Interaction simulation and experimental physico-mechanical analysis of distinct polarity blends of polyethylene and polyvinyl alcohol

Abstract: This paper aimed to investigate the interaction of distinct polarity polymer blends of polyethylene and polyvinyl alcohol (PVOH). Molecular mechanics and dynamics simulation were employed to determine the stability of polyethylene and PVOH complexes. It was found that the binding energies $\Delta E$ for all complexes of polyethylene and PVOH are negative values indicating that the interactions between both components are favorable to achieve a lower energy hierarchy. Such interactions are induced by the high polarity hydroxyl groups of PVOH which caused weak distortion to the dipole moment of inherently non-polar polyethylene. Furthermore, the molecular simulation results were compared with tensile strength, X-ray diffraction and morphology analyses. Tensile strength analysis revealed there was a reduction of magnitude for varying PVOH before achieving a maximum value. Adding small quantities of PVOH in polyethylene as the different polar elements would affect the ordered structure within the blends. Nevertheless, the reduction is insignificant due to the polarity of PVOH which has a slightly distorted polar network of polyethylene. The addition of PVOH (5–15 parts per hundred) into a polyethylene matrix has significantly reduced the crystallinity of the polyethylene matrix by disturbing the highly ordered arrangement structures.

Keywords: mechanical properties; molecular simulation; polyethylene; polyvinyl alcohol; stability.

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1 Introduction

The blending of two or more components is recognized as an effective approach to producing novel polymer materials that possess superior characteristics. However, the mixing of different polymers does not guarantee yielding the desired properties due to the presence of distinct polymer miscibility and the kinetics of phase separation [1]. The thermodynamic interaction parameter ($\chi_{AB}$) between two polymeric components can be altered by the blending compositions [2]. Intrinsically, phase separation occurs in the blending of polymers due to the immiscibility of high molecular weight polymer blends which depend on entropy of mixing. The occurrence of phase separation of polymer blends can cause substantial change of morphologies such as discontinuous structure, islands, or holes that can affect the characteristics of the entire polymer system [3]. Even miscible polymer blends will experience phase separation with increasing temperature or molecular weight of the resins [4]. Particularly, the size domains of the dispersed phase, its dispersibility and interfacial interactions control the physical properties of the polymer blends [5]. Two different polymers are expected to be miscible only when there is a very close match in cohesive energy density or in specific interactions which produces a favorable enthalpy of mixing [6]. Many polymer pairs are known to be miscible or partially miscible, and many have become commercially important. In fact, polymers such as acrylonitrile-butadiene-styrene copolymer (ABS), high impact polystyrene (HIPS) and others employed the theory of phase separation that enables polymers to be used as engineering materials.
Since the 1970s, much research has been conducted to pinpoint the importance of polymer blends [3]. For instance, Braun and Böhringer [7] studied the blending of polyvinyl chloride (PVC) with various types of polymer to reduce the tendency of dehydrochlorination when thermally processed at >180°C. The results showed that the presence of ester groups, nitrile groups and C=C double bonds can improve the thermal stability of PVC in these blends. Besides, it was interesting to find out that the stabilizer as stated can be solubilized either in the PVC phase [PVC/poly(methylacrylate)] or in both phases of the blends [PVC/poly(styrene-co-acrylonitrile)]. Conversely, Wang et al. [8] have investigated the changes of physical and mechanical properties of polypropylene/ethylene octene copolymer (EOC) blends that correspond to various amounts of EOC and extrusion passes to determine the changes of properties. After several melt extrusion cycles, it was reported that there was an increment of the melt flow index (MFI) and crystallinity, whereas the decomposition temperature reduced slightly, and no significant oxidation was noted. The EOC inclusions stabilized the tensile elongation at breakup to three extrusion cycles due to a decrease of their size and a homogenization of their shape, whereas the neat polypropylene continuously decreased with increasing of extrusion.

Conversely, the polarity of polymer components also played important roles to ensure good compatibility among the components. For instance, the compatibility of polyvinyl alcohol (PVOH) and starch were studied by Sin et al. and coworkers [9, 10]. The synergistic interaction of PVOH and starch was determined by differential scanning calorimetry (DSC) method. Originally, starch film did not show presence of any endothermic peaks in DSC thermogram. However, after adding PVOH to starch, the PVOH–starch blend films showed obvious endothermic peaks with onset and end-point temperatures higher than neat PVOH film. In addition, the PVOH–cassava starch blends have experimental enthalpy of melting higher than theoretical values. This evidence shows that the interactions between PVOH and cassava starch molecules are extensively strong.

