The main objective of the present work was to study the effect of electron beam radiation on the morphology stabilization and properties of polystyrene (PS) and polyvinyl methyl ether (PVME) blends both in single and two-phase state, formed during spinodal decomposition process. Morphology development in particular, the domain growth rate of PVME dispersed phase was studied by using optical microscopy. The increasing rate of the interphase thickness resulted from interdiffusion of the samples produced by melt mixing was studied by differential scanning calorimetry. Radiochemistry and Flory-Rhener analysis were performed to determine the cross-link density of samples. The cross-link density of the interphase was measured using FTIR. A combination of thermal analysis techniques and physical properties measurement were used to study the effect of electron beam radiation dose on morphology stabilization due to interfacial modification and properties of both single and two-phase polymer blends. The phase separation rate of PS/PVME miscible blend was found to be a power law type function of separation time with an exponent 0.77. The interphase growth rate was found to be about 3.5 nm.min⁻¹. It was demonstrated that the irradiation process can play significant role in stabilization of PS/PVME blend morphology through immobilization of interphase resulting from copolymerization and/or cross-linking.

INTRODUCTION

The type of morphology, dispersion phase size and interfacial adhesion between two phases are among parameters which play significant roles in determining the mechanical performance of immiscible blends [1]. In many cases the induced morphology is not stabilized enough for further required process and, therefore, needs to use an appropriate method to fix morphology. One method to be used for producing multiphase polymer blend is to freeze and stabilize the microstructure.
formed during spinodal decomposition process of the lower critical solution temperature (LCST) blend system [2]. The electron beam (EB) radiation of two-phase polymer blend in their solid state has been used as one of the most successful method for morphology stabilization. Irradiation process can stabilize the spinodal decomposition induced morphology system through different mechanisms including cross-linking of dispersed phase, enhancement of interfacial interaction or both [2] depending on the nature of blend components. Van Gisbergen and coworkers [3] used electron beam radiation process for stabilization of PP/EPDM blend morphology. According to these authors the stabilization of this system is mainly established by electron beam induced cross-linking of EPDM dispersed phase. Tran-Cong et al. [4] studied the controlling of morphology of anthracene labeled PS/PVME blend by using laser beam photocross-linking, where the PS phase was cross-linked as the blend matrix. The effect of cross-linking on phase diagram, microstructure and properties of IPNs have been studied by many researchers in IPNs systems in which the cross-linking occur between the same molecules (A-A or B-B) [5, 6]. However, there are other cases in which the cross-linking may occur between A-A, B-B or A-B. The EB radiation has also been used to increase the extent of miscibility region (evaluating LCST) through cross-linking reaction [7]. Polystyrene (PS) and polyvinylmethyl ether (PVME) are a rather unique pair of polymers in that they are chemically dissimilar and also dissimilar in their response to irradiation, on the other hand the PS/PVME blend exhibits an LCST behaviour [8] i.e., phase separation upon heating. This combination of dissimilarity and compatibility provides the necessary prerequisites for a unique and informative radiation study. Nishi and Kwei [7] have reported that the electron beam irradiation can cross-link PS/PVME compatible film to form an IPN. Briber and Bauer [9] studied the effect of cross-linking by gamma irradiation in miscible state of deuteriated polystyrene (PSD) and PVME blend on the phase behaviour. It should be noted that the PSD/PVME phase behaviour is not equivalent to the hydrogenated PS/PVME [10]. McHerron and Wilkes [11] have published results of study on the effect of electron beam irradiation on the gel content of PS/PVME blends. It was reported that relatively large amounts of PS must be added to pure PVME in order to influence the gel content.

The aim of the present work was to study the capability of electron beam irradiation for producing PS/PVME two-phase polymer blends with defined and stabilized morphology. An attempt was also made to study the mechanism of electron beam radiation on morphology stabilization and its role in controlling interfacial enhancement and physical performance of blend samples.

