CHAPTER VI

THERMAL CONDUCTIVITY OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES
VI THERMAL CONDUCTIVITY OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES

Natural rubber is considered as a poor conductor of heat and electricity. With the exception of a few items, all rubber products have to undergo the process of vulcanisation during manufacture. Vulcanisation is effected by heating the rubber compound at higher temperature. Due to its poor heat conductivity, a thick article takes a very long time to get its centre portion vulcanised, during which the surface gets degraded. Several methods have been adopted to get an even cure of thick articles. These included microwave heating [1], use of heat resistant efficient vulcanisation systems [2], use of delayed action accelerators [3] use of retarders [4], two stage heating, etc. It is known that use of fillers such as carbon blacks and zinc oxide improves the thermal conductivity of rubber compounds to a certain extent [5]. However, even rubber compounds containing a good amount of carbon black are to be heated for very long periods to vulcanise thick articles such as rubber covered rolls, tyre retreads, etc. (2 to 6 hours depending on thickness). Rubber products generate heat due to high frequency flexing during service. Unless the heat generated is dissipated away from inside, it gets accumulated, causing
severe thermal degradation of the polymer. Thus the study of improving thermal conductivity of rubber vulcanisates assumes importance.

Even though a lot of work has been reported on heat transfer and vulcanisation of rubber products [6], studies on thermal conductivity of rubber vulcanisates are very few. The influence of degree of vulcanisation on thermal conductivity has already been reported [7,8]. Studies conducted by Neskoromnyi et al. [9] showed that as the extent of vulcanisation increases, the thermal conductivity decreases. Orientation of polymer chains and dispersion of fillers were also found to have significant effect on thermal conductivity of rubber vulcanisates [5,10]. Several methods have been described to measure thermal conductivity of rubber vulcanisates [11,12]. In this chapter of the thesis, the results of the thermal conductivity measurements of natural rubber vulcanisates containing aluminium powder are presented in comparison with those of HAF and acetylene black-filled vulcanisates. The details of the equipment used for the measurement of thermal conductivity are given in Section II.9.

VI.1 Effect of Fillers on Thermal Conductivity

The effects of quantity of aluminium powder, HAF black and acetylene black on thermal conductivity at 30°C
are shown in Figure VI.1. Among the three fillers aluminium powder showed the highest increase in thermal conductivity at equal volume loading. The straight line graphs obtained indicates almost linear increase in thermal conductivity with loading of aluminium powder. From the slope of the straight lines, the following equations were found good to calculate the thermal conductivity in the range of loading of fillers studied.

\[
y = 0.0185x + 0.167 \text{ for aluminium powder} \quad \ldots (VI.1)
\]

\[
y = 0.008x + 0.167 \text{ for acetylene black} \quad \ldots (VI.2)
\]

\[
y = 0.004x + 0.167 \text{ for HAF black} \quad \ldots (VI.3)
\]

where

\[
y = \text{Thermal conductivity } \lambda \text{ at } 30^\circ C \text{ in w/m.k.}
\]

\[
x = \text{Quantity of filler added in volume per cent.}
\]

The slightly higher values at the third decimal range, obtained by using the above equations (Table VI.1) may be due other variables such as extent of crosslinking and extent of filler dispersion in the vulcanisate. As pointed out earlier, these two factors also affect the thermal conductivity of the rubber vulcanisates and hence the experimental values are slightly less than the calculated values.
Table VI.1  Effect of fillers on thermal conductivity at 30°C (W/m.k)

<table>
<thead>
<tr>
<th>Quantity volume per cent</th>
<th>Aluminium powder</th>
<th>Acetylene black</th>
<th>HAF black</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.255</td>
<td>0.259</td>
<td>0.205</td>
</tr>
<tr>
<td>10</td>
<td>0.350</td>
<td>0.352</td>
<td>0.245</td>
</tr>
<tr>
<td>15</td>
<td>0.443</td>
<td>0.445</td>
<td>0.284</td>
</tr>
<tr>
<td>20</td>
<td>0.531</td>
<td>0.537</td>
<td>0.319</td>
</tr>
</tbody>
</table>

Thermal conductivity of gum vulcanisate is 0.167 W/m.k.

VI.2  Effect of Temperature on Thermal Conductivity

The thermal conductivity of the samples containing different loadings of aluminium powder, HAF black and acetylene black decreased with increase in temperature (Figures VI.2 to VI.4). The decrease was pronounced with increase in filler loading. The change in thermal conductivity of the gum compound was much less compared with the filled samples. Even at a higher temperature of 70°C, the thermal conductivity of the vulcanisates followed the order, aluminium powder > acetylene black > HAF black > gum, at all loadings. The thermal conductivity of the aluminium powder-filled vulcanisates was almost 40 to 50% higher than that of the acetylene black-filled samples at higher loadings of the fillers.
Figure VI.1  Plot of thermal conductivity at 30°C Vs filler loading
Figure VI.2  Plot of thermal conductivity Vs temperature
Figure VI.3  Plot of thermal conductivity Vs temperature
Figure VI.4 Plot of thermal conductivity Vs temperature
VI.3 Effect of Thermal Conductivity on Extent of Crosslinking

The significance of thermal conductivity of rubber compounds is more relevant with the vulcanisation of thick articles. Hence the $V_r$ values of the test pieces taken from the surface and centre of a cube of $5 \times 5 \times 5$ cm$^3$, vulcanised at different intervals of time, were determined for the vulcanisates containing different loadings of these three fillers. These results are presented in Tables VI.2 and VI.3 respectively.

