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THE PHYSICAL AND THERMAL PROPERTIES OF MODIFIED ROTATIONAL MOLDING GRADE SILANE CROSS-LINKED POLYETHYLENE COMPOUND

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Abstract. This study is aimed at investigating the physical and thermal properties of the modified rotational molding grade cross-linked polyethylene compound with respect to process ability. Rotational molding grade High Density Polyethylene (HDPE) was blended at various compositions with HDPE and Low Density Polyethylene (LDPE) using twin screw extruder. The melt index of the blends was studied according to ASTM D 1238. The blended compositions were chemically cross-linked with various amount of silane cross-linking agent using two roll-mill. Water curing was then undertaken at 100°C in water bath for 4 and 8 hours. Gel content was measured according to ASTM D 2765 to determine the degree of cross-linking. For thermal analysis, only samples cross-linked with 2.0 phr silane cross-linking agent were investigated on the Differential Scanning Calorimetry (DSC) according to ASTM D 3417. The thermal stability test of the silane Cross-linkable Polyethylene (XLPE) was performed by Thermogravimetric Analyzer (TGA) according to ASTM D 3850. Results on melt index (MI) indicated that the rotational molding grade HDPE blended with HDPE showed higher MI compared to that with LDPE thus improved process ability. The density of rotational molding grade HDPE with HDPE was slightly increased whereas that blended with LDPE was slightly decreased. Samples blended with HDPE, melting temperature, T_m, barely changed and degree of crystallinity, X_c, decreased with compositions. Samples with LDPE T_m and X_c decreased with compositions thus improved process ability. As the silane concentrations increased, the gel content after curing was also increased but independent of compositions. Longer curing time resulted in higher gel content. Thermal stability of the cross-linked HDPE was higher than the uncross-linked HDPE, thus silane cross-linking help to stabilize the blends.

Keywords: Silane cross-linked high density polyethylene, rotational molding, thermal properties, physical properties and process ability

Abstrak. Uji kaji ini dijalankan untuk mengkaji sifat fizikal dan terma bagi formulasi campuran polietilina berangkai silang gred acuan putaran berasaskan kebolehprosesan. *High Density Polyethylene* (HDPE) gred acuan putaran dicampur dengan pelbagai komposisi HDPE dan *Low Density Polyethylene* (LDPE) menggunakan penyemperit skru pendua. Indeks Aliran Lebur (MI) campuran dikaji berasaskan ASTM D 1238. Komposisi campuran tersebut disambung silang secara kimia dengan agen penyambung silang silane menggunakan '*two roll mill*'. Kemudian sambung silang lembapan dilakukan di dalam *water bath* selama 4 jam dan 8 jam. Kandungan gel diukur mengikut ASTM D 2765 bagi menentukan darjah penyambungan silang. Bagi analisis terma,

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hanya sampel yang disambung silang dengan 2.0 phr agen penyambung silang silane dikaji dengan Kalorimetri Pengimbasan Pembeza (DSC) berdasarkan ASTM 3417. Ujian kestabilan terma bagi XLPE silane dilakukan dengan menggunakan Penganalisa Termogravimetri (TGA) mengikut ASTM D 3850. Keputusan bagi Indeks Aliran Lebur (MI) menunjukkan campuran antara HDPE gred acuan putaran dengan HDPE lebih tinggi berbanding LDPE, dengan itu menambahbaik kebolehprosesan bahan. Ketumpatan campuran antara HDPE gred acuan putaran HDPE meningkat sedikit manakala campuran dengan LDPE menurun sedikit. Sampel yang dicampur dengan HDPE tidak menunjukkan perubahan bagi suhu lebur, T_m manakala darjah penghabluran, X_c, mengalami penurunan. Sampel campuran dengan LDPE pula, T_m dan X_c menurun dengan bertambahnya komposisi LDPE menunjuk kepada kebolehprosesan yang lebih baik. Kandungan gel meningkat dengan penambahan kepekatan silane dan tidak bergantung kepada komposisi campuran. Masa pengawetan yang lebih panjang menghasilkan nilai gel yang tinggi. Kestabilan terma PE yang dirangkai silang lebih tinggi berbanding HDPE yang tidak dirangkai silang. Oleh yang demikian, penyambungan silang secara silane menambahkan kestabilan campuran.

Kata kunci: HDPE rangkai silang silane, acuan putaran, sifat fizikal, sifat terma dan kebolehprosesan

1.0 INTRODUCTION

Rotational molding is a rapidly developing processing technique for producing large, hollow articles [1]. It has a unique feature among plastics molding processes because the heating, shaping and cooling the plastic are done inside the mould with no application of pressure. It has advanced to the stage where it is capable of producing complex, stress-free, dimensionally stable articles with surface finished comparable with those achieved in injection molding. Wall thickness distribution is more uniform with rotomolding and part size can go well beyond anything which is impossible in blow molding [2]. A rotational mold costs around ten times less than a blow mold to produce a similar item. Compared to injection molding, rotomolding has very low mold cost and the ability to produce complex hollow articles. Compared to blow molding, rotomolding allows much complex and asymmetrical shapes. Rotomolded parts are found in industries ranging from recreational to medical to automotive such as vehicle crash bar which is lighter, traffic sign, coolant reservoir tank, inflatable oxygen mask seal and others [3].