Theory

DeGennes has conducted a theoretical analysis on the effect of A-B cross-linking on phase diagram on concentration fluctuation for UCST polymer blend [12]. In this report he defines the limit of the UCST phase diagram. Briber and Bauer [9] investigated the effect gamma radiation cross-linking on the phase behaviour of miscible PSD/PVME blend and compared their finding with the results predicted from DeGennes theory. According to DeGennes theory the radiation dose will lead to decrease in spinodal temperature while Briber and Bauer experimental results show a reverse effect. The main reason for such discrepancy was that the DeGennes analysis was based on UCST behaviour while Briber and Bauer experiments were on the basis of LCST behaviour. According to the DeGennes a critical interaction parameter of uncross-linked polymer blend ($\chi_0$) is larger than that of cross-linked LCST polymer blend ($\chi$) define as follows [13]:

$$\chi_c = \chi_0 - \frac{2\sqrt{\delta}}{N_c}$$  \hspace{1cm} (1)

where $N_c$ is cross-link density and $\chi$ is given by [1]:

$$\chi_{ab} = \frac{V_r}{RT} (\delta_a - \delta_b)^2$$  \hspace{1cm} (2)

where $V_r$ is reference volume which is taken as close to molar volume of the smallest polymer unit, $R$ is universal gas constant, $T$ is absolute temperature and $\delta$ is solubility parameter of polymers.

The probability of a repeating unit of a chain being branched is proportional to the dose [9]:

$$P = KD$$  \hspace{1cm} (3)

where $P$ is the probability, $D$ is dose and $K$ is the probability constant. The probability that a chain is not
branched can be determined from the following relation:

\[(1-P)^N = (1-KD)^N\]  \(4\)

where \(N\) is the chain repeat unit number. Thus the fraction of unbranched polymer with MWD equal to \(W(N)\) for dose \(D\) can be determined by using the following equation:

\[\frac{W_D}{W_0} = (1 - KD)^N W(N) \text{d}N\]  \(5\)

where \(W_D\) is weight of unbranched fraction at dose \(D\) and \(W_0\) is the initial weight.

The unreacted fraction at dose \(D\) will be:

\[\frac{W_D}{W_0} = \left(\frac{y}{y + KD}\right)^k\]  \(6\)

where

\[k = \frac{N_W}{N_W - N_n}\]  \(7\)

In this equation \(N_n\) is number average molecular weight and \(N_w\) is weight average molecular weight.

By plotting \((W_D/W_0)^{-1/k} - 1\) against \(D\) the value of \(K/y\) can be obtained. Therefore, by having \(K/y\) value, the probability constant \((K)\) and hence the cross-link density can be calculated.

**EXPERIMENTAL**

**Materials**

Commercial grade of PVME was obtained from BASF Co. and PS was supplied by Scientific Polymer Product Co. with specification listed in Table 1.

**Sample Preparation**

Two sets of blends samples with constant composition 30/70 PS/PVME were considered: solution cast samples and melt blend samples.

The melt blend samples were prepared using a laboratory 350 mL internal mixer (Brabender, Germany) equipped with a Banbury type rotor at 170°C and rotor speed of 30 rpm. The molten blend was immediately passed through a two roll mill with 2 mm nip gap in order to prepare suitable sheet for preparing samples for further studies.

The solution cast sample was prepared in toluene as co-solvent. The solution samples were cast on Teflon sheet and kept at room temperature for 24 h, then it was placed in 675 mmHg vacuum oven for 24 h in order to remove residual solvent. The characteristics of samples are given in Table 2.

In order to find cloud point for obtaining phase diagram five blend samples containing 10, 30, 50, 70 and 90 percent of PS were prepared by solution method. The solution samples were cast onto glass slides and fully dried as described in sample preparation section. The cloud points temperature of the blends were determined by isothermal heating and visual observation of turbidity of the sample films according to the reference [11].

