CHAPTER V - MELT FLOW BEHAVIOUR AND EXTRUDATE MORPHOLOGY OF NR-EVA BLENDS.

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(1) Polymer Engineering and Science

Melt flow studies of polymers are of paramount importance in optimising the processing conditions and in designing processing equipments such as extruders injection moulding machines and dies required for various products. Therefore the viscosity functions of a polymer i.e., the shear viscosity as a function of shear rate or shear stress and temperature have become more and more important. A large number of indepth studies have been reported on the melt flow behaviour of elastomers and their blends. Several studies have also been reported on die swell, melt fracture and deformation of extrudates.

The properties of polymer blends depend on their morphology. During the last few years, several studies have been reported on the morphology-property relationship of polymer blends. The existence of phenomena such as segregation and stratification during extrusion of the heterogeneous polymer blends has been established through morphological studies. Since NR-EVA blends find applications in products such as cables, tubing and hoses, studies on the flow characteristics and the extrudate morphology of these blends become very important.

This chapter of the thesis presents the results of the studies on the melt flow behaviour and extrudate morphology of NR-EVA blends. The melt flow characteristics such as viscosity, flow behaviour index, melt elasticity and deformation of the extrudates
have been studied with special reference to the effects of blend ratio, crosslinking system, temperature and shear stress. The elastic parameters such as principal normal stress difference, recoverable shear strain and shear modulus were calculated. The extrudate morphology of the blends has been studied as a function of blend ratio and shear rates. The experimental techniques for assessing the rheological characteristics and extrudate morphology are given in Chapter II.

V.1 EFFECT OF BLEND RATIO AND SHEAR STRESS ON VISCOSITY

The effect of blend ratio and shear stress on the viscosity of uncrosslinked NR-EVA blends at 120°C is shown in Figures V.1a and V.1b. It can be seen that the viscosity of all the blends decreased with increase in shear stress, indicating pseudoplastic behaviour. The pseudoplastic behaviour is due to the fact that at zero shear the molecules are extensively entangled and randomly oriented. Under the application of shear, the molecules become oriented and get disentangled, as a result of which the viscosity decreases.

It is interesting to note that at low shear stress region ($< 3 \times 10^5$ Pa), when EVA content is less than 50 per cent (Figure V.1a), the viscosity of the blends is a non-additive function. NR exhibits slightly higher viscosity than EVA and the viscosity of the blends is higher than that of the components. This is clear
from Figure V.2 where the apparent viscosity of the blends at a low and high shear rate is plotted as a function of the weight percent of EVA. It can be seen that this phenomenon is observed only at a lower shear region and also at lower proportions of the EVA phase where it formed the dispersed phase in the continuous NR matrix. The non-additive nature in the viscosity function of NR-EVA blends at the low shear stress region can be explained as follows.

At low shear stress region, there would be little deformation of the EVA domains and strong interactions among domains can be expected. Therefore, such a state of interaction can give rise to structural build up of EVA domains in the NR matrix. This can lead to a bulk viscosity greater than that of the constituent components. As the level of shear stress is increased, the structure breaks down and the chances of interactions between the domains are reduced. Some support for such a model can be drawn from the scanning electron micrograph (Figure V.3) of 20:80 EVA:NR blend, extruded at a low shear rate. The figure shows aggregates of EVA domains resting on the NR surface. It is also important to note that the increase in viscosity at low shear stress region is more pronounced at lower proportion of EVA in the blend (Figure V.2) where the domain size is minimum. This is due to the fact that smaller domains give rise to strong structure build up and as the proportion of EVA increases, the domain size increases and it tends to become a continuous phase. It is seen that when the EVA phase becomes fully
continuous, the anomaly disappears completely (Figure V.1b). This sort of positive deviation in the viscosity of polymer blends has been reported by many researchers.  