In Malaysia, no compounder has ever developed and compounded the cross-linked polyethylene for rotational molding process, although the demand for such compound worldwide is extensive in the application, especially for harsh outdoor weather conditions. Basically, cross-linking can change the thermoplastic to thermoset and improve the properties of polyethylene (PE) thus extend their applications [4, 5].

There are three major ways to crosslink PE which are by silane cross-linking, peroxide cross-linking and irradiation cross-linking. Among the three cross-linking methods, silane cross-linking is cost-effective and easily operated. Now, silane cross-linkable polyethylene (XLPE), especially low density polyethylene is widely used to produce wires and cables, generally extruded products [6, 7].

Cross-linking of PE changes the chemical structure of the original polymer. The initial thermoplastic material consisting of linear polymer chains is transformed into a polymer network with rubber elastic properties [8, 9]. The cross-linking leads to an increase in the viscosity of the polymer melt, increased tensile strength, improvement of creep properties and an increase in the resistance to environmental stress cracking [10]. In addition, cross-linking can extend the uses of thermoplastic PE by raising the upper temperature limit of application and improving the mechanical properties of this polymer. This was due to the fact that XLPE has better mechanical characteristics at high temperatures. Thus, the use of XLPE allows the cable to withstand temporary overload conditions during which the temperature of the insulation may rise above the melting point of polyethylene; an uncross-linked polymer would flow away from the conductor under these conditions causing the cable to fail [11]. This is similar to rotational molding XLPE compounds, which can withstand higher temperature, thus open for harsh conditions application.

In rotational molding, increasing of MFI will be an advantage to the process ability of the materials making product with good surface finish and more homogenous as the flow of materials improved. Improving the MFI without sacrificing the material cost, energy consumption during processing and thermal properties will be an added advantage. With this in mind, the existing local rotational molding grade HDPE was modified to achieve improved process ability and cross-linked for properties improvement without additional cost.

2.0 EXPERIMENTAL

2.1 Materials

There are three types of polyethylene that were used and shown in Table 1.

Table 1 Specification for the HDPE materials

Materials	**Description**	**Suppliers**
Etilinas HD3840UA	HDPE, density 0.938 g/cm^3, melt index 4.0 g/10 min	Polyethylene Malaysia Sdn. Bhd
Etilinas HD5218AA	HDPE, density 0.952 g/cm^3, melt index 18.0 g/10 min	Polyethylene Malaysia Sdn. Bhd
Petlin LD M050X	LDPE, density 0.919 g/cm^3, melt index 50.0 g/10 min	Petlin (Malaysia) Sdn. Bhd

2.2 Sample Preparation

Polyethylene HD 3840UA was used as a base and reference material. The HD 3840UA was blended with HD5218AA and LD M050X by using twin screw extruder.

The composition of blending formulation is shown in Tables 2 and 3. For Formulation 1, HD3840UA resins were blended with HD5218AA resins and for Formulation 2, HD 3840UA resins were blended with LD M050X resins and extruded accordingly. The temperature of extrusion was 180°C, 190°C and 200°C from feeding zone to die zone respectively and screw speed was 50-55 rpm.

After extruding, samples were pelletized with a pelletizer. At this stage, samples were in the thermoplastic state. Melt index test and density test were then undertaken for all formulations. A silane cross linking agent was added at various concentration (1.3, 1.5, 1.7 and 2.0 phr) to the HD 3840UA, Formulations 1 and 2 in a high speed mixer respectively to a homogeneous mixture before melt mixing on a two roll mill at 200°C. Samples were finally cured in a curing tank for 4 and 8 hours at 100°C using hot water.

Table 2 Blending composition for Formulation 1

Polyethylene	**Formulation**			
HD3840UA	95%	90%	85%	80%
HD5218AA	5%	10%	15%	20%

Table 3 Blending composition for Formulation 2

Polyethylene	**Formulation**			
HD3840UA	95%	90%	85%	80%
LD M050X	5%	10%	15%	20%

3.0 TEST AND ANALYSIS

3.1 Melt Index

The melt index (MI) of the modified and unmodified samples was measured to determine which formulations fall in the rotational molding grade, according to ASTM D 1238 [12] using Ceast MI Tester model 7026.000. The MI measurements were carried out at temperature 190°C under 2.16 weight and the values are expressed in g/10 min.