The samples were irradiated in air at room temperature by using Rhodotoron TT200 (Belgium) with specification given in Table 3. The samples were imposed to irradiation of 10, 25, 50, 100, 150 and 200 kGy at room temperature.

The cross-link density of irradiated samples was determined by using swelling technique according in conjunction with the Flory-Rhener theory [14]. The equilibrium swelling theory of Flory-Rhener proposed for sample polymer network in the presence of small molecules is expressed as follow:

\[-\ln (1-v_2) + v_2 + \chi_1v_2^2] = V_r \left[ v_2^{1/3} - v_2 \right]\]

Where \(v_2\) is the volume fraction of polymer in swollen state, \(V_r\) is the molar volume of solvent, and \(\chi_1\) is the Flory-Huggines polymer-solvent dimensionless inter-

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Commercial name</th>
<th>Supplier</th>
<th>(M_w)</th>
<th>Density (g/mL)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>PS25</td>
<td>S.P.P</td>
<td>250000</td>
<td>1.050</td>
<td>P1</td>
</tr>
<tr>
<td>PVME</td>
<td>Lutonal M40</td>
<td>BASF</td>
<td>87000</td>
<td>1.057</td>
<td>P2</td>
</tr>
</tbody>
</table>
The parameter \( n \) represents the number of active network chain segments per unit volume and its value can be determined from relation \( n = \frac{\rho}{M_c} \), where \( \rho \) is the density and \( M_c \) the molecular weight between cross-links.

A quantity correlation was made between the ratio of the blends which constitutes weight fraction and their characteristic peak intensity that appeared at 3026 and 2819.7 cm\(^{-1} \) for PS and PVME, respectively as shown in eqns (9) and (10) for low PS and high PS content, respectively:

\[
\frac{W_{PS}}{W_{PVME}} = -0.035 + 1.328 \frac{h_{PS}}{h_{PVME}} \quad (9)
\]

\[
\frac{W_{PVME}}{W_{PS}} = -0.033 + 1.103 \frac{h_{PVME}}{h_{PS}} \quad (10)
\]

where \( W \) is the weight fraction of component, and \( h \) is height of the peaks mentioned above.

Thermal analysis of the samples was performed using DSC (Shimadzu DSC-50) in a temperature range -60 to 120°C and heating rate 10°C min\(^{-1} \).

The radiochemistry yields (G values) of cross-linked polymer blends samples were measured by using Charlesby-Pinner equation in the following form [15]:

\[
S + S^{0.5} = \frac{G(s)}{2G(x)} + \frac{0.96 \times 10^6}{G(x) M_w D} \quad (11)
\]

where \( S \) is sol fraction (\( S = 1 - \) gel fraction ), \( G(s) \) is chain scission radiochemistry yield, \( G(x) \) is cross-linking radiochemistry yield, \( M_w \) is initial weight average molecular weight , \( D \) is absorbed dose (kGy). The ratio \( G(s)/G(x) \) can be estimated from the intercept and the value of \( G(x) \) from the slope of the Charlesby-Pinner plot (\( S + S^{0.5} \) vs. \( D^{-1} \)). The gelation dose value (\( D_g \)) value can also be estimated from the same plot when \( S + S^{0.5} = 2 \). Having known the \( G(x) \) the number of cross-link formed in the blend sample can be calculated by using following relation [15]:

\[
N_c = \frac{0.96 \times 10^6}{m G(x) D} \quad \text{(12)}
\]

where \( m \) is molecular weight of repeat unit.

For gel fraction measurement, the irradiated samples were extracted by THF by means of Soxhlet extractor for 24 h at ambient temperature. The insoluble fraction was dried at 80°C for 3 h. The gel fraction was then calculated using eqn (13):

\[
\text{Gel fraction} = 1 - \frac{w_2}{w_1} \quad \text{(13)}
\]

where \( w_1 \) is the initial weight of the sample, and \( w_2 \) is weight of the insoluble residue.