V.2 EFFECT OF CROSSLINKING SYSTEM ON VISCOSITY

The viscosity of NR-EVA blends containing three vulcanising systems, namely sulphur, peroxide and a mixed one, at different shear stress is given in Figures V.4, V.5(a6b) and V.6(a6b), respectively. Since the experiment was conducted at 120°C, no cross-linking reaction is expected to take place during extrusion. Therefore, the flow behaviour of these compounds are similar to those of unvulcanised blends. However, slight variation is observed in certain cases due to the presence of compounding ingredients.

V.3 EFFECT OF PRECIPITATED SILICA ON VISCOSITY

The effect of precipitated silica (INSIL VN₃) on the viscosity of NR-EVA blends at three apparent shear rates is shown in Figure V.7. It is seen that the filled systems exhibit higher viscosity than the pure polymers at all shear rates. This is an expected trend in silica filled systems since it has good physico-chemical interaction with the polymers. The decrease in viscosity at high shear rates is due to the orientation of polymer chains in the direction of shear. In the presence of filler this alignment becomes more restricted. Therefore, the viscosity increases as filler loading increases.
V.4 EFFECT OF TEMPERATURE ON VISCOSITY

Figure V.8 illustrates the effect of temperature on the viscosity of NR-EVA blends at different shear rates. As expected, the viscosity decreased with the increase of temperature for all the blends. However, at low shear rate region, the decrease in viscosity is more predominant than that at high shear rate. It is also noticed that temperature has only marginal effect on viscosity whereas the effect of shear rate on viscosity is substantial as seen from Figure V.8.

In order to further understand the influence of temperature on the viscosity of the blends, Arrhenius plots at a constant shear rate were made (Figure V.9). In this figure, the logarithm of viscosity is plotted as a function of reciprocal temperature. It can be noticed that the points for all the systems lie on straight lines. The activation energies of flow, calculated from the slopes of these lines are given in Table V.1. The activation energy of a material provides valuable information on the sensitivity of the material towards the change in temperature. The higher the activation energy, the more temperature sensitive the material will be. Such information is highly useful in selecting the processing temperature during the shaping process. It can be noticed from Table V.1 that EVA has the maximum value of activation energy and that it is unaffected by the addition of small quantities of NR where it remained as
domains. However, when the proportion of NR in the blend is more than 40 per cent, where it formed a continuous phase, the activation energy decreased sharply. Therefore, it can be concluded that the viscosity of EVA rich blends exhibits greater temperature dependence than those blends having a higher proportion of NR.

V.5 FLOW BEHAVIOUR INDEX ($n'$)

The effect of temperature and blend ratio on the flow behaviour indices of the samples can be assessed from the data given in Table V.2. The extent of non-Newtonian behaviour of polymeric materials can be understood from $n'$ values. Pseudoplastic materials are characterised by $n'$ below 1. Therefore a high value of $n'$ shows a low pseudoplastic nature of the material. The results indicate that as the proportion of EVA in the blend is increased, $n'$ values are increased. It can also be noted that in all cases, $n'$ values increased with the increase of temperature and this effect is predominant in the case of pure EVA and high EVA blends. Therefore, it can be concluded that pseudoplastic nature of NR-EVA blends decreased with temperature and that the high EVA blends are less pseudoplastic than low EVA blends.

The effect of addition of filler on the $n'$ value is given in Table V.3. The results show that in all cases, increase of filler loading decreased the $n'$ values. However, the decrease is pronounced in the case of high EVA blends. This is due to the fact that silica has more affinity towards the EVA phase.
V.6 MELT ELASTICITY

Properties such as extrudate swell, principal normal stress difference ($\tau_{11} - \tau_{22}$), recoverable shear strain ($S_R$) and elastic shear modulus ($G$) characterise the elasticity of polymer melts.

