5.1 Introduction

In this chapter, the effects of unsaturated polyester resin (UPR) on the properties of natural rubber vulcanizates are investigated. UPR was prepared with varying \textit{MA}/PA ratios and blended with natural rubber. The mechanical and ageing properties were studied. Commercial UPR and isophthalic resin (IUPR) were also used for modification. The effects of adding the resins were studied in gum as well as filled compounds.

5.2 Experimental

5.2.1 Materials

GP grade UP resin (HSR 8113M), isophthalic polyester resin (HSR 8131D), styrene, methyl ethyl ketone peroxide (MEKP), and cobalt naphthenate were of commercial grade, supplied by M/s Sharon Engineering Enterprises, Kochi. Dimethyl aniline, benzoyl peroxide, 1,2 propylene glycol (PG) (B.P=188°C, d\textsuperscript{20}=1.04), maleic anhydride (MA) (M.W = 98.06, 98.5% assay), phthalic anhydride (PA) (M.W = 148.12, 99% assay), xylene (B.P = 137-142°C, 95% assay), hydroquinone (M.P=169°C) and triphenyl phosphate were laboratory reagent (LR) grade supplied by E. Merck India Ltd, Bombay.

Specifications of commercial UP resin are given below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number</td>
<td>10-30 mg KOH/g</td>
</tr>
<tr>
<td>Styrene content</td>
<td>25-45%</td>
</tr>
<tr>
<td>Viscosity at 25°C</td>
<td>0.2-4.5 Pa.s</td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>1.07-1.3</td>
</tr>
<tr>
<td>Refractive index at 25°C</td>
<td>1.524-1.559</td>
</tr>
</tbody>
</table>

Details of natural rubber (ISNR5) and compounding ingredients, their suppliers and other particulars are given in Section 2.2.1.

5.2.2 UP resin preparation [1]

The principles of preparation of UP resin have already been discussed in Section 1.4. The resin preparation was done by polycondensation [2]. PG, MA and
PA were taken in the molar ratio 1.1:0.60:0.40 in a 1 litre three-necked RB flask equipped with a mechanical stirrer, N\textsubscript{2} inlet and a reflux condenser. A slight excess of PG (10\%) was provided to allow for evaporation losses. The reaction was conducted with an inert blanket of N\textsubscript{2}. 0.05\% triphenyl phosphate was added to protect the light colour. The reaction mixture was heated at 210°C in a temperature-controlled heating mantle for several hours. The temperature was kept at 210°C, the optimum temperature at which MA in the cis configuration is isomerised to the less strained and more planar trans fumaric acid [3]. About 10ml of xylene was used to remove the water of hydration azeotropically. The acid value [4] was monitored every two hours. When the acid value became 40, vacuum was applied to bring it below 30 by removing residual reactants and the water of condensation. At this stage heating was discontinued. When the reaction mixture cooled down to 100°C, 0.02 wt \% hydroquinone and subsequently, 40 wt \% styrene were added and the mass mixed thoroughly. The resin was cooled to room temperature and stored in containers.

The unsaturation in the polyester chain arises from MA employed for the esterification. Hence the relative proportion of MA in the mixture of MA/PA influences the properties of the final blend. To ascertain this, different UP resins were additionally synthesized with varying MA/PA ratios viz. 30/70 & 90/10 and blended with NR.

5.2.3 Blend preparation

Since reports of blending of UPR with natural rubber are not available in literature, some preliminary experiments were conducted to determine the most suitable manner of addition as well as the best catalyst system. The most popular catalyst system for UPR consists of methyl ethyl ketone peroxide catalyst and cobalt naphthenate promoter. But this system was not selected for this study because of the deleterious effects of pro-oxidant cobalt on natural rubber [5]. Hence three other systems namely a) Dicumyl peroxide (DCP) b) Benzoyl peroxide (BPO) and c) Benzoyl peroxide and dimethyl aniline (BPO&DMA) were selected for the study.
Based on the mechanical properties of the rubber vulcanizate obtained (Table 5.2) on employing each of the above catalyst systems, BPO/DMA was selected for further studies.