3.2 Density

The density test was conducted to determine the density of samples after and before modification, since density affects the flow behavior and process ability, by using Mettler Toledo’s density determination kit.

3.3 Gel Content

The gel content that measure the degree of cross-linking of the cross-linked HDPE was determined gravimetrically, using a decahydronapthalene (decalin) as a solvent at 190°C according to ASTM D 2765 [13]. 1% of antioxidant was dissolved in the decalin to inhibit further cross-linking of the specimen. Two samples were used to determine the average gel content for each composition. The cross-linked polymer sample of 0.300 ± 0.015g by weight were cut into small pieces and placed in a 120 stainless steel wire cloth. The specimens were extracted for 6 hours. After the extraction cycle, the samples were dried in a vacuum oven at 150°C for 2 hours. The gel fraction was calculated as follows:

$$\text{Gel fraction} = (W_2/W_1) \times 100 \tag{1}$$

W_1 is the initial weight of sample and W_2 is the weight of sample after extraction.

3.4 Differential Scanning Calorimetry (DSC) Analysis

The tests were conducted according to ASTM D 3417 [14] by using DSC-7 Perkin–Elmer. These tests were used to determine the melting temperature (T_m) and heat of fusion (ΔH_f) that will relate to the formulations processing temperature. Samples of 5 - 7 mg were encapsulated in aluminum pans and treated at a heating, cooling and heating rates of 10°C min^{-1}. The temperature range was 30 - 250°C. The atmosphere used was nitrogen with a flow rate of 20 ml/min. The melting temperature, T_m, was determined as the peak temperature and the enthalpy of fusion, ΔH_m, was determined from the area of DSC endotherm. The degree of crystallinity was calculated via the total enthalpy method, according to the following equation,

$$X_c = \Delta H_m / \Delta H_m^{+} \tag{2}$$

X_c = degree of crystallinity
ΔH_m = the specific enthalpy of melting of the material
ΔH_m^{+} = 288 J/g that of the 100% crystalline PE [1]

3.5 Thermo Gravimetric (TGA) Analysis

Thermo gravimetric technique was used to analyze the thermal stability of the formulations during exposure to a specified environment using a controlled time rate of heating, which was in accordance to ASTM D 3850 [15]. Sample of about 10 to 15 mg was placed in the specimen holder and the initial mass was recorded and heating rate was set to 20°C/min.

4.0 RESULTS AND DISCUSSION

4.1 Melt Index (MI)

The blending is done for the purpose of increasing MI value of base rotational molding grade HDPE which is 4 g/10 min so as the process ability will be better. The values of MI are shown in Table 4, it shows that with increasing percentage of HD 5218AA or LD M050X, the melt index of the blended polyethylene has increased, especially at 20% of HD 5218AA + HD 3840UA. Table 4 also shows that the value for blended melt index HDPE + HDPE was higher than HDPE + LDPE. The lowering of MI for modified HDPE, blended with LD M050X is due to higher molecular weight of LDPE compared to HDPE. Besides, LDPE has a long branching, tend to entangle among themselves, the chain was not properly alligned and bigger free volume compared to modified HDPE, blended with HD 5218AA.

Table 4 Melt index value of samples

Samples	Melt index (g/10 min)
100% HD 3840UA	4.00
95% HD 3840UA + 5% HD 5218AA	4.13
90% HD 3840UA + 10% HD 5218AA	4.33
85% HD 3840UA + 15% HD 5218AA	4.83
80% HD 3840UA + 20% HD 5218AA	5.33
95% HD 3840UA + 5% LD M050X	4.13
90% HD 3840UA + 10% LD M050X	4.25
85% HD 3840UA + 15% LD M050X	4.53
80% HD 3840UA + 20% LD M050X	4.55

4.2 Density

Figure 1 indicates that the densities of the new-modified composition (Formulation 1) slightly increased with HD 5218AA composition. This probably indicates that the molecular chain arrangement in the modified HDPE with HD 5218AA was more compact and there was no destructive effect in chain arrangement. The density of HD 5218AA is 0.952 g/cm^3 when added into HD 3840UA, the densities increased slightly, showing an improvement in the chain arrangement. Figure 2 illustrates that the densities of modified HD 3840UA (Formulation 2) undergo slight decrement after addition of LD M050X. Typically LDPE has long branching and high molecular weight. The density of LD M050X which is 0.919 g/cm^3, when added to HD 3849UA, the densities decreased slightly. The addition of LD M050X probably destructed the chain arrangement in HDPE, making it more random.