Examination of the data in Table VI.2 indicates that for the gum compound, it takes $t_{90}+12$ minutes (where $t_{90}$ is the optimum cure time taken from the rheograph) to reach the maximum $V_r$ values for the sample taken from the surface. It is reduced to $t_{90}+10$ minutes in the case of sample AL05 and $t_{90}+5$ minutes for the samples containing 10, 15 and 20 volume per cent loadings of aluminium powder. In the case of HAF black-filled vulcanisates, sample HF05 took $t_{90}+12$ minutes and all other samples required only $t_{90}+10$ minutes. In the case of acetylene black-filled samples, it took $t_{90}+12$ minutes for AC05, $t_{90}+10$ minutes for AC10 and, $t_{90}+8$ minutes for AC15 and AC20 samples to attain the maximum $V_r$ values.
Table VI.2  \( V_r \) values of sample taken from the outer surface of the cube

<table>
<thead>
<tr>
<th>Cure time at 150°C</th>
<th>Gun</th>
<th>AL05</th>
<th>AL10</th>
<th>AL15</th>
<th>AL20</th>
<th>HF05</th>
<th>HF10</th>
<th>HF15</th>
<th>HF20</th>
<th>AC05</th>
<th>AC10</th>
<th>AC15</th>
<th>AC20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{90} )</td>
<td></td>
<td>0.149</td>
<td>0.189</td>
<td>0.197</td>
<td>0.201</td>
<td>0.221</td>
<td>0.157</td>
<td>0.163</td>
<td>0.160</td>
<td>0.170</td>
<td>0.153</td>
<td>0.165</td>
<td>0.170</td>
</tr>
<tr>
<td>( t_{90+3} )</td>
<td></td>
<td>0.180</td>
<td>0.190</td>
<td>0.203</td>
<td>0.208</td>
<td>0.228</td>
<td>0.171</td>
<td>0.172</td>
<td>0.173</td>
<td>0.173</td>
<td>0.166</td>
<td>0.170</td>
<td>0.177</td>
</tr>
<tr>
<td>( t_{90+5} )</td>
<td></td>
<td>0.181</td>
<td>0.192</td>
<td>0.207</td>
<td>0.216</td>
<td>0.234</td>
<td>0.177</td>
<td>0.178</td>
<td>0.179</td>
<td>0.180</td>
<td>0.170</td>
<td>0.173</td>
<td>0.180</td>
</tr>
<tr>
<td>( t_{90+8} )</td>
<td></td>
<td>0.184</td>
<td>0.193</td>
<td>0.206</td>
<td>0.216</td>
<td>0.234</td>
<td>0.180</td>
<td>0.184</td>
<td>0.184</td>
<td>0.186</td>
<td>0.176</td>
<td>0.175</td>
<td>0.183</td>
</tr>
<tr>
<td>( t_{90+10} )</td>
<td></td>
<td>0.186</td>
<td>0.195</td>
<td>0.204</td>
<td>0.216</td>
<td>0.229</td>
<td>0.182</td>
<td>0.188</td>
<td>0.189</td>
<td>0.193</td>
<td>0.177</td>
<td>0.178</td>
<td>0.184</td>
</tr>
<tr>
<td>( t_{90+12} )</td>
<td></td>
<td>0.187</td>
<td>0.195</td>
<td>0.202</td>
<td>0.215</td>
<td>0.226</td>
<td>0.184</td>
<td>0.189</td>
<td>0.190</td>
<td>0.193</td>
<td>0.181</td>
<td>0.179</td>
<td>0.183</td>
</tr>
<tr>
<td>( t_{90+15} )</td>
<td></td>
<td>0.187</td>
<td>0.194</td>
<td>0.201</td>
<td>0.209</td>
<td>0.220</td>
<td>0.185</td>
<td>0.199</td>
<td>0.191</td>
<td>0.197</td>
<td>0.179</td>
<td>0.178</td>
<td>0.183</td>
</tr>
</tbody>
</table>
Table VI.3 $V_r$ values of sample taken from inside centre of the cube