Since UPR crosslinks to a gel after a few minutes of adding the catalyst and accelerator, it was necessary to find the optimum time interval (Fig.5.1) before adding it to the rubber on a two roll mill. The effect of varying the percentage of catalyst (Fig.5.2) was also investigated.

2.2.4 Rubber compounding and curing

The resin was incorporated into the gum rubber while compounding on a two roll mill. Before addition the resin was mixed with 1.5% by weight of benzoyl peroxide and dimethylaniline as curing agent. Then the compounding ingredients were added in the following order: activators, filler (where applicable), accelerators, and sulphur. Mixes were prepared and cured as already described in Section 2.2.4. The formulations of the mixes are given in Table 3.1, 3.2 and 3.3.

2.2.5 Quality evaluation

The vulcanizates were tested according to relevant ASTM standards. The details of the test procedure as well as the ASTM standards applicable have already been furnished in Section 2.2.5.

2.3 Results and discussion

a) Preliminary studies

Table 5.4 lists the physical properties of natural rubber modified with 2% unsaturated polyester resin using different catalyst systems. These are compared with results obtained when 1) no catalyst is used for UPR and 2) no UPR is used. From an examination of tensile strength the combination of BPO and DMA gives the highest tensile strength to the blend. While in the absence of catalyst the addition of UPR leads to a comparable value of tensile strength, the combination of
MEKP and cobalt naphthenate gives much lower values. Oxidation and consequent chain scission of the rubber molecules due to the presence of cobalt ion may be responsible for this. The combination of BPO and DMA has been used in subsequent studies.

Table 5.1 Properties of natural rubber modified with com. UPR using different catalyst systems

<table>
<thead>
<tr>
<th>Properties</th>
<th>NR+ UPR0%</th>
<th>NR+ UPR2% BPO</th>
<th>NR+ UPR2% DCP</th>
<th>NR+ UPR2% BPO+DMA</th>
<th>NR+ UPR2% MEKP+CoN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>22.56</td>
<td>21.2</td>
<td>23.58</td>
<td>24.6</td>
<td>25.25</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>2.186</td>
<td>1.67</td>
<td>1.58</td>
<td>1.74</td>
<td>1.51</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1001.8</td>
<td>1081</td>
<td>1297</td>
<td>1224</td>
<td>1281</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>41.61</td>
<td>42.59</td>
<td>37</td>
<td>42.2</td>
<td>38.54</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>35</td>
<td>36</td>
<td>35</td>
<td>37</td>
<td>35</td>
</tr>
<tr>
<td>Resilience (%)</td>
<td>63</td>
<td>68</td>
<td>68</td>
<td>74</td>
<td>70</td>
</tr>
<tr>
<td>Abrasion loss (cc/hr)</td>
<td>4.33</td>
<td>5.70</td>
<td>5.64</td>
<td>4.95</td>
<td>5.03</td>
</tr>
</tbody>
</table>

NR—natural rubber
BPO—benzoyl peroxide
DMA—dimethyl aniline
MEKP—methyl ethyl ketone peroxide
CoN—cobalt naphthenate

The effect of time elapsed after addition of BPO/DMA to the resin was studied by choosing different intervals namely 1, 2, or 3 minutes (Fig. 5.1). Beyond 3 minutes the resin became too viscous for addition to rubber. The highest tensile strength is shown when 3 minutes are allowed to elapse.
Fig. 5.1 Variation of tensile strength with time of addition of resin

Fig. 5.2 Variation of tensile strength with benzoyl peroxide content
Hence this procedure was followed for later studies. Similarly the amount of BPO giving the best tensile strength to the vulcanizate for a constant DMA content of 0.5% of the resin was also estimated by following the tensile strength. The optimum value of BPO is found to be 1.5% (Fig. 5.2)

b) Effect of commercial and synthesized UPR on the properties of NR vulcanizate

Figs. 5.3 and 5.4 show the FTIR spectra of gum NR modified by UPR and unmodified NR respectively. The modified rubber shows evidence of C=O stretching frequency by the presence of the ester group (1731 cm⁻¹). The additional absorption peak at 1127 cm⁻¹ can be due to a number of chemical moieties not directly attributable to known chemical changes.