In this study, the characteristics and interaction of polyethylene and PVOH were conducted. As polyethylene is a nonpolar homopolymer, the blending of distinct polarity PVOH can be of great interest to study. The blending of polyethylene and PVOH is expected to cause phase separation due to incompatibility of both components. Although the PVOH will not form hydrogen bonds with the polyethylene, the electronegativity of hydroxyl group (–OH) will induce a distortion of the electron field leading to phenomena such as distortion of molecular electron density [11]. This will directly influence the arrangement of the polyethylene crystalline structure, subsequently affecting the macroscopic properties of the polymer blends. To the best of our knowledge, there is no report on the physical and mechanical properties of HDPE-PVOH blends. Their miscibility is questionable as both of them are almost opposite in nature, where HDPE being hydrophobic with a non-polar nature and PVOH being hydrophilic with a polar nature. Therefore, in this study, the physical and mechanical properties of the HDPE-PVOH corresponding to the composition of PVOH and thermal treatment were reported. The purpose of this study was also to determine and compare the influence of different temperatures used for thermal treatment on the properties of the polymer blends.

2 Materials and methods

2.1 Computational modeling strategy

The computational modeling of polyethylene and PVOH was carried out using Hyperchem® Professional 8.0 (Hyperchem) standard algorithm. The computational modeling procedure is as follows:

1. For modeling purposes and to keep the models computationally manageable [12], the numbers of polyethylene repeating units (i.e. ethylene interacting with PVOH repeating unit, vinyl alcohol) were kept to a minimum. Thus, the monomers of analysis were determined at four to seven units of ethylene (mPE) and vinyl alcohol (mPVOH). The purpose of such combinations was to determine the effect of increasing repeating units that affect the stability of the complexes.

2. Each pair of the molecular complex was constructed in the Hyperchem workplace. Initially, the distance of molecular complexes of mPE and mPVOH was guessed. Then, the semi-empirical quantum mechanics AM1 (Austin Model 1) method was selected for geometrical optimization by Polak-Ribiere algorithm. The distance and conformation of mPE and mPVOH changed by reiterating until the total root-mean-square (RMS) gradient was less than 0.1 kcal/(mol.Angstrom). This indicates that the complexes remain at stable geometrical condition. Conversely, mPE and mPVOH of the complexes also underwent geometrical optimization separately. The change of binding energy, ΔE of each complex was calculated using the following formula:
ΔE=E_{complex}-(E_{5mPE}+E_{5mPVOH}) \quad (1)

3. The molecular thermal effects were analyzed using the molecular dynamics simulation AM1 method. The geometrical optimized complexes of both 5mPE:6mPVOH and 6mPE:5mPVOH underwent molecular dynamics simulation using the AM1 method to analyze the thermal effects when subjected to elevated temperature.

4. For the molecular dynamics analysis, the AM1 method was also being employed for simulation. The geometrical optimized combinations as completed in step 3 were used for the molecular dynamics analysis. The condition of simulation analysis was set at heat time: 0.1 ps; run time: 0.3 ps; cool time: 0.1 ps; step size: 0.001 s; starting temperature: 298.15 K; simulation temperature: 393.15 K; temperature step: 10 K and in vacuo. The kinetic energy (EKIN), potential energy (EPOT) and total energy (ETOT) of the system were calculated and recorded. Subsequently, the deviation of all the energies was calculated as in Eq. (2):

\[ D_x = \sqrt{\left\langle \alpha^2 \right\rangle - \left\langle \beta \right\rangle^2} \quad (2) \]

where \( \left\langle \alpha^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \alpha_i^2 \)

\( \left\langle \beta \right\rangle = \left( \frac{1}{N} \sum_{i=1}^{N} \beta_i \right)^2 \)

and \( x = \text{value of } E_{\text{kin}}, \text{EPOT} \) and \( E_{\text{TOT}} \).

2.2 Materials

High density polyethylene (HDPE) used as polymer resin in this study is Titanex®HB0972 (Melt Index 0.1) produced by Lotte Chemical Titan Holdings Sdn. Bhd. (Malaysia). Fully hydrolyzed polyvinyl alcohol Sekisui Selvol™ polyvinyl alcohol 103 with 4% solution viscosity at 20°C 4.00 cP and hydroysis 98.40 mole% manufactured by Sekisui Specialty Chemicals America, LLC (USA) was used in this study.