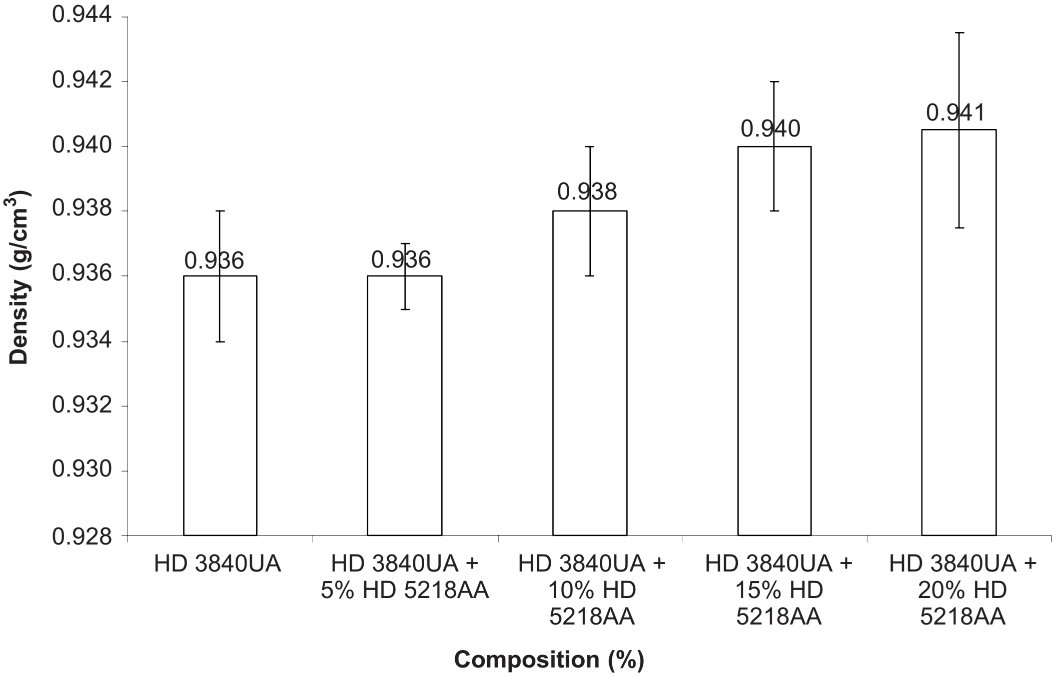

Figure 1 Density of modified HDPE with HD 5218AA at different compositions (Formulation 1)

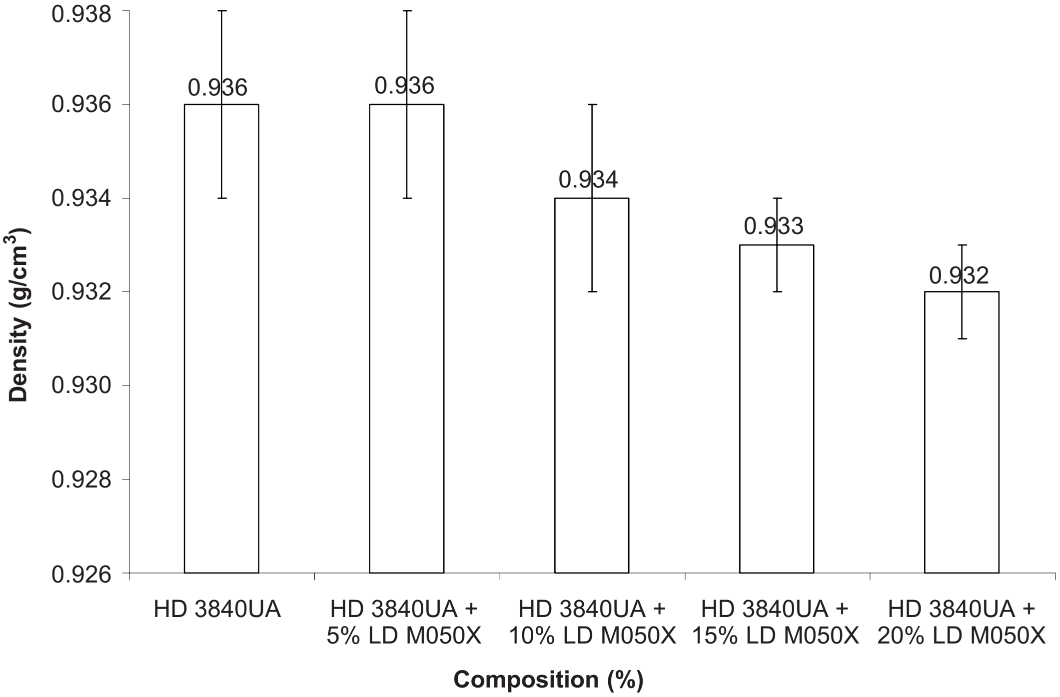

Figure 2 Density of modified HDPE with LD M050X at different blend compositions (Formulation 2)

In general, the densities of the modified HDPE barely change with compositions showing that HDPE or LDPE added has only a slight effect on the density, thus barely affect the cost effectiveness of the materials and process ability.