Fig.5.3 FTIR spectrum of vulcanized NR+4% UPR
Fig. 5.4 FTIR spectrum of NR vulcanizate.

Cure characteristics of NR with UPR are given in Table 5.2. Fig. 5.5 shows the variation of cure time with UPR content. Cure time increases with resin content. This indicates that unlike epoxy resins UPR does not activate the curing reaction. The increase in cure time may be due to the retarding effect of residual acidity in the resin on the crosslinking reaction.

Figs. 5.6 to 5.10 represent the plots of \( \ln (M_h - M_t) \) vs time of various UPR modified samples. Cure rate constants are given in Table 5.3. They indicate that cure rate decreases when the MA/PA ratio increases which means that the amount of unsaturation has a bearing on the retarding effect on the crosslinking reaction.
Table 5.2 Cure characteristics of gum NR vulcanizate with UPR

<table>
<thead>
<tr>
<th>Resin content (%)</th>
<th>Scorch time(min)</th>
<th>Cure time (min)</th>
<th>Maximum Torque(dNm)</th>
<th>Cure rate index (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.62</td>
<td>5.62</td>
<td>2.69</td>
<td>33.33</td>
</tr>
<tr>
<td>Commercial UPR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.13</td>
<td>6.62</td>
<td>2.35</td>
<td>28.65</td>
</tr>
<tr>
<td>4</td>
<td>3.56</td>
<td>6.94</td>
<td>2.26</td>
<td>29.58</td>
</tr>
<tr>
<td>6</td>
<td>3.95</td>
<td>9.03</td>
<td>2.21</td>
<td>19.68</td>
</tr>
<tr>
<td>8</td>
<td>4.27</td>
<td>11.63</td>
<td>2.18</td>
<td>13.58</td>
</tr>
<tr>
<td>UPR 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.52</td>
<td>8.01</td>
<td>2.31</td>
<td>22.27</td>
</tr>
<tr>
<td>4</td>
<td>3.62</td>
<td>8.98</td>
<td>2.15</td>
<td>18.66</td>
</tr>
<tr>
<td>6</td>
<td>4.09</td>
<td>12.96</td>
<td>2.29</td>
<td>11.27</td>
</tr>
<tr>
<td>8</td>
<td>4.10</td>
<td>16.96</td>
<td>2.05</td>
<td>7.77</td>
</tr>
<tr>
<td>UPR 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.67</td>
<td>9.23</td>
<td>2.25</td>
<td>17.98</td>
</tr>
<tr>
<td>4</td>
<td>3.89</td>
<td>10.99</td>
<td>2.04</td>
<td>14.08</td>
</tr>
<tr>
<td>6</td>
<td>3.97</td>
<td>15.07</td>
<td>2.05</td>
<td>9.01</td>
</tr>
<tr>
<td>8</td>
<td>4.05</td>
<td>17.71</td>
<td>1.82</td>
<td>7.32</td>
</tr>
<tr>
<td>UPR 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.95</td>
<td>8.71</td>
<td>2.27</td>
<td>21.01</td>
</tr>
<tr>
<td>4</td>
<td>4.01</td>
<td>11.32</td>
<td>2.14</td>
<td>13.68</td>
</tr>
<tr>
<td>6</td>
<td>4.49</td>
<td>18.01</td>
<td>1.76</td>
<td>7.39</td>
</tr>
<tr>
<td>8</td>
<td>4.43</td>
<td>18.77</td>
<td>1.68</td>
<td>6.97</td>
</tr>
</tbody>
</table>

Fig. 5.5 Variation of cure time with resin content
Fig. 5.6 $\ln(M_h-M_t)$ vs t for NR compound