2.3 Sample preparation

The samples were prepared by blending HDPE with various compositions [5, 10, 15 and 20 parts per hundred (phr)] of PVOH using twin screw extruder Nanjing Giant SHJ-20 at 7 rpm with all zones set at 190°C. The extrudate was cooled in water and fed into a pelletizer to obtain polymer pellets. The pellets were then dried at 60°C for 24 h. The polymer pellets were then compression moulded by using a hot press machine under a heating temperature of 180°C to form polymer sheets. The polymer sheets were cut into dumbbell-shaped polymer samples in accordance to ASTM D1822 standard. Then, the dumbbell-shaped polymer samples were placed into ovens for thermal treatment at 120°C for 8 days. The selection of 120°C for thermal treatment was based on the softening point of polyethylene which produces significant vibration of chains to interact with PVOH. The polymer samples for each formulation were collected once every 2 days.

2.4 Tensile test

Tensile test was conducted to evaluate the tensile strength, Young’s modulus of elasticity, and elongation at break of the polymer samples. The samples that were cut into dumbbell shape in accordance to ASTM D1822 standard were tested using Instron Universal Testing Machine (Model 4302 Series IX). The tensile test was carried out at room temperature (25°C) using 2 kN load cell with cross-head speed of 50 mm/min. The final value of the tensile property data for each sample was obtained from the average of five specimens.

2.5 X-ray diffraction analysis (XRD)

The dispersion and crystallinity of MMT in the PVOH matrix were tested by using the XRD-6000 Shimadzu X-ray Diffractometer at 40 kV and 40 mA with the scanning rate of 1°/min. The samples were scanned over a range of 2θ=0–40°. The crystallite size of the samples was calculated by using the following (Scherrer formula):

\[ L = \frac{k\lambda}{b \cos \theta} \quad (3) \]

where \( L = \text{crystallite size, } \AA; k = \text{Scherrer constant; } b = \text{FWHM, radian.} \)

2.6 Scanning electron microscopy (SEM)

The surface morphologies of fractured samples were investigated by using an SEM Hitachi S3400N with a voltage of 15 kV. The fractured surfaces of the samples were observed under the microscopy at magnification of 1000 times, 8000 times and 15,000 times.
3 Results and discussion

3.1 Binding energies and molecular dynamics analyses

Table 1 shows the binding energies of the mPE and mPVOH interactions for various repeating unit complexes. It was found that all complexes exhibited negative values of \( \Delta E \), indicating that the interactions are favorable towards lower energy hierarchy [13]. This is different from the general perspective that blending different polarities of polymers can cause instability of the blending system. Indeed, most of the commercial polymers can undergo a blending process without exhibiting substantial visible phase separation unless observed using a microscopy method [14]. From the geometrical optimization analysis for 5mPE:5 mPVOH complexes (see Figure 1), it can be found that the geometrical orientation of the 5mPE is not linearly exhibited (referring to the linear line), in other words, slightly distorted by the influence of the polarity 5mPVOH. The simulation output of 5mPE also showed that the dipole moment of non-polar mPE gradually increased to 0.005 debyes. Since the formation of a chemical bond is non-existent, it can be postulated that the weak distortion is caused by the high polarity of hydroxyl groups of 5mPVOH. Therefore, the small electronic force attraction would present between 5mPE and 5mPVOH molecular which promotes inter-molecular interactions. Although the interactions complexes are favorable in terms of negative values of the \( \Delta E \), the magnitude of value is still relatively small compared to the previous studies by Sin et al. [9] who found that magnitude of \( \Delta E \) can be larger when the complexes are inherently highly compatible which leads to enhancement of mechanical properties.

Further detailed analysis on the binding energies at increasing repeating unit of mPE corresponding to 5mPVOH found that the 4mPE and 7mPE have the highest magnitude of \( \Delta E \). The large negative value of \( \Delta E \) indicates more stable complexes have been formed. Hence, in relation to this statement, the low repeating unit 4mPE would not disrupt the high polarity of 5mPVOH to form strong and stable network interactions as induced by a hydroxyl functional group. Meanwhile, the 7mPE has shown higher magnitude of \( \Delta E \) (compare to 5mPE and 6mPE interactions with 5mPVOH) which indicates that the mildly distorted polar network (i.e., weak dipole moment) of 7mPE has predominated to interact amongst themselves. However, such interaction is still unlikely to interact as strongly as the network formed when the repeating unit of mPVOH is high; thus, the \( \Delta E \) is still lower than 4mPE. Conversely, when the repeating unit increases from 4mPVOH to 6mPVOH, the magnitudes of \( \Delta E \) are higher. This shows that the formation of a stable blending system is dependent on the composition of PVOH in the binary PVOH-polyethylene blends. High polarity of PVOH not only induces small electronic distortion of the polyethylene in the blends, it interacts through its strong hydroxyl functional group.

