Development of marine grade radiation cross-linked high density polyethylene (HDPE) floater pontoon material

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Abstract. Crosslinked High Density Polyethylene (HDPE) was developed using electron beam radiation techniques. The crosslinked HDPE can be used as marine grade cross-linked HDPE floater pontoon material. Thermoplastic resin, HDPE blended with Ethylene Vinyl Acetate (EVA) in various weight percentage compositions before being radiate with electron beams irradiation. These composites showed significant changes in mechanical properties and temperature stability after the irradiations. From this study, the optimum dose for HDPE and HDPE/EVA blends will be obtain. This study also will provide the optimum irradiation dose in order to have a good, high strength and impact for the production of pontoon material. The present of EVA in the blend will act as impact modifier also being investigated in this study. From the study, the result showed some significant changes in thermal and mechanical properties after being irradiated with electron beam. The comparison of the result between these composite composition of irradiated and non-irradiated HDPE composite used for floater pontoon material is presented in this paper

1. Introduction
High Density Polyethylene (HDPE) is a thermoplastic that provide a high strength-to-density ratio, and has been widely used in the production of plastic bottles, pipes, geomembranes, and plastic lumber. HDPE is known for its large strength to density ratio. The density of HDPE can range from 930 to 970 kg/m³. Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving it stronger intermolecular forces and tensile strength than Low Density Polyethylene (LDPE) [1]. The difference in strength exceeds the difference in density, giving HDPE a higher specific strength. It is also harder and able to withstand somewhat higher temperatures (120 °C/248 °F for short periods) [2].

In order to obtain more excellent material properties of HDPE, Ethylene vinyl acetate copolymer (EVA) can be used to strengthen HDPE. Ethylene vinyl acetate copolymer (EVA) being used in this project are as an impact modifier for improving impact properties due to the presence of olefinic segments and interactive vinyl acetate groups in EVA[3]. In addition, the vinyl acetate concentration (VA %) may provide an additional variable to EVA for its role as impact modifier of HDPE. Furthermore, the glass
transition temperature of EVA is quite low, which also indicates the possibility of achieving better low
temperature impact properties for the HDPE/EVA blend

Radiation technology used is based on the use of high energy ionizing radiation, mainly high energy
electrons (0.2-10 MeV) from electron accelerators as a source of energy in different industrial
applications. The scientific basis of radiation technology is the reactive chemical species produced by
absorbed radiation resulting in changes of chemical, physical and biological properties.

In many industrial applications radiation processing has proven to be a technology of choice either
because of its economic competitiveness or its technical superiority. Although the chemical effects of
ionizing radiation have been known for more than a century its industrial applications become possible
only after the availability of reliable gamma source and powerful electron accelerator during the last
couple of decades. Worldwide there are approximately 200 Co-60 gamma irradiators and 100 electron
beam accelerators being used in major fields of industry namely health-care, polymers, food and
environmental applications [4]. This project is intended to develop irradiated HDPE and of High Density
Polyethylene (HDPE) and Ethylene vinyl acetate (EVA) (HDPE/EVA) blends for pontoon material
purposes. The main objective of blending is to enhance the material properties that will meet the
sufficient material requirement for HDPE/EVA resin. Pontoon or floats are the airtight hollow structures,
similar to pressure vessel, designed to provide buoyancy in water. Their principal applications are in
marine engineering applications such as watercraft hulls, aircraft floats, floating pier and pontoon
bridge construction. So, in order to meet the standard of pontoon production, it must have a high strength
and impact properties and also high temperature resistance.

For the blending of HDPE/EVA, the blends will be processed using different formulation in high
speed mixer. The process then will be followed using electron beam in order to expose the blends onto
various kinds of doses before characterized. In order to characterize and investigate the properties of this
polymer blend, the testing will be involved in aspect of mechanical, thermal and morphological. The
blends will undergo Gel Content, DSC, tensile, flexural, hardness and impact testing.

2. Experimental

2.1. Materials
High Density Polyethylene (HDPE), Ethyl Vinyl Acetate (EVA) and Trimethylolpropane triacrylate
(TMPTA) was used in this project. HDPE that been used in the study is HDPE HD5201AA as it is for
extrusion grade material.