All gel fraction results repeated here are an average of three samples. The measured results were compared with those predicted from simple mixture additive rule as shown eqn (14):

\[
G_t = G_{ps} \phi_{ps} + G_{PVME} \phi_{PVME} \quad \text{(14)}
\]
where \( G_t \), \( G_{ps} \) and \( G_{pvme} \) are theoretical, PS and PVME gel fraction, respectively and \( \phi \) is components’ weight fraction.

In order to determine the growth rate of separated phase, the samples prepared at different time within the phase separation period were examine by optical microscopy (Nikon model SMZ-1500).

**RESULTS AND DISCUSSION**

Figure 1 shows the phase diagram of PS/PVME blend sample obtained on the basis of the cloud point results in conjunction with Flory-Huggins theory is expressed in the following form [16, 17]:

\[
\chi = -0.29209 + \frac{0.4968 - \frac{45.971}{T}}{1 - 0.04874 \phi_{PVME}}
\]  

(15)

Here \( \chi \) represents the Flory-Huggins interaction parameter, \( T \) is absolute temperature and \( \phi \) is weight fraction.

From these results one may notice that the LCST temperature of these blends samples is approximately 140°C where the corresponding PS weight fraction \( \phi_{ps} \) is equal to 0.30.

Two typical optical micrographs indicating the growth rate of PVME separated phase are shown in Figures 2 and 3.

Figure 4 illustrates the result of variation of separated phase size region as a function of time obtained from five optical micrographs of the samples taken in different separation times. As it is clearly seen the growth rate of the PVME separated phase linearly increase with increasing the separation time with power law type kinetic equation as follow:

\[
d = 3.9 \times 10^{-4} t^{0.77}
\]

(16)

here \( d \) (\( \mu \)m) is phase separated regions mean size and \( t \) (s) is separation time.

On the other hand according Chan’s kinetics theory
spinodal decomposition [17]:

\[ d_0^2 = 2 D t \]

when \( d_0 \) is the size of the original fluctuations in concentration which was assumed large enough to enable segregation to take place in the spinodal region, \( D \) is the diffusion coefficient, and \( t \) is the separation time.

Thus from the above it is possible to estimate the diffusion coefficient \( (D) \) of these samples. The calculated value was found to be:

\[ D = 6.7 \times 10^{-9} \text{ cm}^2/\text{s} \]

It should be noticed that the diffusion coefficient value for any other temperature can be calculated by using following relation [17]:

\[ d(T, \varphi) = L(\varphi) \left( \frac{T - T_c}{T_c} \right)^{-\nu} \]  

where \( \nu = 1/2 \) base on the mean field assumption [18] and estimated value of \( L(\varphi) \) is 10 Å [19].

Figure 5 shows the variation of heat flow corresponding to \( T_g \) of blends constituent with annealing time measured at 120°C by using DSC. It is believed that when PS and PVME as miscible polymers come into contact with each other mutual diffusion across the interphase between the two polymers may occur. The composition's inhomogeneous decrease may be due to the interdiffusion, until theoretically a homogeneous molecular mixture of both components is reached [20]. Thus the interdiffusion process can occur during annealing of the quenched two-phase melt blended samples at a temperature above the \( T_g \) of PS but below the LCST it follows as described in Figure 6.

Therefore, the interdiffusion rate can be calculated from the heat flow results shown in Figure 5 and using the following relation:

\[ h(t_a) - h(t_a = 0) / h(t_a = 0) \]  

where \( h \) is the height of peak at \( T_g \) of each blend's constituent and \( t_a \) is annealing time.