Table 1  Binding energies \( \Delta E \) (kcal/mol) of the complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>( E_{\text{mPE}}^\dagger ) (kcal/mol)</th>
<th>( E_{\text{mPVOH}}^\dagger ) (kcal/mol)</th>
<th>( E_{\text{complet}}^\dagger ) (kcal/mol)</th>
<th>Binding energy, ( \Delta E ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4mPE:5mPVOH</td>
<td>-2363.8147</td>
<td>-3445.3538</td>
<td>-5812.6022</td>
<td>-3.4337</td>
</tr>
<tr>
<td>5mPE:5mPVOH</td>
<td>-2927.7765</td>
<td>-3445.3538</td>
<td>-6375.6489</td>
<td>-2.5186</td>
</tr>
<tr>
<td>6mPE:5mPVOH</td>
<td>-3491.7418</td>
<td>-3445.3538</td>
<td>-6940.1681</td>
<td>-3.0726</td>
</tr>
<tr>
<td>7mPE:5mPVOH</td>
<td>-4055.7040</td>
<td>-3445.3538</td>
<td>-7504.2761</td>
<td>-3.2183</td>
</tr>
<tr>
<td>5mPE:4mPVOH</td>
<td>-2927.7765</td>
<td>-2778.7009</td>
<td>-5790.0240</td>
<td>-2.5466</td>
</tr>
<tr>
<td>5mPE:6mPVOH</td>
<td>-2927.7765</td>
<td>-3445.3538</td>
<td>-6375.6489</td>
<td>-2.5186</td>
</tr>
<tr>
<td>5mPE:7mPVOH</td>
<td>-2927.7765</td>
<td>-4113.0542</td>
<td>-7044.3971</td>
<td>-3.5664</td>
</tr>
</tbody>
</table>

\( \xi \) mPE and \( \xi \) mPVOH, \( \zeta \), number of repeating unit.
group network by formation of hydrogen bonds to provide a stable environment in the blends. Nevertheless, it was also found that the ΔE dropped when the repeating unit reached 7mPVOH. This can be explained when the ability of PVOH to induce the polarity effect of mPE has reached its saturation level; subsequently the interaction of mPE with mPVOH would not be pursued harmonically due to large variation in dipole moment between 7mPVOH (8.863 debyes) and 5mPE (0.005 debyes). In other words, the mPE would disrupt the continuity of the PVOH matrix. This would cause substantially different morphology, as well as loss of mechanical properties, as reported in the next section.

In addition, the molecular dynamics simulation analysis was conducted to determine the thermal effect of the lowest and highest stability complexes as stated, namely 5mPE:7mPVOH and 6mPE:7mPVOH, respectively. In this analysis, the deviation of the kinetic energy (DEKIN), potential energy (DEPOT) and total energy (DETOT) of both of the complexes were compared and analyzed. The analysis of the deviation of energy is important for evaluating the stability of a simulation and the extent of equilibration. It also helps to identify possibly interesting low energy conformations with thermal effect. Figure 2 shows the deviation of energies corresponding to simulation starting from 25°C to 120°C and finally a return to 25°C. The deviation of total energy, D_{ETOT} for the low stability of 5PE:7PVOH complex is noticeably higher than 5PE:6PVOH. This indicates that the interaction of the components in 5PE:7PVOH complex produced a higher energy hierarchy that can fluctuate vigorously when subjected to thermal effect. This is due to the lack of intermolecular interaction of both components that enables their motions to act more freely. Subsequently, the components tend to take the opportunity to separate when reaching an excited stage. The elevation of temperature is able to transform the thermal energy into kinetic energy which enables the components of the complexes to undergo vibration and move freely to achieve a molten state. Further analysis on D_{EKN} and D_{EPOT} of 5PE:6PVOH and 5PE:7PVOH found that the differences are larger for D_{EKN} (~2.8 at the end of simulation) than D_{EPOT} (~1.1 at the end of simulation). This indicates application of the thermal effect changes the characteristics of the complexes on the structural interaction compared to the bonding interaction at different amounts of mPVOH. Indeed, this is considered to be reasonable due to weak bonding between the mPVOH and mPE as discussed. When subjected to the thermal effect, the complexes undergo separation as well as diminished substantial entangled-ordered structure which weakens the interaction of the components. Subsequently, the complexes undergo a substantial thermal aging effect. The geometrical orientations of both complexes upon completion of simulation are shown in Figure 3. Figure 3A shows that the 6mPVOH chain has distorted and attracted to the 5mPE molecule. Meanwhile, the molecules of 5mPE and 7mPVOH as shown in Figure 3B have separated to a larger distance after undergoing molecular dynamics simulation at 393.15 K (120°C). This also indicates that 5mPE:7mPVOH complex possesses strong deviation of kinetic energy which results in a more pronounced aging effect after prolonged thermal exposure.