The principal normal stress difference ($\tau_{11} - \tau_{22}$) was calculated from the extrudate swell values and shear stress according to Tanner's equation:

$$\tau_{11} - \tau_{22} = 2\tau_w [2(\frac{d_e}{d_c}) - 2]^{1/2}$$

Recoverable shear strain ($S_R$) and the apparent shear modulus ($G$) were calculated from the following equations:

$$S_R = \frac{(\tau_{11} - \tau_{22})}{2\tau_w}$$

$$G = \frac{\tau_w}{S_R}$$

V.6.1 Extrudate swell

As molten polymer flows through the capillary, orientation of polymer chains occurs due to shear. When the melt emerges from the die, polymer molecules tend to recoil leading to the phenomenon of die swell or extrudate swell. This is a relaxation imposed in the capillary. Factors such as chain branching, stress relaxation,
crosslinking, presence of fillers and plasticizers etc. control the elastic recovery. Table V.4 shows the die swell values of uncross-linked NR-EVA blends extruded at 120°C at two shear rates. It can be noticed that EVA shows the lowest die swell due to its low elastic recovery and the addition of NR increases the die swell of the blend. It can also be noted that for a given blend, die swell increased with shear rate. This is due to the fact that at high shear rates, the residence time of the material in the capillary decreases and hence more elastic energy is stored by the polymer. This results in an increase in die swell. The die swell values of silica filled blends containing mixed cure system, extruded at 120°C at an apparent shear rate of 3330 s⁻¹ are given in Table V.5. It is seen that, in general, die swell decreased with filler loading. Silica filler increases the rigidity and stiffness of the polymer chain. This results in low mobility of the polymer chains under the influence of applied shear stress. Hence the elastic recovery and consequently die swell decrease with the increase of filler loading.

V.6.2 Deformation of extrudates

Figure V.10 shows the photograph of the blends extruded at two different shear rates. At low shear rate most of the extrudates have smooth surfaces. However, at high shear rates, extrudate surfaces exhibit different extent of distortion. These extrudates have rough surfaces and are of non-uniform diameter.
This is associated with melt fracture which occurs at high shear forces where the shear stress exceeds the strength of the melt. The effect of silica filler on the deformation of the crosslinkable extrudate can be understood from Figure V.11. It is seen that the addition of silica decreased the deformation of the extrudates.

V.6.3 **Principal normal stress difference** \( (\tau_{11} - \tau_{22}) \)

Table V.6 shows the principal normal stress difference of uncrosslinked blends extruded at low and high shear rates. The temperature of extrusion was 120°C. EVA showed the lowest value of principal normal stress difference. Addition of NR increased the normal stress difference of EVA. The principal normal stress difference increased with the increase of shear rates. The higher value of \( \tau_{11} - \tau_{22} \) implies higher elasticity of the blends. This is reflected in higher die swell values also.

V.6.4 **Recoverable elastic shear stress** \( (S_R) \)

It has been reported\(^{115}\) that when the stored elastic strain energy of a polymer melt exceeds a critical value, the excess amount may be converted into surface free energy yielding distortion to the extrudate. Table V.6 shows the \( S_R \) values of the blends at two different shear rates. It is seen that \( S_R \) increases with the increase of shear rates. This is related to the extent of extrudate distortion of the blends (Figure V.10). At low and high shear rates, the \( S_R \)
values of the blends increase with the increase of NR content.

V.6.5 Elastic shear modulus (G)

The elastic shear modulus of the blends as shown in Table V.6 indicated that the melt elasticity of EVA is increased by the addition of NR. The elastic shear modulus increased with the increase of shear rate, especially in the case of blends containing a higher proportion of EVA.