<table>
<thead>
<tr>
<th>Cure time at 150°C</th>
<th>Gum</th>
<th>AL05</th>
<th>AL10</th>
<th>AL15</th>
<th>AL20</th>
<th>HF05</th>
<th>HF10</th>
<th>HF15</th>
<th>HF20</th>
<th>AC05</th>
<th>AC10</th>
<th>AC15</th>
<th>AC20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{90}$</td>
<td>0.080</td>
<td>0.178</td>
<td>0.194</td>
<td>0.197</td>
<td>0.215</td>
<td>0.111</td>
<td>0.128</td>
<td>0.120</td>
<td>0.144</td>
<td>0.132</td>
<td>0.158</td>
<td>0.164</td>
<td>0.170</td>
</tr>
<tr>
<td>$t_{90}+3$</td>
<td>0.149</td>
<td>0.189</td>
<td>0.202</td>
<td>0.208</td>
<td>0.227</td>
<td>0.152</td>
<td>0.163</td>
<td>0.151</td>
<td>0.169</td>
<td>0.159</td>
<td>0.167</td>
<td>0.174</td>
<td>0.180</td>
</tr>
<tr>
<td>$t_{90}+5$</td>
<td>0.169</td>
<td>0.191</td>
<td>0.202</td>
<td>0.209</td>
<td>0.230</td>
<td>0.169</td>
<td>0.174</td>
<td>0.166</td>
<td>0.180</td>
<td>0.166</td>
<td>0.171</td>
<td>0.180</td>
<td>0.183</td>
</tr>
<tr>
<td>$t_{90}+8$</td>
<td>0.182</td>
<td>0.192</td>
<td>0.205</td>
<td>0.214</td>
<td>0.230</td>
<td>0.179</td>
<td>0.180</td>
<td>0.176</td>
<td>0.185</td>
<td>0.173</td>
<td>0.174</td>
<td>0.181</td>
<td>0.192</td>
</tr>
<tr>
<td>$t_{90}+10$</td>
<td>0.186</td>
<td>0.193</td>
<td>0.205</td>
<td>0.214</td>
<td>0.226</td>
<td>0.181</td>
<td>0.184</td>
<td>0.187</td>
<td>0.188</td>
<td>0.174</td>
<td>0.179</td>
<td>0.185</td>
<td>0.197</td>
</tr>
<tr>
<td>$t_{90}+12$</td>
<td>0.189</td>
<td>0.194</td>
<td>0.204</td>
<td>0.214</td>
<td>0.225</td>
<td>0.183</td>
<td>0.186</td>
<td>0.188</td>
<td>0.190</td>
<td>0.176</td>
<td>0.179</td>
<td>0.183</td>
<td>0.197</td>
</tr>
<tr>
<td>$t_{90}+15$</td>
<td>0.190</td>
<td>0.197</td>
<td>0.204</td>
<td>0.215</td>
<td>0.222</td>
<td>0.185</td>
<td>0.192</td>
<td>0.191</td>
<td>0.191</td>
<td>0.178</td>
<td>0.179</td>
<td>0.183</td>
<td>0.198</td>
</tr>
</tbody>
</table>
The effect of thermal conductivity is more evident from the $V_r$ values of the samples taken from inside centre of the cube of 5 x 5 x 5 cm$^3$. To get maximum or almost stable $V_r$ values, it took more than $t_{g0}+15$ minutes for the gum, AL05, HF05, HF10, HF15 and AC05 compounds. While compounds containing 10, 15 and 20 volume loadings of acetylene blacks (AC10, AC15 and AC20) took $t_{g0}+10$ minutes, only $t_{g0}+8$ minutes and $t_{g0}+5$ minutes were required for compounds containing 10, 15 and 20 volume per cent loadings of aluminium powder. It is worth mentioning here that as pointed out in Chapter III, $t_{g0}$ values of the aluminium powder-filled compounds were lower than that of the other compounds. This observation clearly indicates that use of aluminium powder reduce the vulcanisation time of thick articles through improvement in thermal conductivity imparted by this filler.

VI.4 Effect of Aluminium Powder on Electrical Resistivity

Usually there exists a correlation between electrical conductivity and thermal conductivity [5]. In order to examine this, vulcanisates containing 10 volume per cent of HAF black, acetylene black and aluminium powder (HF10, AC10 and AL10) were tested for volume resistivity under the application of 500 V DC supply. The volume resistivity values (ohm. cm) obtained were $57 \times 10^4$, $16 \times 10^4$ and $6 \times 10^4$ respectively for HF10, AC10 and AL10.
samples. This indicated that electrical conductivity also showed the same trend as that of thermal conductivity with the addition of aluminium powder. The above values are in the range for antistatic application.

VI.5 Conclusions

The following conclusions could be drawn from the results contained in this chapter.

1. Thermal conductivity of rubber is increased by the addition of HAF black, acetylene black and aluminium powder. At equal volume per cent, aluminium powder gives the highest conductivity.

2. Thermal conductivity decreases with increase in temperature.

3. The time required for attaining the maximum extent of crosslinking (as measured by $V_r$) for a thick rubber article will be the least when appropriate quantity of aluminium powder is incorporated in the compound.
References