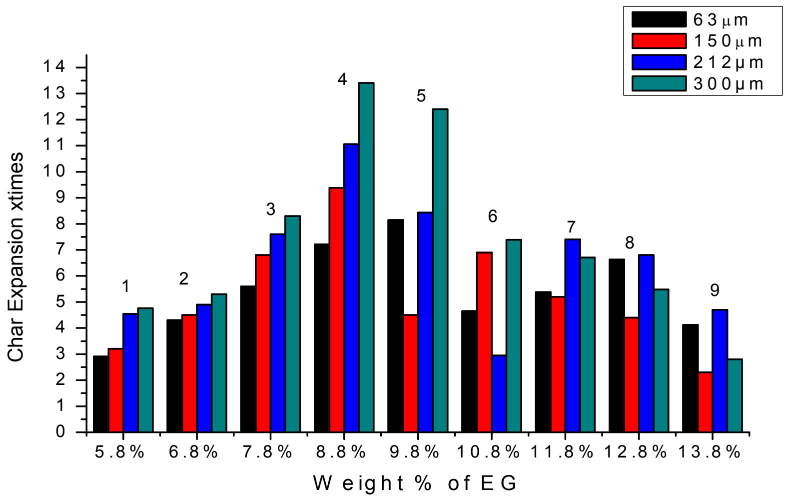


Figure 4.68: Comparison of char expansion with different particle size of EG

4.5.5 Conclusion

Based on this study, the effect of particle size of EG on char expansion and char morphology. The results showed char expansion is increased as the particle size of EG is increased. The IF4-5-63µm gives the char expansion 8.15 times with 9.8% of EG. The char expansion was obtained 9.38 time of IF4-4-150µm with 8.8wt of EG. The char expansion was obtained 11.0 times from formulation IF4-4-212µm with 8.8wt% of EG.

EG with 300µm particle size showed the best results in char expansion 13.4 times from the original thickness of the coating with 8.8 wt%. SEM image showed char morphology of burnt coating contained cavities, cracks, in the char structure, while in some structures it was also shown the smooth surface without any crack and thick char flakes which are strong barrier between fire and substrate. The 300µm EG char samples showed the better char structure with better char expansion which help to the thermal stability of the coatings.

4.5.6 Characterization of selected ICF of 300µm EG

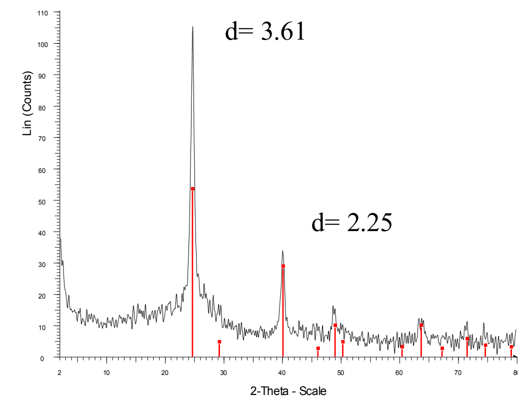
From Table 3.16 four formulations were selected for further characterization to study the chemical composition of char residue using X-Ray diffraction, functional group present in the char residue using FTIR and the residual weight using TGA.

4.5.6.1 Composition of 300µm EG ICFs char

The residue char of sample IF1, IF2, IF3 and IF4 are analyzed by X-ray diffraction using EVA software illustrated in Figure 4.69, 4.70, 4.71 and 4.72 respectively. Figure 469 illustrated the XRD analysis of IF1 char which shows two peaks represents the presence of borophosphate and boron oxide peaks at 2θ=25, 40^{o} and d spacing value is 3.61 and 2.25 respectively in the char while Figure 4.70 of IF2 showed the presence of graphite at 2θ=26.5^{o}, d value 3.47 and the borophosphate and boron oxide are at the same position such as in IF1.