$y = -0.2257x + 1.0725$
$R^2 = 0.9756$

Fig. 5.7 $\ln(M_h-M_t)$ vs t for NR compound with 4% UPR

$y = -0.6357x + 2.9076$
$R^2 = 0.9922$

Fig. 5.8 $\ln(M_h-M_t)$ vs t for NR compound with UPR-1

$y = -0.6024x + 2.6582$
$R^2 = 0.9875$
Fig. 5.9 $\ln(M_h-M_t)$ vs $t$ for NR compound with UPR-2

Fig. 5.10 $\ln(M_h-M_t)$ vs $t$ for NR compound with UPR-3

Table 5.3 Cure rate constants of UPR modified samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate constant (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>0.2257</td>
</tr>
<tr>
<td>NR+com. UPR (4%)</td>
<td>0.6357</td>
</tr>
<tr>
<td>NR+UPR 1 (4%)</td>
<td>0.6024</td>
</tr>
<tr>
<td>NR+UPR 2 (4%)</td>
<td>0.4429</td>
</tr>
<tr>
<td>NR+UPR 3 (4%)</td>
<td>0.2377</td>
</tr>
</tbody>
</table>
Figures 5.11 to 5.20 show variation in different properties of vulcanizate on addition of UPR. Each of these figures also indicates the effect of using UPR of varying MA: PA ratios for NR modification. For comparison purposes the effect of using commercial UPR is also shown.

**Fig. 5.11** Variation of tensile strength with resin content

**Fig. 5.12** Variation of 300% modulus with resin content
Modification using unsaturated polyester resin

Fig. 5.13 Variation of elongation at break with resin content

Fig. 5.14 Variation of tear strength with resin content
Fig. 5.15 Variation of hardness with resin content

Fig. 5.16 Variation of resilience with resin content
Modification using unsaturated polyester resin

**Fig. 5.17** Variation of retention of tensile strength with resin content on ageing at 70°C for 72 hrs.

**Fig. 5.18** Variation of retention of tear strength with resin content on ageing at 70°C for 72 hrs.
Fig. 5.19 Variation of weight loss with resin content on Soxhlet extraction

Fig. 5.20 Variation of mass of oil absorbed with resin content

Fig. 5.11 shows the variation of tensile strength with resin content. Until about 4% of the resin the tensile strength is more or less unchanged in most cases. Higher
percentages of the resin show a negative effect on the tensile strength. Commercial UPR shows a slight superiority over the synthesized samples at 4%. A high MA:PA ratio is found to affect the tensile strength value negatively. This is evident from the position of the MA:PA = 90:10 curve. The presence of more and more unsaturation in the resin can lead to vulcanization and loss of curatives. This is a possible explanation. It is also possible that as more and more polystyrene crosslinks are established across polyester chains the crosslinking of rubber chains is inhibited, especially at higher resin concentrations and higher degree of unsaturation (higher MA content).

The effect on 300% modulus (Fig. 5.12) is more dramatic. The presence of the resin in increasing amounts causes a more rapid fall in modulus than tensile strength. This can also be explained in the light of the above arguments.

Elongation at break (Fig. 5.13) shows a gradual increase with increase in resin content. This can also be a consequence of the inhibiting effect of polystyrene crosslinks earlier discussed. A high MA content on the other hand does not permit high elongation because of extra crosslinks between polyester chains. Commercial UPR leads to higher elongation, a probable reason being a lower styrene content which leads to fewer numbers of crosslinks or shorter crosslinks between polyester chains.

Fig. 5.14 shows that tear strength falls on addition of polyester. Crystallinity is one factor that affects the tear strength directly [6]. The presence of polyester chains can prevent NR from attaining higher levels of crystallinity. The role of MA/PA ratio is not very clear in this case.

The effect of resin content on surface hardness is shown in Fig. 5.15. There is a gradual fall in surface hardness with increasing resin content. This can also be a consequence of reduced crosslinking between the rubber chains.