2.2. Preparation of crosslinked HDPE
Crosslinking of HDPE was carried out by electron beam in various doses 50, 100, 150 and 200 kGy
respectively. HDPE pellet been dried first at 60°C for 24 hours to eliminate moisture. The HDPE pellets
were blends with the internal mixer melting for about 10 minutes before the 3 weight percent of TMPTA
was added. The mixture compounded using internal mixer with a 190°C in temperatures and screw speed
of 50 rpm. The compound been allowed to cool in room temperature for a few minutes before
subsequently been hot pressed into a 1mm and 4mm thickness sheet using hot press machine. The hot
press machine operated at 170°C for about 15 minutes. The press samples undergo the electron beam
irradiation at various doses which are 50, 100, 150 and 200 kGy respectively. The prepared samples are
being cut before being used for the characterizations. The cross-linked HDPE samples being prepared to
the standard and requirements of each characterization respectively. The process flow details showed in
the figure 1 below.
2.3. Preparation of HDPE/EVA blends with crosslinker agent

The project continued with blending of HDPE and EVA blend with present of TMPTA. Firstly, the HDPE and EVA pellets put into the internal mixer and let it to melt before the TMPTA was added. The compositions of TMPTA that used for the mixing with HDPE/EVA is 3 weight percent meanwhile the HDPE/EVA is 90/10 weight percent. The mixture compounded using internal mixer with a 190°C in temperatures and screw speed of 50 rpm. The compound was allowed to cool in room temperature for a few minutes before subsequently been hot pressed into a 1mm and 4mm thickness sheet using hot press machine at 170°C for about 15 minutes before being irradiated with 50, 100, 150 and 200 kGy. The prepared sample then being characterized and the optimum composition of HDPE/EVA were collected. The process flow details showed in the Figure 2 below.

![Figure 1. Process flow of preparation of crosslinked HDPE.](image-url)
2.4 Gel Content
The crosslink degree of HDPE and HDPE/EVA was determined by a gel content method. The products obtained from electron beam were cut into 0.2 cm² with three time repetitions before being put into a wire mesh. Then, the samples prepared were being boiled in 40 mL xylene, at 60°C. The solution was being left for about 24 hours. Then, the sample were collected and washed by ethanol to get rid the excessive ethanol after being boiled. The samples then were being dried at 70°C in a vacuum oven for 4 hours.

To measure the crosslink degree, the dried sample then collected and measured it final weight in order to obtain the mass of sample that do not dissolve, that indicate the crosslink part of the samples. The crosslink degree was calculated using the following equation. Each sample were tested in triplicate and average values were reported.

\[
\text{Gel Content} = \frac{\text{(Wt. of sample after boiling)}}{\text{(Wt. of sample)}} \times 100\% \tag{1}
\]

Figure 2. Process flow of preparation of HDPE/EVA blends with crosslinker agent.
2.5 Differential Scanning Calorimetry (DSC)

The miscibility of the blends was investigated by means of differential scanning calorimetry in inert atmosphere. The sample of 4 to 7 mg will be pressed in Aluminium pan and were being heated at a rate of 10°C/min from 25°C to 200°C. The crystallization (T_c) and melting temperature (T_m) had being taken as those corresponding to the peak values of the crystallization exotherms and melting endotherms, respectively. The percentage of crystallinity X_c was calculated using the following equation:

\[
\% \text{Crystallinity} = \frac{\Delta H_m}{f \Delta H_{m \text{ ideal}}} \times 100\%
\]

where, \(\Delta H_m\) is measured heat fusion, \(f\) is the weight fraction of the component in equation, and \(\Delta H_{m \text{ ideal}}\) is the enthalpy of fusion for 100% crystalline (\(\Delta H_m\) (PLA) =288 J/g).

2.6 Tensile Test

Tensile test was carried out according to ASTM D638 (Standard Test Method for Tensile Properties). The tensile properties were measured at environment temperature and humidity on the universal testing machine. The testing was being performed under ambient conditions. The cross head speed was fixed in a value of 50 mm min\(^{-1}\). Five specimens for each formulation were tested and average values will be recorded.

2.7 Hardness Test

Hardness test were done according to ASTM D2785 by using Shore D Rockwell Hardness tester. The test was done under ambient conditions. The samples standard dimensions are 6mm. Hardness values were being calculated. Five specimens were tested and the average value was being calculated.