3.2 Tensile properties

Figure 4 shows the tensile strength and elongation of HDPE-PVOH blends when treated at 120°C for 8 days. It was found that prior to the thermal treatment process, pristine HDPE exhibits the highest tensile strength at 30.4 MPa. With the initial addition of 5 phr of PVOH into HDPE, the tensile strength has drastically dropped to 22.9 MPa.
was followed by reduction of tensile strength to 15.3 MPa while subsequently returning to 17.1 MPa and 19.6 MPa for 10, 15 and 20 phr of PVOH, respectively. Such a trend can be well observed from the molecular mechanics geometrical optimization analysis where there is a reduction of magnitude for varying from mPVOH before achieving a maximum value. The high tensile strength of pristine HDPE is mainly due to the high ordered crystalline structure of HDPE [15]. However, the addition of small quantities of PVOH in HDPE as the different polar elements would affect the ordered structure within the blends. Nevertheless, the reduction is insignificant due to the polarity of PVOH which has a slightly distorted polar network, as mentioned. Such “weak linkage” would form minor interactions among the molecules without exhibiting substantial deterioration of the entire blending system. Further addition of PVOH to the level of 10 phr exhibited the lowest tensile strength of the blend. At this level, the PVOH portion with a high polarity characteristic causes negative impact to the structural arrangement of HDPE. Subsequently, increments of PVOH portions up to 15 and 20 phr showed improvement of tensile strength. This shows that the high polarity intermolecular interaction among PVOH components in the matrix of HDPE improves the tensile strength of the binary blends. The high polarity network can be contributed by the interaction of the hydroxyl group of PVOH via hydrogen bonding that strengthens the loosely packed HDPE structure.

When HDPE-PVOH blends were thermally treated at 120°C, it was found that all the compositions shared a common trend. There is an increment of tensile strength to maximum value on the initial aging period (i.e., second

![Figure 3](image1.png)  
**Figure 3** Geometrical orientation of (A) 5mPE:6mPVOH complex, (B) 5mPE:7mPVOH complex after molecular dynamics simulation using AM1 method.

![Figure 4](image2.png)  
**Figure 4** Tensile strength of HDPE-PVOH blends thermally treated at 120°C.
and fourth days followed by declining afterwards). This phenomenon can be explained where re-crystallization occurred at this period [16]. When HDPE-PVOH blends were subjected to the thermal effect, a randomized order of the polymer chains obtained sufficient energy to rearrange into a highly ordered structure, thus improving the tensile strength of the polymer blends. Furthermore, it was also found that when the blends contained higher amounts of PVOH, they would undergo such rearrangement in a faster manner compared to pristine HDPE and 5 phr PVOH blends. This is in agreement with the molecular dynamics simulation where the larger deviation of total energies ($D_{TOT}$) indicates polymer chains tend to react vigorously with the thermal effect. In other words, this would result in highly active movement of polymer chains to rearrange into highly ordered structures within shorter periods of time. In addition, most of the blends also exhibited reductions of tensile strengths throughout the thermal treatment period. The prolonged thermal effect diminished the entangled-ordered structure due to different characteristics of PVOH and HDPE reactions to the thermal effect. This would cause substantial molecular chains separations that weakened the mechanical properties of the polymer. However, in the current analysis, the degradation resulting from chain scission and decomposition were not considered, because the thermal treatment temperature did not even reach the melting point of HDPE (180°C) and PVOH (210°C). There was an exception for the 20 phr PVOH blend with the increment of tensile strength at the end of treatment period. This might be due to application of thermal effects onto high amounts of PVOH, increasing the possibility of formation of a hydrogen bonding network as a result of substantial rearrangement of polymer chains which strengthened the tensile properties of the blend [17].

3.3 X-Ray diffraction (XRD) analysis

The XRD pattern of HDPE-PVOH blends added with increasing of PVOH loading levels is illustrated in Figure 5A. Two significant diffraction peaks (peak A and peak B) are observed in the XRD patterns of the blends.

