CHAPTER VIII - EFFECT OF BLEND RATIO AND FILLERS ON THE CELL STRUCTURE AND PROPERTIES OF MICROCELLULAR SOLES FROM NR-EVA BLENDS.

The results included in this chapter have been accepted for presentation at the International Natural Rubber Conference, scheduled for 5-8 February 1992, Bangalore, India.
Various types of polymers and their blends are used in footwear to achieve specific combination of properties such as light weight, wearing comfort, stiffness and durability. Conventionally a blend of natural rubber (NR) or styrene-butadiene (SBR) with high styrene resin (SBR 1958) is used for making microcellular soles. Supply of styrene for the production of SBR is reported to be decreasing\textsuperscript{126}. Attempts have been going on to develop a substitute for SBR 1958 in footwear application. A promising alternative for SBR 1958 in microcellular soles appears to be ethylene-vinyl acetate copolymer (EVA), which possesses an overall balance of properties.

This chapter discusses the effect of blend ratio and fillers on the mechanical properties of microcellular soles based on NR-EVA blends. Scanning electron microscopic observations were made on microcellular sheets to study the variation in cell structure with blend ratio and type of filler. The details of the experimental procedures adopted for studying the mechanical properties and for scanning electron microscopic observations are given in Chapter II.

For preparing microcellular sheets, blends having NR:EVA ratios 50:50, 40:60, 30:70, 20:80 and 0:100 were used. These blends are designated as F, G, H, I and J, respectively (Table VIII.1). The effect of fillers was evaluated in blend G only. This was because, for DCP cured NR-EVA blends, better technological properties were shown by those blends which contained a higher proportion of EVA.
(Chapter III). The concentration of blowing agent was varied so as to get the same expansion for the microcellular sheets prepared from various blends. Linear expansion of the sheets before post-curing was controlled to about 100 per cent of the mould dimensions.

VIII.1 CELL STRUCTURE

VIII.1.1 Effect of blend ratio on cell structure

Figures VIII.1 to VIII.5 are the photomicrographs of the cut edges of the microcellular sheets prepared from blends F to J, respectively, as seen under a scanning electron microscope. From these figures, it is evident that as the proportion of EVA in the blend is increased, the size of the cells becomes larger and the cells attain a more uniform structure. The larger cell size of the EVA rich blends is due to the lower melt viscosity of such blends which facilitates increased blowing with unit weight of the blowing agent. The non-uniformity of the cells in those blends in which the proportion of EVA is reduced can be due to the non-uniform distribution of blowing agent between EVA and NR phases. In the NR phase, distribution of the blowing agent can be less due to its non-polar nature. But the dispersion of the blowing agent in this phase will be better since the viscosity of the blend increases as the proportion of NR is increased. This will lead to smaller size for the cells formed in such blends. The non-uniformity in cell structure of such blends can also be due to the difference in extents of blowing of the two phases.
VIII.1.2 **Effect of filler on cell structure**

Figure VIII.6 is the photomicrograph of the microcellular sheet in which china clay was used as the filler. Comparing with figure VIII.2, which contained the same loading of precipitated calcium carbonate, it is seen that the china clay filled compound gave a slightly larger cell size. The uniformity of cell structure is almost identical. From the rheographs of calcium carbonate and china clay loaded compounds it is seen that the compound containing the former has a higher viscosity (Figure VIII.7). Hence in this compound the blowing agent will be more finely dispersed which will result in smaller cell size for the expanded sheet.

VIII.2 **PHYSICAL PROPERTIES**

VIII.2.1 **Relative density and shrinkage**

The relative density decreased with increase in EVA content and the extent of decrease was higher when EVA content increased from 50 to 70 per cent (Figure VIII.8). Further increase of EVA content did not cause any appreciable change in relative density. But shrinkage of microcellular sheets showed steady increase with increase in proportion of EVA in the blend. In microcellular soles, shrinkage that occur on post-curing or long term storage is due to loss of gases by diffusion process. The larger cell size and reduced wall thickness of the cells facilitate diffusion of gases from blends.
having higher proportions of EVA. The combined effects of high permeability and faster diffusion of gases in high EVA blends are reflected in higher shrinkage of such blends.

VIII.2.2 Hardness and compression set

Hardness of the microcellular soles decreased and the compression set increased with increase in EVA content (Figure VIII.9). The increase in compression set is due to the residual thermoplastic nature of EVA.

VIII.2.3 Abrasion loss and split tear

The increase of EVA content in the blend enhanced the abrasion resistance and split tear strength of the microcellular sole (Figure VIII.10). These two properties are very important as far as the service life of the product is concerned. The factors which contribute to the improvement in these properties are uniform cell structure of the sole having higher proportion of EVA and the crystalline nature of EVA. Uniform cell structure helps to take up higher loads by equal distribution of the applied force. Crystalline regions in EVA impart high tear resistance to the product by arresting/diverting the propagation of the tear path.

VIII.2.4 Effect of filler on properties

The effects of china clay and precipitated calcium carbonate
on the physical properties of the microcellular soles were evaluated by varying the filler content. All other ingredients, including the blowing agent were kept at the same dosage as that for compound G, except the oil content which was varied in proportion to the filler level. Diethylene glycol (DEG) was added in those compounds which contained china clay as the filler.