2.8 Impact Test

The Izod impact test was carried out according to the ASTM D256 (A) standard test method to determine the pendulum impact resistance of notched specimens for the composites. The testing machine, Izod impact tester consists of a heavy base with a vise for clamping the specimen in place during the test. The samples is in rectangular bar which was held vertically at half of it length and notch according to standard. Five specimens of each formulation will be tested and the average impact strength was calculated.

3. Results and discussion

3.1. Characterization of HDPE

3.1.1. Gel Content. From the graph shown in Figure 3, the degrees of crosslinking were increased with increasing of irradiation dose. From 0% of gel content degree, it is increased up to 70% when being irradiated with electron beam with dose of 50, 100, 150 and 200kGy respectively. This showed that HDPE blends undergo the crosslinking process throughout the irradiation using electron beam.
Crosslink with 3 phr TMPTA with 50kGy irradiation dose have a 51% of crosslink degree and increase slightly when the sample bombarded with 100kGy. With the presence of 100kGy of electron beam irradiation, the crosslinking degree is about 59%. For dose 150kGy, the result also showed the increment in crosslinking degree from 59% to 70% and it decrease slightly with the 200kGy as shows in the Figure 1. This shows the irradiation dose of 150kGy of HDPE is the optimum dose for HDPE crosslinking. Increasing the dose would enhance the chances of crosslinking process occurs in the backbone of HDPE, hence the crosslink degree increased $^{(5)}$. Since the available sites on the HDPE backbone are limited, the higher dose of electron beam irradiation will degrade the rather than crosslink.

3.1.2. Differential Scanning Calorimetry (DSC). The thermal properties of samples were determined by DSC analysis. Figure 4, 5, 6, 7 and 8 shows the DSC curve of heat flux versus temperature at different dose. The value of melting temperature, $T_m$, glass transition temperature, $T_g$ and degree of crystallinity, $\%X_c$ of each samples were summarized in Table 1.

![Figure 3. The crosslink degree of HDPE.](image)

![Figure 4. DSC thermogram at of HDPE pure.](image)
Figure 5. DSC thermogram at of HDPE50.

Figure 6. DSC thermogram at of HDPE100.
Table 1. Tm, Tg and Xc value for different irradiation dose (HDPE)

| Sample Description | Tm (°C) | Tg (°C) | Xc (%) |
|--------------------|---------|---------|--------|
| HDPE pure          | 131.38  | 67.34   | 54.41  |
| HDPE50             | 131.98  | 66.70   | 55.62  |
| HDPE100            | 131.98  | 66.28   | 55.51  |
The Tm value of the HDPE pure is increase in increasing of the irradiation dose but decreasing when being bombarded with 200kGy. For the Tg, the Tg for the HDPE pure is decreased when bombarded with electron beam. The reduction of Tg could be attributed to chain branching due to a crosslinking reaction between HDPE backbones. Researcher also reviewed that the endothermic peaks at Tg could be attributed to the enthalpy relaxation effects coming from the thermal history of the samples (6). The Xc showed in table were increasing when the HDPE is been irradiate with electron beam. From the result, this is indicated that by exposed the blend to the electron beam, the Tm of HDPE increase but decreasing their Tg.

### 3.1.3. Tensile Test

Tensile strength with different dose was summarized in Figure 9 below. Tensile strength of the HDPE increased with increasing of irradiation dose. Tensile strength of pure HDPE was 30.1 MPa. When undergo the irradiation dose from 50 up to 200kGy, the tensile strength increasing to 30.3, 31.3, 32.2 and 32.1 MPa respectively. This occurred due to the cross linking of the HDPE. The highest tensile strength recorded is 32.2 MPa with irradiation dose of 150 kGy.

![Figure 9. Tensile strength.](image)

### 3.1.4. Impact

The impact strength with the different dose of irradiation is shown in Figure 10. It can be seen that with increasing of irradiation dose, the impact toughness increase for prepared sample.
3.1.5. Hardness. The hardness test was carried out and the results shown in the Figure 11 below. From the figure, the hardness of cross linked HDPE showed at 150 kGy achieved the highest value and decreasing when being radiated with 200 kGy.