V.7 EXTRUDATE MORPHOLOGY

The factors such as component ratio, their melt viscosity, rate of shear during melt mixing and presence of other ingredients such as lubricants, extenders, plasticizers, fillers etc. control the final morphology of the polymer blends. Danesi and Porter\textsuperscript{22} have reported that for the same processing history, the composition of the blend and the melt viscosity difference determine the morphology. Figure V.12a gives the core region of the extrudate of 80:20 EVA:NR blend extruded at a shear rate of 330 s\textsuperscript{-1}. The holes in the surface correspond to the NR phase which had been extracted by benzene. It is quite evident that the NR phase exists as domains in the continuous EVA matrix. The average domain size measured from the photograph was 14.5 \textmu m. The dispersed nature of the NR phase is associated with its lower proportion and slightly higher viscosity than EVA. Figure V.12b shows the morphology of the core region
of the same composition (80:20 EVA:NR) extruded at a shear rate of 3330 s⁻¹. It is interesting to note that the particle size has been considerably reduced at a high shear rate. The measured particle size was 7.8 µm. Figure V.12c shows a clear demarcation between periphery of the extrudate which is occupied mostly by EVA phase and the centre by NR phase.

Figures V.13 and V.14 show the morphology of the blends of 30:70 and 40:60 NR:EVA, respectively, extruded at a shear rate of 330 s⁻¹. In these blends also, it can be seen that NR phase is dispersed as domains at the core of the extrudate which is surrounded by an EVA sheath. The size of the NR domain is considerably higher. A further increase in the proportion of NR to 50 per cent makes the two phases co-continuous. This is seen from the photomicrograph of core region of 50:50 NR:EVA blend extruded at a shear rate of 330 s⁻¹ (Figure V.15). A clear phase inversion can be seen from the morphology of 70:30 NR:EVA extruded at a shear rate of 330 s⁻¹ (Figure V.16). It is interesting to note that the aggregates of EVA domains having size of 24 µm are resting on the NR surface. From the above observations it can be concluded that the morphology of NR-EVA blends exhibits a two phase structure in which the minor component is dispersed as domains in the continuous phase of the major component. However, at 50:50 composition both the components exist as continuous phases.
The stratification (division into periphery and core) of the extrudate may be associated with the migration of the low viscosity EVA phase towards the periphery of the extrudates and the resulting encapsulation of the high viscosity NR phase. The stratification phenomenon has been reported in the case of binary polymer blends by many researchers. These include the studies of Yu and Han, Southern and Ballman, Danesi and Porter, and Thomas et al. All these authors concluded that the differences in shear viscosity between the components lead to interphase distortion, with the lower viscosity component encapsulating the high viscosity component.

The decrease in domain size with the increase of shear rate is associated with particle break down. During extrusion, the dispersed domains are elongated at the entrance of the capillary under the action of shear force. At sufficiently high shear forces, the elongated domains are broken down into small particles. However, under low shear forces, the elongated domains retain their morphology and are not broken down into smaller sizes.