Figure 7 shows the variation interdiffusion mass percent as a function of annealing time. For early interdiffusion stages (where interphase thickness is very smaller than PVME particle size, \( \delta_{ip} \ll d_p \)) the fractional interdiffused volume \( (\nu_{ip}) \) can be calculated by following relation:

\[ \nu_{ip} \sim 6 \delta_{ip}/d_p \]  

By knowing the interdiffusion mass fraction of each blend's components at given annealing time from Figure 8 the total interdiffusion mass can be calculated which was found to be 0.8500 for annealing time of 100 min. Thus from the above and considering the mean particle diameter of PS dispersed phase found to
be 2.5 μm the $v_{ip}$ can be calculated. The value of interphase thickness growth rate obtained from calculated $v_{ip}$ is about 3.5nm.min$^{-1}$. This result was found to be in good agreement with that reported by Sauer and Walsh [21] for the same blend system but by using different methods.

On the other hand, the required time for complete interdiffusion at 120°C can be predicted from eqn (17). The value of D predicted from eqn (17) for 120°C was found to be about $D = -4.27 \times 10^{-14}$ cm$^2$/s and corresponding required time for complete interdiffusion time at 120°C calculated based on particle size 2.5 μm was 20000 min.

However, the results obtained from interdiffusion test shown in Figure 7 suggest much longer time for a complete interdiffusion. Such a disagreement observed between the results of these two methods suggest that the interdiffusion rate measured at an early stage here in this work may not necessarily remain unchanged during later stages of the interdiffusion process.

**Radiochemical Analysis**

The results of $G(x)$, $G(s)$, $D_g$ and $N_{cg}$ of the PS, PVME and blend samples which were obtained from the Charlesby-Pinner plot (Figure 8) according to procedure described before are given in Table 4.

In order to study the effect of EB radiation on stabilization of two-phase morphology of PS/PVME blends it is probably the most appropriate way to use the irradiation induced copolymerization and/or cross-linking of blend interphase as a criterion. To do this, two-phase blend samples prepared by using the phase separation method were irradiated at different doses. Each of these samples was then dissolved in toluene as the co-solvent and the obtained clear solution was separated in two PS and PVME rich liquid phases after adding methanol. The PS weight fraction in the irradiated blend samples measured by FTIR are given in Table 5.

It should be noted that dose 7.5 kGy was the maximum radiation dose used in this method, and above this dose the blend components fractionation could not be carried out.

The amount of minor component in each phase (e.g., PS in PVME rich phase) can be considered as a measure of copolymerization induced by irradiation in the samples. Thus from the results given in Table 5 one may notice that the extent of the copolymerization is increased by increasing the irradiation dose.

As described in the theory section the copolymerization probability constant (K) can be obtained from plotting the $1 - (W_{PVME})^{1/1.7_{PVME}}$ against dose. Then, the interphase cross-link density $N_c$ can be calculated from $N_{ci} = (KD)^{-1}$. The value obtained for $N_{C1}$ represents the cross-link density of the interphase closed to

---

**Figure 7.** Interdiffused mass content of PS and PVME as function of the annealing time ($t_a$) at 120°C obtained from DSC measurements.

**Figure 8.** Charlesby-Pinner plots for PS, PVME and blends.

---

**Table 4.** Radiochemical analysis data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G(s)$</th>
<th>$G(x)$</th>
<th>$D_g$</th>
<th>$N_{cg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.089</td>
<td>0.32</td>
<td>228.5</td>
<td>4539</td>
</tr>
<tr>
<td>P2</td>
<td>0.68</td>
<td>1.18</td>
<td>12.8</td>
<td>19000</td>
</tr>
<tr>
<td>bm</td>
<td>0.21</td>
<td>0.52</td>
<td>45.6</td>
<td>1396</td>
</tr>
<tr>
<td>bs2</td>
<td>0.29</td>
<td>0.81</td>
<td>41.3</td>
<td>1116</td>
</tr>
<tr>
<td>bs5</td>
<td>0.24</td>
<td>1.34</td>
<td>33.7</td>
<td>944</td>
</tr>
<tr>
<td>ba240</td>
<td>0.7</td>
<td>1.96</td>
<td>15.6</td>
<td>1224</td>
</tr>
<tr>
<td>ba0</td>
<td>0.81</td>
<td>2.27</td>
<td>14.55</td>
<td>11300</td>
</tr>
</tbody>
</table>
PS phase while NC2 close to the PVME rich phase can be obtained from plotting 1- \((W_{ps})^{-1/3.75}\) against dose. The value of NC1, NC2 and NCi as a function of dose calculation from the above described method are given in Table 6.