Figure VIII.11 shows the effect of loading of china clay and calcium carbonate on expansion of the moulded sheets. Filler loading reduced the expansion of the sheets and this effect was almost identical for both the fillers. However, calcium carbonate showed better expansion ratio than clay. Compression set of the microcellular sheets increased with filler loading (Figure VIII.12). In this case, the behaviour of both the fillers are almost identical. However, calcium carbonate showed comparatively lower set. The split tear strength (Figure VIII.13) was also better for the calcium carbonate loaded sheets. But the relative increase in split tear with loading was less for calcium carbonate loaded microcellular sheets. Figure VIII.14 shows the effect of filler on shrinkage of expanded sheets. Shrinkage was more for the calcium carbonate loaded compounds at higher filler loadings. This is due to the fact that these sheets had higher expansion ratios compared with clay loaded samples. However, at 45 phr level, the calcium carbonate loaded compound showed lower shrinkage. Hardness (Figure VIII.15) and relative density (Figure VIII.16) also increased with filler loading. Both
these properties were lower for the sheets containing calcium carbonate since these sheets had higher expansion than those containing china clay. Abrasion loss decreased with increase in filler loading (Figure VIII.17). But in this case, calcium carbonate loaded sheets showed higher abrasion loss than china clay loaded samples. Comparatively less increase in split tear and higher abrasion loss of the calcium carbonate loaded sheets is due to higher expansion of the sheets. These two properties depend very much on the strength of the matrix. When expansion is higher, the actual volume of the matrix to take up the load will be lower.

FORMULATION OF COMPOUND MEETING BIS SPECIFICATIONS

With an understanding of the changes in properties with blend ratio and filler loading, a formulation which can yield microcellular sheets that meet Bureau of Indian Standard specifications for Hawai sheets, was developed. The formulation developed and the properties of the sheets prepared using the same are given in Tables VIII.1 and VIII.2, respectively.
Table VIII:1. Formulation to meet BIS specifications.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer (blend consisting of 40% NR and 60% EVA)</td>
<td>100.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>2.0</td>
</tr>
<tr>
<td>Styrenated phenol type of antioxidant</td>
<td>1.0</td>
</tr>
<tr>
<td>Dicumyl peroxide*</td>
<td>4.0</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>90.0</td>
</tr>
<tr>
<td>Paraffinic oil</td>
<td>3.6</td>
</tr>
<tr>
<td>Azodicarbonamide</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*40 per cent active.
Table VIII.2. Physical properties.

<table>
<thead>
<tr>
<th></th>
<th>NR-EVA</th>
<th>BIS Specifications limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Relative density</td>
<td>0.45</td>
<td>0.4 to 0.5</td>
</tr>
<tr>
<td>2. Hardness (Shore A)</td>
<td>46.0</td>
<td>45±5</td>
</tr>
<tr>
<td>3. Change in hardness after ageing at 100°C for 24 hours</td>
<td>+2</td>
<td>+5</td>
</tr>
<tr>
<td>4. Split tear strength (N)</td>
<td>53</td>
<td>50</td>
</tr>
<tr>
<td>5. Shrinkage, 100±1°C, 1 h (%)</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>6. Flex resistance: Kilocycles to crack initiation</td>
<td>&lt;400</td>
<td>&lt;60</td>
</tr>
<tr>
<td>7. DIN abrasion loss 5 N load (mm³)</td>
<td>440</td>
<td>--</td>
</tr>
<tr>
<td>8. Compression set (%)</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>9. Room temperature shrinkage at 27°C for 2 weeks (%)</td>
<td>1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Figure VIII.1
Photomicrograph of NR:EVA (50:50) blend.

Figure VIII.2
Photomicrograph of NR:EVA (40:60) blend.

Figure VIII.3
Photomicrograph of NR:EVA (30:70) blend.
Figure VIII.4
Photomicrograph of NR:EVA (20:80) blend.

Figure VIII.5
Photomicrograph of NR:EVA (0:100) blend.

Figure VIII.6
Photomicrograph of NR:EVA (40:60) clay filled blend.
Figure VIII.7
Rheographs of calcium carbonate and china clay filled compounds.

Arc 3°
Chart motor 30 min
Range Sel: 50
Temp 160°C

TORQUE, dNm

TIME, MINUTES

CaCO₃ Filled
Clay filled
Figure VIII.8
Variation of relative density and shrinkage with EVA content.
Figure VIII.9
Variation of hardness and compression set with EVA content.
Figure VIII.10
Variation of abrasion loss and split tear strength with EVA content.
Figure VIII.11
Effect of china clay and calcium carbonate on expansion.
Figure VIII.12
Effect of china clay and calcium carbonate on compression set.
Figure VIII.13
Effect of china clay and calcium carbonate on split tear strength.
Figure VIII.14
Effect of china clay and calcium carbonate on shrinkage.
Figure VIII.15
Effect of china clay and calcium carbonate on hardness.
Figure VIII.16
Effect of china clay and calcium carbonate on relative density.
Figure VIII.17
Effect of china clay and calcium carbonate on abrasion loss.
SUMMARY AND CONCLUSIONS