4.3 Gel Content

Figures 3 and 4 show plots of the gel content with respect to blend compositions for various concentration of silane cross-linking agent after 8 hours curing for Formulations 1 and 2 respectively. The plots indicate that the gel content increased with increasing silane concentration and unaffected by the presence of HDPE or LDPE modifier. Cross-linking occurs mainly in the amorphous phase [11]. Compositions of HD 5218AA and LD M050X in the blend also did not show any effect on the gel content, thus the degree of cross-linking.

Gel content for 1.3 phr silane concentration is in the range of 5% to 9%, 1.5 phr silane concentration is in the range of 13% to 18% and 1.7 phr silane concentration is in the range of 23% to 28%. Gel content for 2.0 phr silane concentration is in the range of 35% to 40%. The value of gel content for 2.0 phr silane concentrations is still insufficient to be used in certain application with respect to the standard where the standard requirement is at least 65% gel content for silane cross-linked method. This is probably due to the silane incorporated in the blend formulation is not enough or not fully cured. At 4 hours curing for both Formulations 1 and 2, the plots follow the

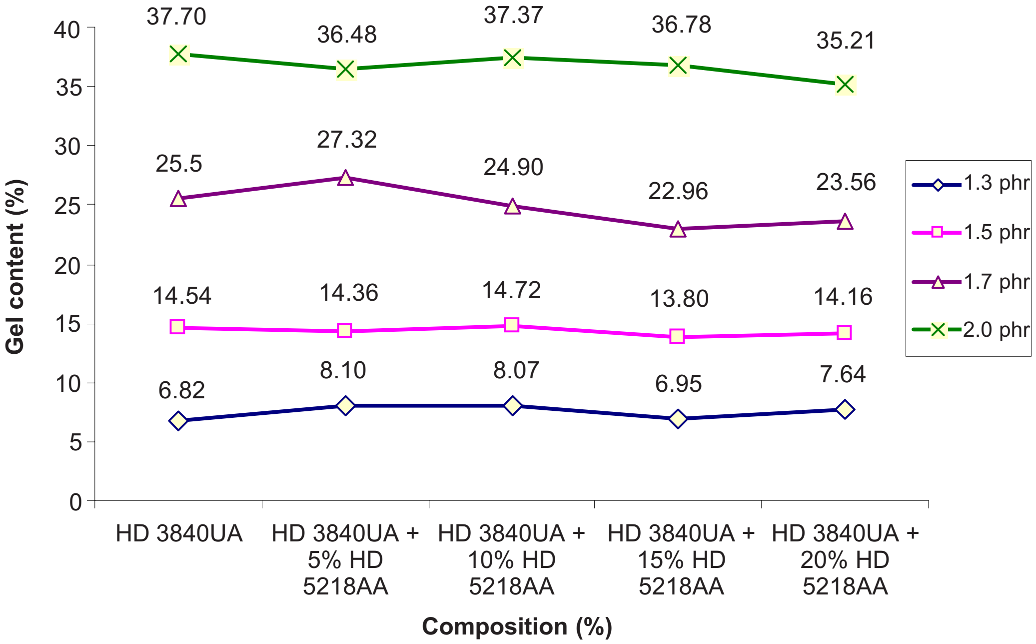

Figure 3 Gel content after 8 hours curing for different silane concentrations (Formulation 1)

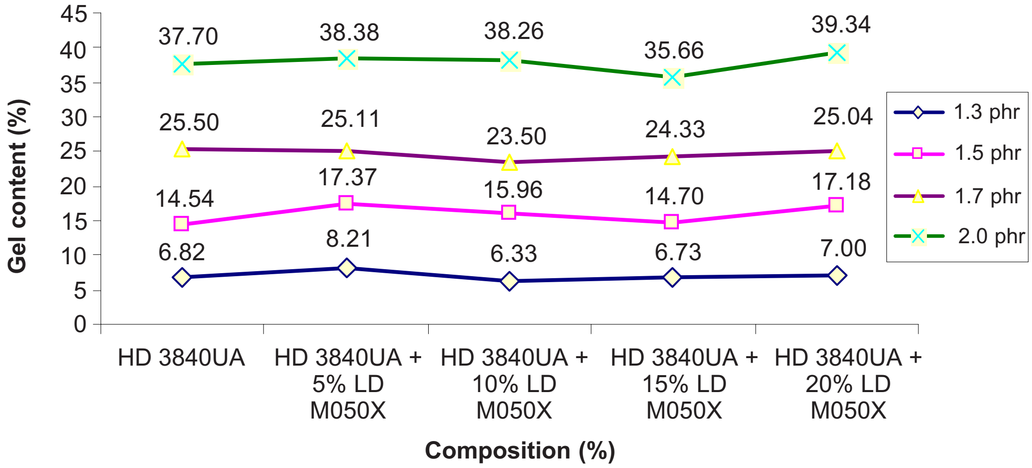

Figure 4 Gel content after 8 hours curing for different silane concentrations (Formulation 2)

trend for 8 hours curing. However, the value is slightly lower than 8 hours curing. Longer curing time is probably preferred for the formulation to reach the required standard.