Finally, the increase of NR domain size with increasing concentration of NR phase is associated with recombination and coalescence of the dispersed domains. The occurrence of coalescence at high concentration of one of the components in a binary blend has been reported. Thomas et al. have reported similar phenomenon in the case of hytrel-PVC blends.
Table V.1. Activation energy.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Blend ratio (NR:EVA)</th>
<th>E x 10^{-3} (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>90:10</td>
<td>0.4145</td>
</tr>
<tr>
<td>C</td>
<td>80:20</td>
<td>0.4606</td>
</tr>
<tr>
<td>D</td>
<td>70:30</td>
<td>0.5066</td>
</tr>
<tr>
<td>E</td>
<td>60:40</td>
<td>0.5066</td>
</tr>
<tr>
<td>F</td>
<td>50:50</td>
<td>0.6440</td>
</tr>
<tr>
<td>G</td>
<td>40:60</td>
<td>0.8751</td>
</tr>
<tr>
<td>H</td>
<td>30:70</td>
<td>0.9212</td>
</tr>
<tr>
<td>I</td>
<td>20:80</td>
<td>0.9212</td>
</tr>
<tr>
<td>J</td>
<td>0:100</td>
<td>0.9212</td>
</tr>
</tbody>
</table>
Table V.2. Flow behaviour index ($n'$)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$120^\circ C$</th>
<th>$170^\circ C$</th>
<th>$180^\circ C$</th>
<th>$190^\circ C$</th>
<th>$200^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.165</td>
<td>0.195</td>
<td>0.220</td>
<td>0.220</td>
<td>0.237</td>
</tr>
<tr>
<td>B</td>
<td>0.171</td>
<td>0.208</td>
<td>0.221</td>
<td>0.230</td>
<td>0.244</td>
</tr>
<tr>
<td>C</td>
<td>0.183</td>
<td>0.208</td>
<td>0.238</td>
<td>0.261</td>
<td>0.354</td>
</tr>
<tr>
<td>D</td>
<td>0.188</td>
<td>0.218</td>
<td>0.240</td>
<td>0.270</td>
<td>0.360</td>
</tr>
<tr>
<td>E</td>
<td>0.194</td>
<td>0.239</td>
<td>0.248</td>
<td>0.275</td>
<td>0.376</td>
</tr>
<tr>
<td>F</td>
<td>0.223</td>
<td>0.245</td>
<td>0.270</td>
<td>0.280</td>
<td>0.382</td>
</tr>
<tr>
<td>G</td>
<td>0.233</td>
<td>0.309</td>
<td>0.303</td>
<td>0.314</td>
<td>0.398</td>
</tr>
<tr>
<td>H</td>
<td>0.245</td>
<td>0.327</td>
<td>0.362</td>
<td>0.358</td>
<td>0.437</td>
</tr>
<tr>
<td>I</td>
<td>0.296</td>
<td>0.358</td>
<td>0.360</td>
<td>0.415</td>
<td>0.439</td>
</tr>
<tr>
<td>J</td>
<td>0.289</td>
<td>0.371</td>
<td>0.436</td>
<td>0.452</td>
<td>0.484</td>
</tr>
</tbody>
</table>
Table V.3. Effect of silica on flow behaviour index of NR-EVA blends.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Silica loading, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>0.166</td>
</tr>
<tr>
<td>C</td>
<td>0.198</td>
</tr>
<tr>
<td>E</td>
<td>0.239</td>
</tr>
<tr>
<td>F</td>
<td>0.249</td>
</tr>
<tr>
<td>G</td>
<td>0.282</td>
</tr>
<tr>
<td>I</td>
<td>0.318</td>
</tr>
<tr>
<td>J</td>
<td>0.344</td>
</tr>
</tbody>
</table>