Figure 4.71 shows four peaks of IF3, first peak observed at 2θ=15 and d value 4.56, represents the presence of sassolite in the char residue where sassolite is the mineral acid of boric acid. The second and third peaks represent the boron phosphate and graphite at 2θ=25, 26.5°, d value 3.61 and 3.47 respectively. Figure 4.72 represents three peaks of IF4 with 11.76wt% of EG, first peak represents the presence of borophosphate and second peak represents the graphite and third one represents boron oxide at 2θ=25, 26.5°, 40, d value 3.61, 3.47 and 2.25 respectively. The formation of H_3BO_3 that has been shown due to the dehydration to aid the formation of B_2O_3, glass-like material which increase the viscosity and avert the gaseous decomposition products evading to feed the flame [12].

All these XRD results showed that intensity of graphite peak is gradually increased with EG weight percentage increased. The results of XRD show that the reaction between boric acid with melamine, APP and O_2 can enhance the performance of anti-oxidation of the intumescent fire retardant coating due to the protective char layered on steel substrate.



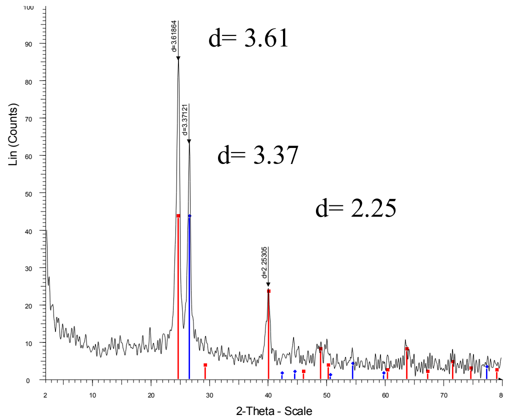
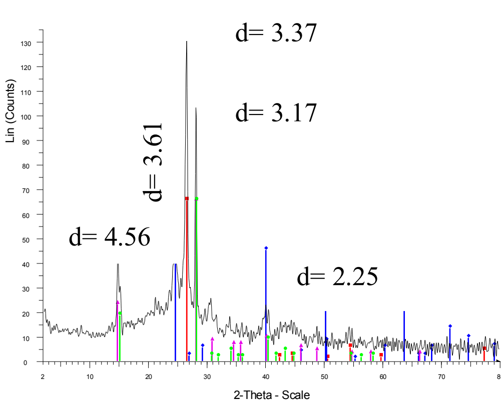


Figure 4.69: IF1 XRD spectra of the char, Figure 4.70: IF2 5.88wt% EG



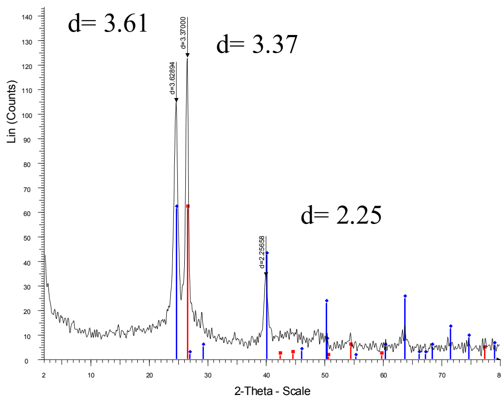


Figure 4.71: IF3 with 8.2wt% of the EG, Figure 4.72 IF4 with 11.76wt% of the EG

4.5.6.2 Functional groups of 300µm EG ICFs char

The residues char have been analyzed using spectroscopic tools to know the mechanism of interaction between, EG APP, melamine, boric acid, epoxy and hardener. FTIR spectra are shown in Figures 4.73, 4.74 and 4.75 of coatings IF1, IF3 and IF4, respectively. The FTIR spectrum of IF1 represents the phosphate and melamine region in Figure 4.73. In the region of phosphate P-O-P 800---1400 cm^{-1} the symmetric vibration phosphate PO_4^{-1} occurred at $1084cm^{-1}$ and three bands of amino groups C-N---2903, C=N --2346, C≡N---$1622Cm^{-1}$. The region 1380–$1700cm^{-1}$ at 1619, 1521, $1429cm^{-1}$ due to the amino groups (NH_2) and to the ring(C, N) [147].