Silane crosslinking leads to a more complex situation. A possible separation of the grafted compound during crystallisation into silane rich (preferentially the amorphous phase) and silane depleted fractions (crystalline phase) as well as crosslinking in the solid state with limited mobility will lead to an overall more heterogeneous network [6, 10].

4.4 Differential Scanning Calorimetry (DSC)

4.4.1 Melt Temperature

Figures 5 and 6 indicate that melting temperature of the XLPE formulations compounded with 2.0 phr silane cross-linking agent. There were not much different between 100% HD 3840UA with melting point of 128°C to that of other XLPE formulations. Increasing the HD 5218AA content did not affect the melting temperature of the formulation, therefore crystalline region was maintained. Two roll mills mixing probably give poor dispersion of the cross-linking agent, thus HD 5218AA added to the HDPE was unable to form good crosslink and change the morphology [9]. Furthermore, HDPE resin itself is highly crystalline therefore, for melt temperature to vary will be less probable. Melt temperature is related to the crystallinity.

With the addition of LD M050X resin into the HD 3840UA, a drop in melt temperature was observed with increasing percentage of LD M050X resin. This

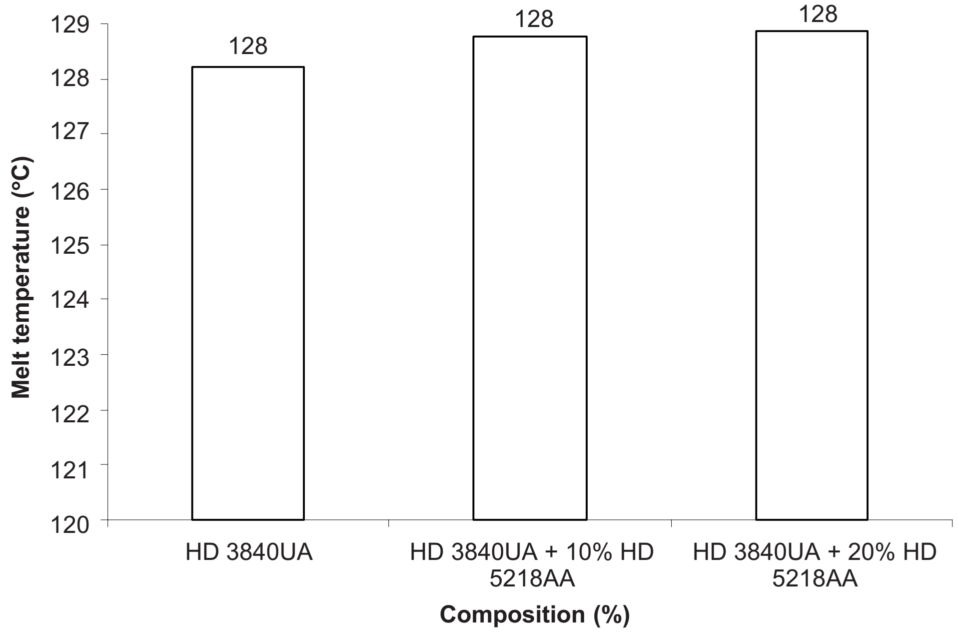

Figure 5 Melting temperature of modified HDPE with HD 5218AA (Formulation 1)

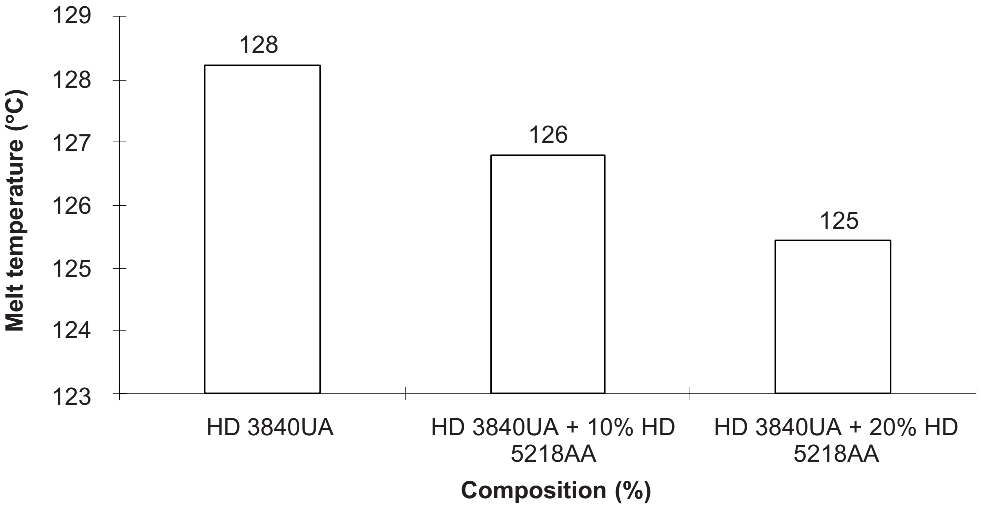

Figure 6 Melting temperature of modified HDPE with LD M050X (Formulation 2)