![Figure 5](image-url)

**Figure 5** XRD pattern of (A) un-aged HDPE-PVOH blends with increasing PVOH percentages, and (B) HDPE-PVOH blends (added with 10 phr and 20 phr PVOH) under thermally aged at 120°C for 4 days and 8 days.
Two significant diffraction peaks, peak A and peak B, were also observed to appear on XRD pattern curves of all thermal treated HDPE-PVOH blends at 2θ≈22.1° and 24.5°, respectively, as shown in Figure 5B. Referring to Figure 5B, the intensities of peak A and peak B for 20 phr PVOH added HDPE-PVOH blends were observed to increase when thermally treated at 120°C for 8 days. This also indicates that the application of thermal effect could increase the crystallinity of 20 phr PVOH added HDPE-PVOH blends by promoting the occurrence of re-crystallization of the polymer matrix. As indicated in Figure 6, the crystallinity of all thermally treated HDPE-PVOH blends was observed to gradually increase when the thermal treatment duration increased up to 4 days. This also indicates the occurrence of re-crystallization in HDPE-PVOH matrix when exposed to high temperature (120°C) for up to 4 days. This might be attributable to the random arrangement of polymer chains in the HDPE-PVOH matrix where their movements are initially restricted in the crystal lattice which could effectively absorb sufficient thermal energy during thermal treatment. This could cause the polymer chains in random arrangement to receive sufficient kinetic energy to break through the bonding force of the crystal lattice and to align themselves into highly packed structures [21]. Thus, the crystallinity of HDPE-PVOH blends has been increased when thermally treated for up to 4 days. However, further increasing in thermal treatment duration from 4 days to 8 days has significantly reduced the crystallinity of all HDPE-PVOH blends except HDPE-PVOH blend added with 20 phr PVOH. This might be due to the continuous absorption of high thermal energy by the polymer chains in crystallite structures that highly increase the kinetic energy of polymer chains and thus cause the reduction in bonding force of crystal lattice [21]. The reduction in bonding forces could affix the polymer chains at the crystal lattice structure and
cause the breakdown of the crystal lattice structure into a more randomized order arrangement.

The crystallite sizes of peak A and peak B for all thermally untreated and treated HDPE-PVOH blends were calculated using Eq. 3 and depicted in Table 2. In Table 2, the crystallite sizes of peak A and peak B for HDPE-PVOH blends were significantly increased when 5 phr PVOH was added into the HDPE-PVOH matrix. The increase in crystallite sizes of peak A and peak B is due to the interaction of crystallites in the PVOH matrix with the original crystallites in HDPE matrix that could significantly increase the size of crystallites [18]. However, further increasing the PVOH loading level has gradually decreased the crystallite size of HDPE-PVOH blends. This might be attributed to the further addition of PVOH which could disturb and rupture the highly ordered arrangement of the crystallites and thus reduce the crystallite sizes of peak A and peak B. As shown in Table 2, increasing of the thermal treatment duration up to 4 days did not exhibit significant effect in the crystallite size of peak A for pristine HDPE. However, when the thermal treatment duration increased to 8 days, the crystallite size of peak A for pristine HDPE was slightly decreased. This could be due to the application of thermal energy which could increase the kinetic energy of polymer chains and cause the slight breakdown of crystallites. Thus, the crystallite size was decreased due to the poor interaction between crystallites.

Referring to Table 2, the crystallite size of peak A and peak B for all HDPE-PVOH blends was rapidly increased when thermally treated for 4 days. This shows that the application of thermal energy to the HDPE-PVOH matrix could exhibit the polymer chains to reach sufficient kinetic energy and enable alignment of themselves in more ordered arrangement to form new crystallites in the polymer matrix. The interaction of these newly formed crystallites with the existing crystallites could significantly increase the crystallite size. At lower loading levels of PVOH (<5 phr), further increasing the thermal treatment duration from 4 to 8 days has rapidly reduced the crystallite size of peak A and peak B. This also indicates that further thermal aging could rupture the highly ordered structures in the polymer matrix and cause the reduction in crystallite size. At higher loading levels of PVOH (≥10 phr PVOH), the crystallite size of peak A and peak B was gradually increased when further thermally treated from 4 days to 8 days. This might be due to the increasing in PVOH loading level which could significantly increase the tendency of the -OH pendant of PVOH to form hydrogen bonding with other PVOH in polymer matrix [20]. Thus, this could lead to higher ordered chains arrangement in the polymer matrix and also increase the crystallinity. Besides, the increment in crystallinity also might be attributable to the polymer chains in a random arrangement structure of higher loading level of PVOH which could absorb more thermal energy during thermal treatment. This could cause these polymer chains to obtain sufficient kinetic energy to break through the bonding force of the crystal lattice and converge towards