IF2 has different spectrum compared to IF1 spectrum illustrated in Figure 4.74. The ingredients are the same with the same environment of fire test, except the difference of EG weight%. In region of P-O-P $800\text{-}1400cm^{-1}$ the symmetric vibration is presented at $1084cm^{-1}$. The asymmetric vibration of P-O group occurred at the region of $890\text{-}950cm^{-1}$ and the P-O symmetric region of P-O-P chain is within $1400\text{-}1080cm^{-1}$ [134, 136]. In the 2nd region $1380\text{-}1700cm^{-1}$, there are two peaks at $1417cm^{-1}$ and $1615cm^{-1}$ represent the stretching vibration of CH_2 or CH_3 deformation vibration, and polyaromatic compound respectively. In the 3rd region above than $2100cm^{-1}$ there are two bending peaks first two weak bending peaks occurred at 2257, $2367cm^{-1}$ which represent the bending vibrations of (-CH_3- CH_2-) groups. The peak observed at $1194cm^{-1}$ and $3213cm^{-1}$ are showed the presence of boric acid in char residue.

The results recommend that there are two major phase of the thermal degradation of coating formulations, the degradation at 400-500°C fit in the first stage and at 600-700°C stay with the second stage. As illustrated in Figure 4.75, the second stage leading to form a compact char with the absorption of polyaromatic (due to epoxy resin) and phosphorous compounds with borophosphate and boron oxide that are the main component of the char. These results have the same opinion with the analysis of X-ray diffraction.