3.2. Characterization of HDPE/EVA blends

3.2.1. Gel Content. From the graph shown, the degree of crosslinking was increased with increasing of irradiation dose. From 0% of gel content degree, it is increased up to 42% when being irradiated with electron beam with dose of 50, 100, 150 and 200kGy respectively. This showed HDPE/EVA blends undergo the crosslinking process throughout the irradiation using electron beam.
Crosslink with 50kgy irradiation dose have a 42% of crosslink degree and increase slightly when the sample bombarded with 100kGy. With the presence of 100kGy of electron beam irradiation, the crosslinking degree is about 57%. For dose 150kGy, the result also showed the increment in crosslinking degree from 57% to 62% and it increase slightly with the 200kGy as shows in the Figure 11. Increasing the dose would enhance the chances of crosslinking process occurs in the backbone of HDPE/EVA, hence the crosslink degree increased.

3.2.2. DSC. The thermal properties of samples were determined by DSC analysis. Figure 3 and 4 shows the DSC curve of heat flux versus temperature at different dose. The value of melting temperature, Tm, glass transition temperature, Tg and degree of crystallinity, %Xc of each samples were summarized in Table 2.

| Sample Description | Tm (°C) | Tg (°C) | Xc (%) |
|--------------------|---------|---------|--------|
| HDPE/EVA           | 131.38  | 67.34   | 54.33  |
| HDPE/EVA50         | 132.78  | 65.69   | 55.87  |
| HDPE/EVA100        | 132.40  | 67.22   | 54.32  |
| HDPE/EVA150        | 131.86  | 66.30   | 55.97  |
| HDPE/EVA200        | 131.08  | 66.16   | 55.23  |

The Tm value of the HDPE/EVA is increase in increasing of the irradiation dose but decreasing when being bombarded with 150 and 200kGy. For the Tg, the Tg for the HDPE/EVA is decreased when bombarded with electron beam. The reduction of Tg could be attributed to chain branching due to a crosslinking reaction between HDPE and EVA. The Xc showed in table were increasing when the HDPE/EVA is being irradiate with electron beam. It seems that, by exposed to electron beam, had increase it Tm and but decreasing their Tg.
3.2.3. Tensile Test. Tensile strength with different dose was summarized in Figure 13 below. When undergo the irradiation dose from 50 up to 200kGy, the tensile strength does not have significant changes but decreasing from lower dose to higher, the tensile strengths are 28, 25, 25, 25 and 24 MPa respectively. This occurred due to the presence of EVA onto HDPE. The tensile strength of HDPE/EVA blend is decreasing significantly with increasing of radiation dose. This is due to the formation of voids and poor interaction between HDPE/EVA blends caused the poor in tensile strength. These showed that higher dose applied on the HDPE/EVA blends will reduce it tensile strength.

![Figure 13. Tensile Strength.](image)

3.2.4. Impact. The impact strength with the different dose of irradiation is shown in Figure 14 below. It can be seen that with increasing of irradiation dose, the impact toughness increase for prepared sample, and from the figure, the impact strength for HDPE/EVA blend showed an increment in impact strength value compared to pure cross linked HDPE. This is due to the present of EVA in HDPE blends as an impact modifier.

![Figure 14. Impact strength.](image)
3.2.5. Hardness. The hardness test was carried out and the results shown in the Figure 15 below. From the figure, the hardness of cross linked HDPE/EVA blend showed at 100 kGy achieved the highest value and uniform when being irradiated further. This showed that 100 kGy of radiation dose is the optimum dose for the blend.

![Figure 15. Hardness.](image)

4. Conclusions

From the results of the study, the crosslinking degree of the HDPE with TMPTA as crosslinker showed the optimum grafting degree is at 150 kGy of irradiation dose with degree of crosslinking is 70%. For the thermal test, DSC showed that the Tm value increased and the Tg is decreased with increasing of %Xc. This result also supported by tensile and hardness testing that indicated that 150kGy is the optimum dose in order to have a good, high strength and impact for the production of pontoon material as the normal pontoon used only HDPE. And this property is really critical for every production of pontoon supplier as it is the main issues in making the pontoon. On the other hand, the blends of HDPE/EVA with the presence of 3 phr of TMPTA were being tested. From the result, the tensile strength HDPE/EVA blends decreased gradually with increasing irradiation dose. These results implied that the samples became less stiff and had lower resistance to deformation within these compositions and indicated that higher dose is not suitable for the blends. For the impact strength of HDPE/EVA blends, it showed that with increasing irradiation dose, the impact toughness increase from 40 to 50kJ/m². This is due to the present of EVA in HDPE blends as an impact modifier.

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