<table>
<thead>
<tr>
<th>Loading level of PVOH, phr</th>
<th>Thermal aging duration, day</th>
<th>Peak A (as shown in Figure 5)</th>
<th>Peak B (as shown in Figure 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
<td>4 days</td>
<td>8 days</td>
</tr>
<tr>
<td></td>
<td>2θ, °</td>
<td>Crystallite size (L), Å</td>
<td>2θ, °</td>
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<td></td>
<td>2θ, °</td>
<td>Crystallite size (L), Å</td>
<td>2θ, °</td>
</tr>
<tr>
<td>0</td>
<td>22.22</td>
<td>144.9</td>
<td>22.05</td>
</tr>
<tr>
<td>5</td>
<td>22.23</td>
<td>151.0</td>
<td>22.14</td>
</tr>
<tr>
<td>10</td>
<td>22.13</td>
<td>141.3</td>
<td>22.21</td>
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<td>135.93</td>
<td>22.19</td>
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<td>22.14</td>
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<td></td>
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<td>Crystallite size (L), Å</td>
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<td></td>
<td>2θ, °</td>
<td>Crystallite size (L), Å</td>
<td>2θ, °</td>
</tr>
<tr>
<td>0</td>
<td>24.56</td>
<td>130.6</td>
<td>24.45</td>
</tr>
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<td>5</td>
<td>24.60</td>
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</tr>
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<td>24.51</td>
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<td>24.49</td>
<td>127.3</td>
<td>24.57</td>
</tr>
<tr>
<td>20</td>
<td>24.55</td>
<td>132.9</td>
<td>24.51</td>
</tr>
</tbody>
</table>

*a phr, parts per hundred.
a more ordered arrangement, thus inducing the formation of new crystallites in the polymer matrix [12]. The interaction of the new crystallites due to thermal treatment with the existing crystallites could increase the crystallite size [18].

3.4 Morphological observations

Figure 7 illustrates the fracture surface of HDPE-PVOH blends added with various loading levels of PVOH. As shown in Figure 7A, the occurrence of very thin fibrils can be clearly observed to appear on fractured surfaces of pristine HDPE (or 0 phr PVOH). The appearance of very thin fibrils is mainly attributed to the high rigidity behavior of HDPE polymer which tends to break before the plastic deformation of the polymer matrix. Besides, small voids can also be observed to appear on the matrix of pristine HDPE as shown in Figure 7A. The appearance of small voids in polymer matrix is due to the release of water vapor during hot pressing of samples. As shown in Figure 7B, the HDPE-PVOH matrix was observed to be more continuous than pristine HDPE without the appearance of thin fibrils when added with 5 phr PVOH. Besides, the occurrence of globules also can be clearly observed on the fractured surface of 5 phr PVOH where the added HDPE-PVOH matrix and the formation of globules is mainly due to the rebound effect of polymer matrix during breaking of the sample. This also indicates the reduction in rigidity of the HDPE matrix when adding with 5 phr PVOH. This might be

![Figure 7 Morphologies observation of un-aged HDPE-PVOH blends added with (A) 0 phr PVOH, (B) 5 phr PVOH, (C) 10 phr PVOH, (D) 15 phr PVOH and (E) 20 phr PVOH under 8000 times magnification.](image-url)
due to the addition of PVOH into the HDPE matrix which could slightly rupture the crystallites in the HDPE matrix and thus increase the elongation ability of the matrix by reducing the crystallinity in the polymer matrix. The increase in elongation ability of the matrix is responsible for the rebound effect of the polymer matrix after sample breaking to form globules.

Conversely, the formation of thicker in width but short fibrils can be observed on the fractured surface of the HDPE-PVOH matrix as illustrated in Figure 7C. The formation of fibrils in 10 phr PVOH added HDPE-PVOH matrix indicating the higher plastic deformation of polymer matrix but lower in rigidity. Besides, a higher amount of voids also can be clearly observed in Figure 7A. This observation also was found to tally with the tensile strength results in which the 10 phr PVOH added HDPE-PVOH samples posed the poorest tensile strength compared to other samples. As shown in Figure 7D, higher globules amounts were observed to appear on the HDPE-PVOH matrix when added with 15 phr PVOH. Besides, the polymer matrix of 15 phr PVOH added HDPE-PVOH matrix also was found to have fewer continuities than other HDPE-PVOH samples with the occurrence of voids. This also indicates the poorer properties in tensile strength of 15 phr PVOH added HDPE-PVOH blends. By observing Figure 7E, the polymer matrix of 20 phr PVOH added HDPE-PVOH blends was found to be more continuous than polymer matrices of 10 phr and 15 phr PVOH added.