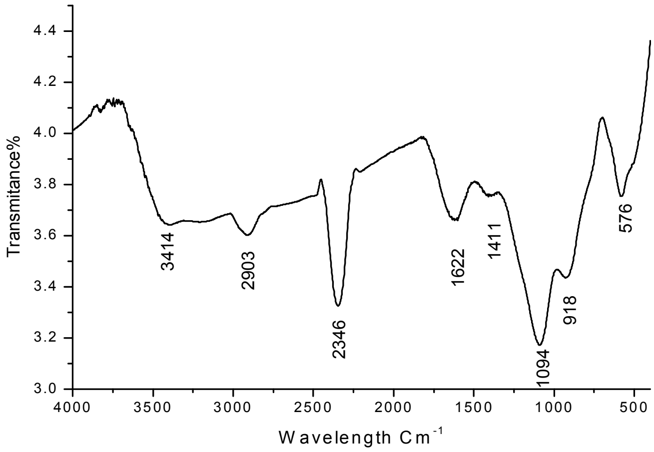


Figure 4.73: IF1 FTIR spectra

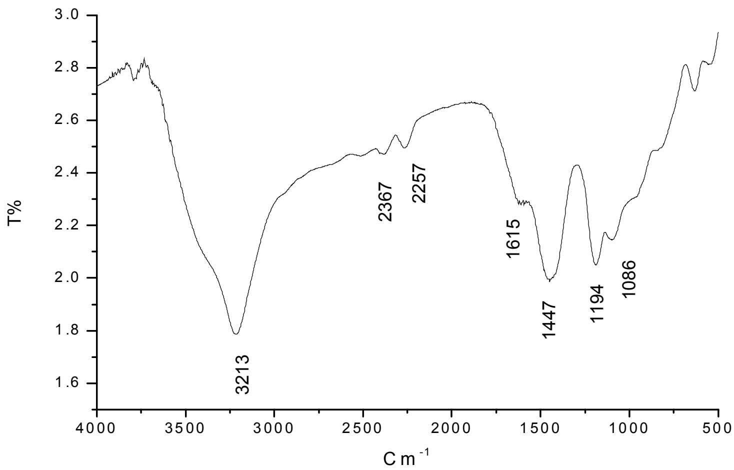


Figure 4.74: IF3 FTIR spectrum of char residue

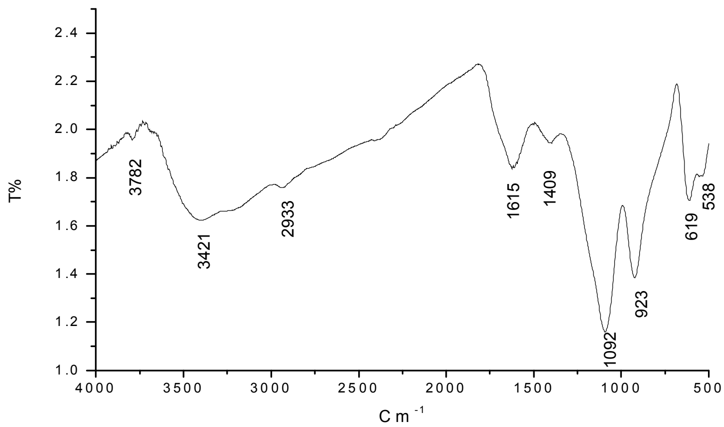


Figure 4.75: IF4 FTIR spectrum of char residue

4.5.6.3 Residual weight and DTGA of 300μm EG ICFs

The residual weight of IF1 is already explained in TGA of three ingredients based intumescent coating in Figure 4.30. Figure 4.76 shows the residual weight loss from TGA analysis of the coating IF2, IF3 and IF4 are 20.18, 29.16 and 31.31 wt%. It showed that increasing the weight% of the EG the residual weight has been increased. The derivative of thermo gravimetricanalysis (DTGA) curves of IF2, IF3 and IF4 are presented in the Figure 4.77 to 4.79. In Figure 4.77, IF2 shows four step thermal degradation at, 116^{o}C, 147^{o}C, 294^{o}C and 422^{o}C which represents the decomposition of boric acid into meta boric acid and then further convert in boron oxide at 116^{o}C and 147^{o}C respectively while 294^{o}C represents the degradation of melamine and maximum degradation observed at 422^{o}C of the other intumescent ingredients such as APP, EG, epoxy and hardener. Melamine starts its decomposition after 290^{o}C and some melamine was reacting with APP and as a result with the formation of melamine phosphate [148].

The DTGA curve of IF3 presents the decomposition occurred at six point 124^{o}C, 152^{o}C, 292^{o}C, 371^{o}C, 418^{o}C and 476^{o}C in Figure 4.78. At 124^{o}C and 152^{o}C showed the degradation of boric acid, from the literature it is clear that boric has two step of thermal degradation. In the first step it will degrade into metaboric acid (HBO_2) at 100-140^{o}C and in the second step is 140- 200^{o}C the dehydration of metaboric acid into boron oxide (B_2O_3) [149]. The 3rd and 4th degradation point which showed the degradation of melamine at 282^{o}C and at 371^{o}C the decomposition of epoxy and EG. The 5th and 6th degradation point represents the degradation of APP and next one is the degradation of boron phosphate and hardener at 422^{o}C and 476^{o}C respectively due the reaction products of the ingredients in coating formulation. Formulation IF4 has shown five degradation temperatures at 126^{o}C, 282^{o}C, 363^{o}C, 416^{o}C and 467^{o}C in Figure 4.79. The decomposition of boric acid into meta boric acid occurred at 126^{o}C, the decomposition of melamine occurred at 282^{o}C; the decomposition of epoxy and EG observed at 363^{o}C and at 416^{o}C APP and boron phosphate reaction product decomposes to boron phosphate oxide respectively. As the weight percentage of EG is gradually increased so there is faintly variation in the temperature derivation. The maximum degradation of IF2, IF3 and IF4 are 422, 418 and 416^{o}C.