shows that the amorphous region increased whereas crystalline region decreased. Furthermore, LDPE exhibits lower crystallinity. As a result, it reduced the melt temperature of the system as LDPE resin was added, thus improve process ability in terms of energy requirements.

4.4.2 Degree of Crystallinity

Figures 7 and 8 illustrate the degree of crystallinity of XLPE at different composition compounded with 2.0 phr silane cross-linking agent. The degree of crystallinity of 100% HD 3840UA is 41%. As the HD 5218AA and LD M050X resin were added into the HDPE, the degree of crystallinity seems to drop. The drop in the degree of crystallinity was probably due to the formation of crosslink which increased the amorphous region and decreased the crystalline region. The drop in the degree of crystallinity for LD M050X was much higher than HD 5218AA. LDPE disturbed and disorganized the arrangement in the structure, thus promoted the formation of

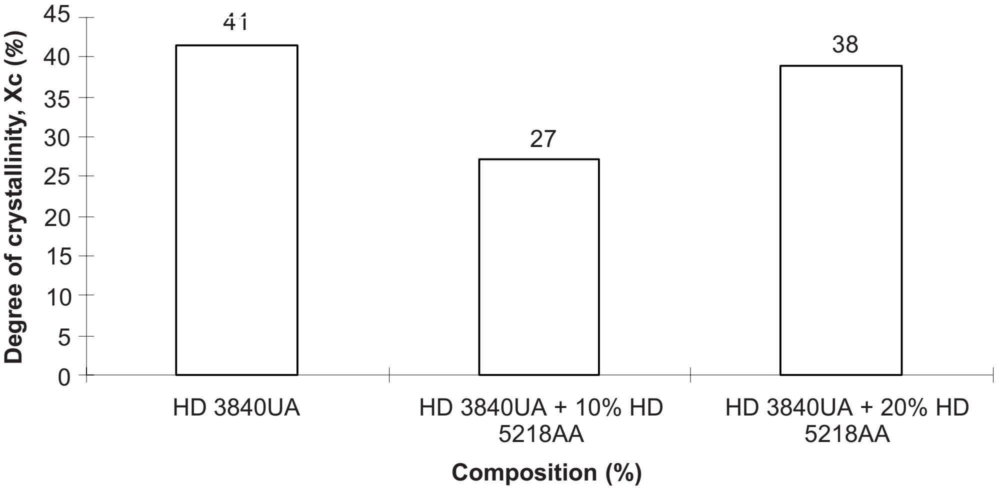

Figure 7 Degree of crytallinity of modified HDPE with HD 5218AA (Formulation 1)

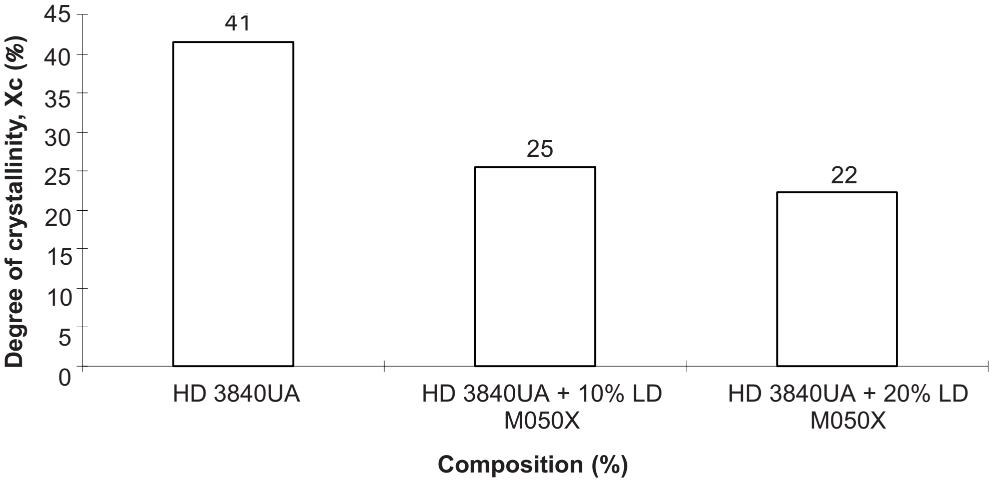

Figure 8 Degree of crytallinity of modified HDPE with LD M050X (Formulation 2)

the amorphous region. Whereas HDPE which itself have high crystallinity did not show much effect on the degree of crystallinity of the formulated blends.