The variations of spinodal decomposition temperature with radiation dose which were predicted from eqn (1) and using the results shown in Table 6 are given in Table 7.

These results indicate that as it is expected increasing the irradiation dose results in decreasing the extent of cross-link density in the interphase which will, in turn, lead to increasing spinodal decomposition temperature. These predicted results are in good agreement with the experimental results measured by using cloud point method. These results suggest that irradiation process can play a significant role in stabilization of these blends morphology through immobilization of interphase resulting from copolymerization and/or cross-linking.

The optical micrograph shown in Figure 9 compares the morphology of a 50 kGy irradiated PS/PVME blend sample before and after annealing. These results indicate that, although, the PVME dispersed phase size becomes smaller as a result of annealing induced interdiffusion, the nature of matrix disperse morphology of the blend is preserved. These results support the role of the irradiation on morphology stabilization of sample

**Table 5.** PS Weight fraction in each rich phase.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Wps</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVME rich</td>
</tr>
<tr>
<td>1.25</td>
<td>-0.072</td>
</tr>
<tr>
<td>5</td>
<td>0.198</td>
</tr>
<tr>
<td>7.5</td>
<td>0.073</td>
</tr>
</tbody>
</table>

**Table 6.** Interphase cross-link density.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>NC1</th>
<th>NC2</th>
<th>NCi</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8822</td>
<td>8244</td>
<td>8537</td>
</tr>
<tr>
<td>25</td>
<td>3407</td>
<td>3184</td>
<td>3297</td>
</tr>
<tr>
<td>50</td>
<td>2008</td>
<td>1876</td>
<td>1943</td>
</tr>
<tr>
<td>100</td>
<td>1004</td>
<td>938</td>
<td>971</td>
</tr>
<tr>
<td>150</td>
<td>669</td>
<td>625</td>
<td>647</td>
</tr>
<tr>
<td>200</td>
<td>502</td>
<td>469</td>
<td>485</td>
</tr>
</tbody>
</table>

**Table 7.** Spinodal temperature \(T_s, ^\circ C\) as function of dose.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>142</td>
<td>141</td>
</tr>
<tr>
<td>25</td>
<td>145</td>
<td>146</td>
</tr>
<tr>
<td>50</td>
<td>149</td>
<td>151</td>
</tr>
<tr>
<td>100</td>
<td>160</td>
<td>162</td>
</tr>
<tr>
<td>150</td>
<td>165</td>
<td>166</td>
</tr>
<tr>
<td>200</td>
<td>182</td>
<td>180</td>
</tr>
</tbody>
</table>

**Figure 9.** Irradiated phase separated blend (dose 50 kGy): (a) before annealing at 120°C; (b) after annealing at 120°C.
The phase separation rate of PS/PVME solution blend measured as an average size of separated domain was found to be a power law type function of separation time with an exponent 0.77. The value of interphase thickness growth rate of this blend calculated is based on the fractional interdiffusion volume fraction \( (\nu_{ip}) \) and it was found to be about 3.5 nm.min\(^{-1}\), which was in agreement with that reported by some other researchers.

The results obtained from gel content measurement performed on the irradiated two-phase cast blend samples suggested that decreasing of interphase cross-link density as a result of increasing the irradiation dose can lead to elevating the spinodal decomposition temperature. This suggested that irradiation process can play a significant role in stabilization of PS/PVME blend morphology through immobilization of interphase resulting from copolymerization and/or cross-linking. It was also found that 100 kGy dose was the minimum required dose for stabilizing the morphology.

**REFERENCES**