The results of the TGA and DTGA showed the similar behaviour of thermal degradation for each of the coating samples. However, the residual weight of IF2, IF3, IF4 has been increased 20.18, 29.16, 31.13% as the weight% of EG increased 5.88, 8.82, 11.76, respectively. This shows that, coating IF3 enhanced intumescent effect compared to other formulations with six degradation temperature curves.

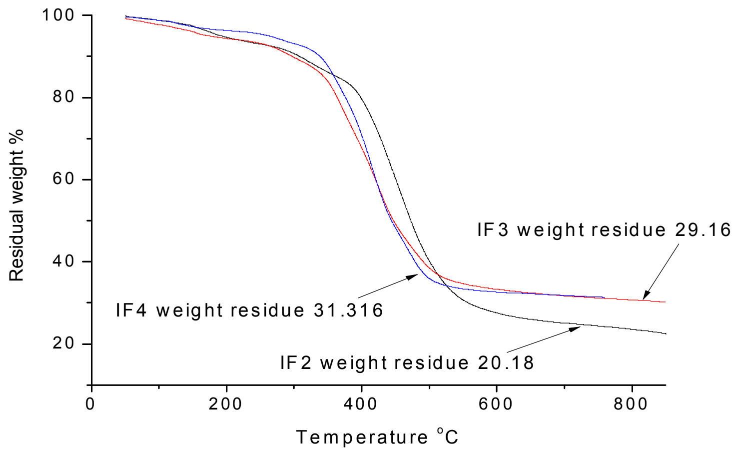


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Figure 4.76: TGA of the IF2, IF3 and IF4