Therefore, the results shown by the melt temperature and degree of crystallinity seem to support each other theoretically. The melting temperature and total crystallinity are related to the crystal size and amount of crystals revealed as endothermic peak temperature and area under the peak in the thermogram respectively. Formation of crosslink junctions while the polymer is at melt state (amorphous phase) disturbs the reorganization and chain folding during crystallization process and this results in formation of imperfect crystallite with smaller size and also less in content, thus lowering the melt temperature [7, 9].

4.5 Thermogravimetric Analyzer (TGA)

The 100% HD 3840UA showed a major weight loss started from 390°C and beyond which showed a sharp loss behavior. However, with the increasing percentage of HD 5218AA resin, the decomposition temperature has increased as shown in Figure 9. This was also observed for increasing percentage of LD M050X resin. An increase in the onset of thermal decomposition is also observed and it increased with the modified compositions.

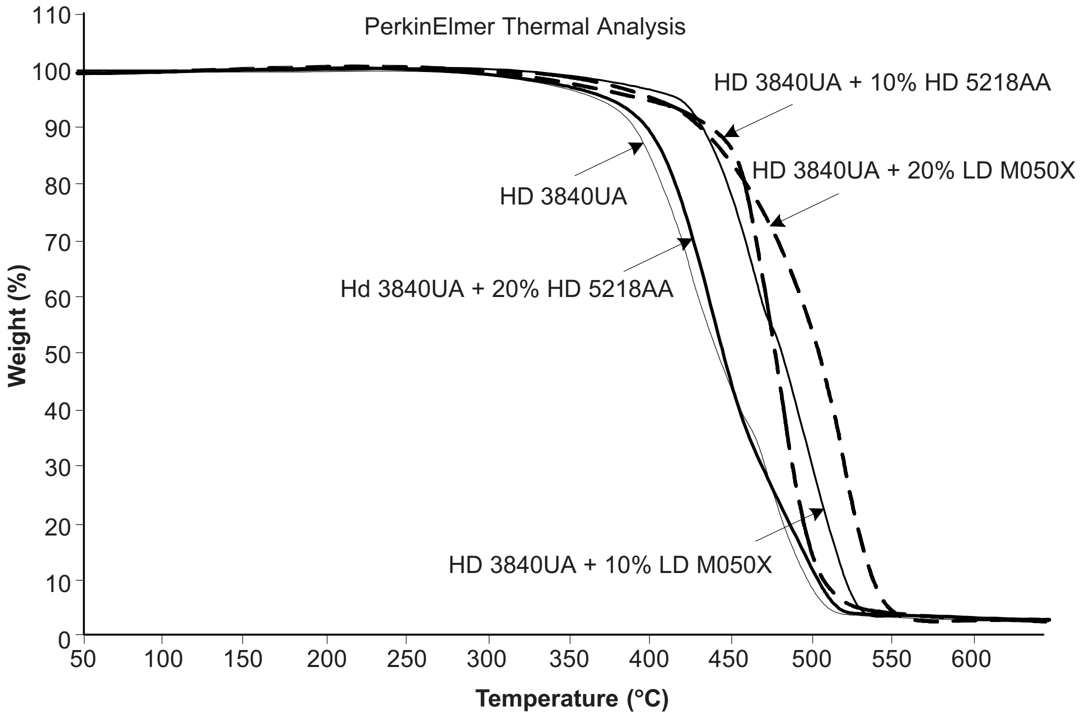

Figure 9 Thermogravimetric curve for different composition of pure HD 3840UA and with silane crosslinking agent 2.0 phr

As gel content increased, it was clearly observed that the thermal degradation temperature was also increased. Weight loss behavior became broad and more time was needed to complete the degradation. Therefore, thermal stability increased as gel content increased which are related to higher crosslinking [10, 16].

5.0 CONCLUSIONS

Melt index (MI) value is basically increased for HD 3840UA blended with HD 5218AA, thus improved process ability. Density value for HD 3840UA blended with HD 5218AA was slightly increased and decreased for HD 3840UA blended with LD M050X that barely affect material cost and process ability. Gel content is increased with increasing silane cross-linking agent concentration only and unaffected by the HDPE or LDPE compositions. Melt temperature is unchanged for cross-linked HD 3840UA with HD 5218AA and decreased for cross-linked HD 3840UA with LD M050X, thus energy consumption during processing is unaffected. The degree of crystallinity is decreased for both modified cross-linked HDPE formulations when compared with base HDPE resulting in possible reduction of strength. Degradation temperature is increased for both modified cross-linked HDPE formulations when compared with base HDPE, indicative of increased stability.

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