- : 98 :-
Table V.4. Extrudate swell of uncrosslinked NR-EVA blends, at 120°C.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Apparent shear rate, s(^{-1}) 3330</th>
<th>330</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.46</td>
<td>1.19</td>
</tr>
<tr>
<td>B</td>
<td>1.61</td>
<td>1.43</td>
</tr>
<tr>
<td>C</td>
<td>1.46</td>
<td>1.35</td>
</tr>
<tr>
<td>D</td>
<td>1.40</td>
<td>1.26</td>
</tr>
<tr>
<td>E</td>
<td>1.36</td>
<td>1.26</td>
</tr>
<tr>
<td>F</td>
<td>1.26</td>
<td>1.25</td>
</tr>
<tr>
<td>G</td>
<td>1.26</td>
<td>1.24</td>
</tr>
<tr>
<td>H</td>
<td>1.25</td>
<td>1.23</td>
</tr>
<tr>
<td>I</td>
<td>1.24</td>
<td>1.23</td>
</tr>
<tr>
<td>J</td>
<td>1.08</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Table V.5. Effect of silica on die-swell values of crosslinkable (mixed) NR-EVA blends extrudated at 3330 s⁻¹.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Silica loading, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>A₃S</td>
<td>1.07</td>
</tr>
<tr>
<td>C₃S</td>
<td>1.07</td>
</tr>
<tr>
<td>E₃S</td>
<td>1.06</td>
</tr>
<tr>
<td>F₃S</td>
<td>1.35</td>
</tr>
<tr>
<td>G₆S</td>
<td>1.35</td>
</tr>
<tr>
<td>I₃S</td>
<td>1.35</td>
</tr>
<tr>
<td>J₃S</td>
<td>1.08</td>
</tr>
</tbody>
</table>
Table V.6. Melt elasticity of NR-EVA blends extruded at 120°C.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Shear rate 330 s(^{-1})</th>
<th>Shear rate 3330 s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\frac{\tau_{11}}{\tau_{22}})</td>
<td>(G)</td>
</tr>
<tr>
<td>B</td>
<td>23.98×10^5</td>
<td>0.80×10^5</td>
</tr>
<tr>
<td>C</td>
<td>18.47×10^5</td>
<td>0.94×10^5</td>
</tr>
<tr>
<td>D</td>
<td>14.06×10^5</td>
<td>1.17×10^5</td>
</tr>
<tr>
<td>E</td>
<td>13.66×10^5</td>
<td>1.14×10^5</td>
</tr>
<tr>
<td>F</td>
<td>12.68×10^5</td>
<td>1.15×10^5</td>
</tr>
<tr>
<td>G</td>
<td>12.41×10^5</td>
<td>1.18×10^5</td>
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<tr>
<td>H</td>
<td>12.02×10^5</td>
<td>1.22×10^5</td>
</tr>
<tr>
<td>I</td>
<td>12.01×10^5</td>
<td>1.22×10^5</td>
</tr>
<tr>
<td>J</td>
<td>3.35×10^5</td>
<td>4.38×10^5</td>
</tr>
</tbody>
</table>
Figure V.1a
Viscosity-shear stress plots of uncrosslinked NR-EVA blends at 120°C.
Figure V.1b
Viscosity-shear stress plots of uncrosslinked NR-EVA blends at 120°C.
Figure V.2
A plot of viscosity vs EVA content at low and high shear rates, at 120°C.
Figure V.3
SEM Photomicrograph of blend C, aggregates of EVA domains resting on NR surface.
Figure V.4: Viscosity-shear stress plots of NR-EVA blends containing sulphur cure system, at 120°C.
Figure V.5a
Viscosity-shear stress plots of NR-EVA blends containing peroxide cure system, at 120°C.
Figure V.5b
Viscosity-shear stress plots of NR-EVA blends containing peroxide cure system, at 120°C.
Figure V.6a
Viscosity-shear stress plots of NR-EVA blends containing mixed cure system, at 120°C.
Figure V.6b
Viscosity-shear stress plots of NR-EVA blends containing mixed cure system, at 120°C.
Figure V.7
Effect of EVA content and shear rate on apparent shear viscosity of NR-EVA blends having different silica content.
Figure V.8
Effect of temperature and shear rate on the apparent shear viscosity of NR-EVA blends.
Figure V.9
A plot of log $\gamma$ versus reciprocal of temperature.
Figure V.10
Effect of shear rate and blend ratio on deformation of extrudates.
Figure V.11
Effect of blend ratio and silica content on the deformation of the extrudates.

Figure V.12a
Morphology of blend I extruded at a shear rate of 330 s⁻¹, showing larger particle size.
Figure V.12b
Morphology of blend I extruded at a shear rate of 3330 s⁻¹, showing lower particle size.

Figure V.12c
Periphery and core structure of blend I.

Figure V.13
SEM Photomicrograph of blend II extruded at a shear rate of 330 s⁻¹.
Figure V.14
SEM Photomicrograph of blend \( G \) extruded at a shear rate of \( 330 \text{ s}^{-1} \).

Figure V.15
SEM Photomicrograph of blend \( F \) extruded at a shear rate of \( 330 \text{ s}^{-1} \).

Figure V.16
SEM Photomicrograph of blend \( D \) extruded at a shear rate of \( 330 \text{ s}^{-1} \).