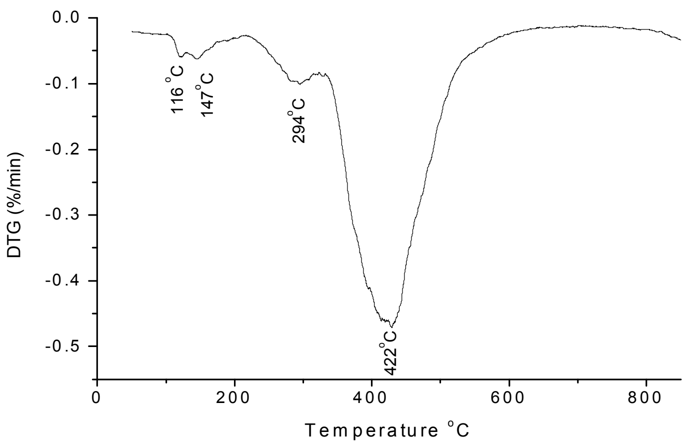

Figure 4.77: DTGA curve of IF2 showing four steps degradations

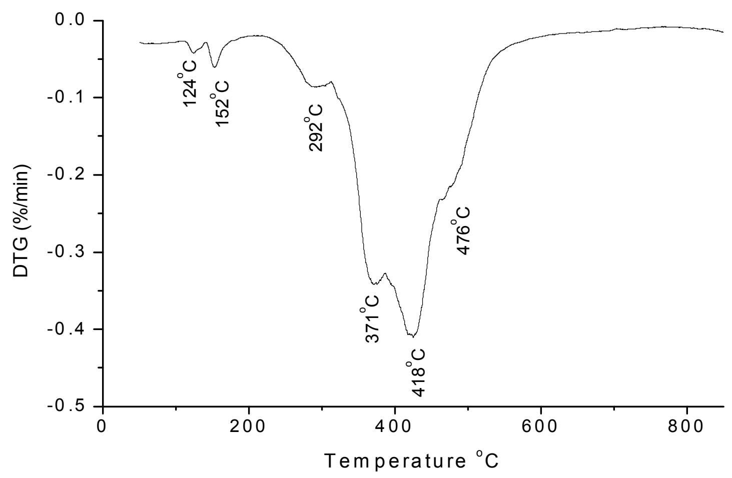

Figure 4.78: DTGA curve of IF3 showing six steps degradations

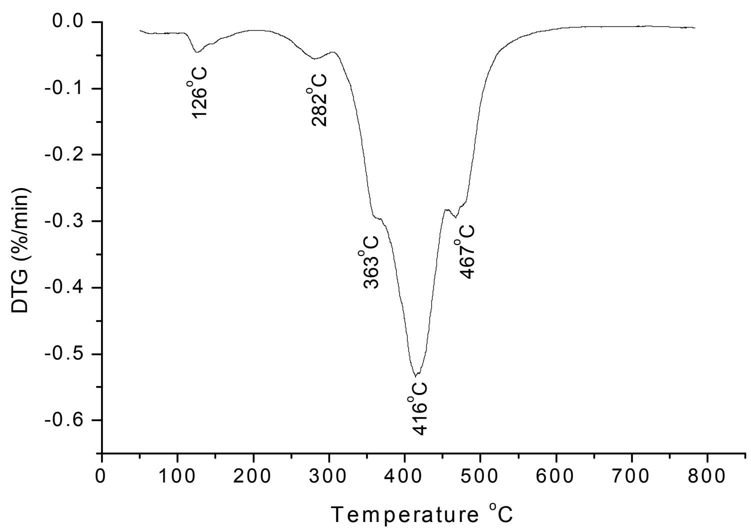

Figure 4.79: DTGA curve of IF4 showing five steps degradations

4.5.6.4 Conclusion of 300μm EG ICF

Based on the results of XRD, it showed the presence of, boron oxide, boron phosphate, graphite (carbon) sassolite in the residual char helped to reduce the fire effects on the underlying substrate. The XRD results are further confirmed by the presence of the respective functional groups in the residual char using FTIR analysis. TGA and DTGA showed that EG enhanced residue weight higher than that of APP-melamine-boric acid-epoxy-hardener coating. EG is a carbon source that will create uniform protective layer on the surface of the insulating substrate. Thus, the efficiency of the heat transfer was reduced and this gave a better intumescent effect into the coating formulations.

4.6 Effect of boric acid and melamine on ICFs with 300µm EG

From Table 3.17, five formulations were prepared to study the effect of boric acid and melamine on heat shielding, char expansion, and char morphology of 300µm EG intumescent fire retardant coating formulations. Their characterizations were carried out using XRD, FTIR, SEM and TGA.

4.6.1 Heat shielding and char expansion of boric acid and melamine ICF

In this study, five samples with different compositions of intumescent ingredients were prepared. Bunsen burner was used as a fire test source according to UL 94standard. Three K-type thermocouples were used to measure the temperature with AMS-850 data logger. The flame temperature of the Bunsen burner was 950^{o}C. Figure 4.80 shows a plot of time (minute) vs temperature of the substrate and Figure 4.81 shows the expansion of char after fire test conducted in the carbolite furnace. The char photographs of IF1-Mel, IF2-BA, IF3-BA-Mel, IF4-BA-Mel and IF5-BA-Mel after fire test are displayed Figure 4.82 (a, b, c, d, and e). The uncoated structural steel substrate can only sustain its property for about 8 minutes after fire; the temperature reaches 500^{o}C after 6 minutes fire as illustrated in Figure 4.80.

Coating IF1-Mel shows a maximum char expansion of 11 times due to the presence of blowing agent (melamine) which expands the char as illustrated in Figure 4.81. Initially, the formulation expands uniformly, as fire sustains with it oxidizes and could no longer protect the steel substrate. The substrate temperature after 30 minutes was 416^{o}C and it increased to 470^{o}C after 60 minutes as reported in Figure 4-65. IF1-Mel formulation contains EG, APP, melamine and epoxy resin with hardener; the char