Figure 8 Morphologies observation of HDPE-PVOH blends added with 0 phr PVOH and thermally treated at 120°C for (A) 4 days, and (B) 8 days; HDPE-PVOH added with 10 phr PVOH and thermal treated at 120°C for (C) 4 days and (D) 8 days; HDPE-PVOH added with 20 phr PVOH and aged for (E) 4 days and (F) 8 days under 8000 times magnification.
HDPE-PVOH blends. The occurrence of globules and voids in a 20 phr PVOH added sample also was observed to be less than 15 phr PVOH added HDPE-PVOH blends. The continuities of the polymer matrix could increase the tensile strength of the polymer matrix by reducing the plastic deformation of that polymer matrix (globules). Thus, the 20 phr PVOH added HDPE-PVOH blends posed better tensile strength results than 10 phr and 15 phr PVOH added HDPE-PVOH blends, as discussed earlier.

The surface morphologies of all thermally treated HDPE-PVOH blends added with various loading levels of PVOH are depicted in Figure 8. As shown in Figures 7A, 8A and 8B, the polymer matrix of pristine HDPE was observed to be more continuous when thermally treated for 4 days and 8 days. The short and very thin fibrils also were found to disappear from the pristine HDPE matrix when thermally treated for 4 days and 8 days. Conversely, the occurrence of globules and thicker fibrils also could be clearly observed on the fractured surfaces of pristine HDPE matrix when thermally treated for 4 days and 8 days. However, the occurrence of voids in pristine HDPE matrix when thermally treated for 8 days was observed to be slightly increased in amounts and size when compared to the voids on the pristine HDPE when thermally aged for 4 days. This also indicates that the application of thermal energy on pristine HDPE matrix for 4 days could significantly enhance tensile strength of pristine HDPE by causing the polymer chains in matrix to obtain sufficient kinetic energy to align themselves into highly ordered arrangement structures.

As shown in Figures 7C, 8C and 8D, when the 10 phr PVOH added HDPE-PVOH blends were thermally treated at 120°C for 4 days, the thick fibrils were observed to disappear on the fractured surface, and this also indicated the reduction in mechanical properties (tensile strength) of polymer properties when under strain. Besides, the number of voids also were observed to significantly increase, and the occurrence of voids tends to weaken the tensile strength of the polymer matrix, as discussed in tensile strength results. The formation of voids is attributed to the release of water vapor during the samples compression moulding process [22]. As shown in Figures 7E, 8E and 8F, the occurrence of short fibrils and high amounts of voids can be observed on the polymer matrix of 20 phr PVOH added HDPE-PVOH blends. The formation of short fibrils on fractured surfaces of a 20 phr PVOH added HDPE-PVOH blend is due to the brittle behavior of the polymer matrix which restricts the elongated polymer matrix from rebound back to its position during sample breaking. Besides, the appearance of voids also could reduce the amount of stress that a polymer can withstand when being strained before breaking [23]. Thus, this observation is consistent with the tensile strength results of 20 phr PVOH added HDPE-PVOH blend when thermally treated to 4 days. However, when the 20 phr PVOH added HDPE-PVOH blends were thermally treated for 8 days, the polymer matrix was observed to be more continuous than the un-aged samples and the samples thermally treated for 4 days. The increasing matrix continuities also led to enhance the mechanical properties such as tensile strength of HDPE-PVOH blend, as shown in the results of tensile strength.

4 Conclusions

The binding energies $\Delta E$ for all complexes of mPE and mPVOH are negative values, indicating the interactions between both components are favorable to achieve lower energy hierarchy. Such interaction is induced by the high polarity hydroxyl groups of mPVOH which caused weak distortion to the dipole moment of inherently non-polar mPE. Furthermore, such simulation results can be evidenced from the tensile strength analysis where there is a reduction of magnitude for varying of PVOH before achieving a maximum value. The addition of small quantities of PVOH in HDPE as the different polar elements would affect the ordered structure within the blends. Nevertheless, the reduction is insignificant due to the polarity of PVOH which has a slightly distorted polar network. Meanwhile, the addition of PVOH (5 phr–15 phr) into the HDPE matrix has significantly reduced the crystallinity of HDPE matrix by disturbing the highly ordered arrangement structures in the HDPE matrix. However, the crystallinity of HDPE-PVOH blends was gradual when the PVOH loading level increased up to 20 phr. This might be because the higher amount of PVOH in the HDPE-PVOH blends could enable the -OH functional group to form the extra hydrogen bonding which contributes towards larger crystallinity of polymer matrix. The crystallite sizes of peak A and peak B were observed to slightly increase as 5 phr PVOH was incorporated into HDPE matrix. This is because the good interaction of the crystallite size in HDPE matrix and crystallite size in PVOH could extend the crystallite size significantly. Hence, the physico-mechanical properties of the HDPE-PVOH have improved.

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References