Resilience (Fig. 5.16) shows a gradual decrease on addition of the resin. The presence of the resin may be responsible for this. This can has a negative impact on heat build up in the rubber.
Fig. 5.17 shows an important positive effect of adding UPR to NR. The retention of tensile strength after ageing at 70°C for 72 hours shows an increasing trend as the resin content goes up. At 0% resin content the percentage retention of tensile strength is only 55% of the original value. The addition of UPR dramatically increases this value to the original tensile strength at 8% resin content. The thermal degradation of natural rubber on the continued action of heat has been arrested to some extent by this modification. There can be several possible explanations for this: (1) Free radical formation which is part of the degradation process has been reduced (2) Polyester network which has better thermal stability is supporting the rubber matrix under stress (3) More crosslinks have been established between the two components or even within the same component on ageing (4) The ageing process may take to completion any incomplete crosslinking reaction especially in the case of the resin.

Fig. 5.18 shows the effect of ageing at 70°C for 72 hours on tear strength. Here also there is a steady increase in the value on addition of resin. The increase in tear strength may be the result of additional crosslinks formed either as a part of the original crosslinking reaction or new crosslinks formed between the two components.

Fig 5.19 is a plot of the weight loss suffered by NR containing different amounts of resin on extraction with acetone. The weight loss on extraction shows an increasing tendency with increasing resin content. This can be attributed to the presence of uncrosslinked polyester chains likely to be present in the blend. A post curing operation (as happens during ageing) may complete the crosslinking of the resin.

Fig 5.20 gives the variation of the mass of oil absorbed by NR as the resin content goes up. The rubber was immersed in oil for three days and the change in weight was observed. There is substantial reduction in the mass of oil absorbed when 2% resin is added. Beyond this concentration there is not much change in the weight of oil absorbed. It is possible that as higher amounts of resin are added there is no proportional increase in crosslinking between the resin chains or between resin and rubber chains.
c) Effect of commercial UPR on the properties of filled NR

Cure characteristics are shown in Table 5.4. In silica filled and HAF black filled NR, cure time increases with UPR content (Fig. 5.21).

![Graph showing variation of cure time with resin content](image)

**Fig.5.21** Variation of cure time with resin content

**Table 5.4** Cure characteristics of filled NR vulcanizate with UPR

<table>
<thead>
<tr>
<th>Resin content (%)</th>
<th>Scorch time(min)</th>
<th>Cure time (min)</th>
<th>Maximum Torque(dNm)</th>
<th>Cure rate index (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica filled</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.73</td>
<td>3.73</td>
<td>2.74</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>2.09</td>
<td>4.60</td>
<td>2.84</td>
<td>39.84</td>
</tr>
<tr>
<td>4</td>
<td>2.33</td>
<td>4.68</td>
<td>2.84</td>
<td>42.55</td>
</tr>
<tr>
<td>6</td>
<td>2.51</td>
<td>4.94</td>
<td>2.59</td>
<td>41.15</td>
</tr>
<tr>
<td>8</td>
<td>2.47</td>
<td>5.01</td>
<td>2.56</td>
<td>39.37</td>
</tr>
<tr>
<td>HAF filled</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.67</td>
<td>3.77</td>
<td>4.26</td>
<td>47.6</td>
</tr>
<tr>
<td>2</td>
<td>1.78</td>
<td>3.99</td>
<td>4.35</td>
<td>45.25</td>
</tr>
<tr>
<td>4</td>
<td>2.02</td>
<td>4.86</td>
<td>4.27</td>
<td>35.21</td>
</tr>
<tr>
<td>6</td>
<td>2.45</td>
<td>5.12</td>
<td>4.21</td>
<td>37.45</td>
</tr>
<tr>
<td>8</td>
<td>2.56</td>
<td>6.01</td>
<td>3.98</td>
<td>28.98</td>
</tr>
</tbody>
</table>
Figures 5.22 to 5.26 show the variation of tensile strength, 300% modulus, elongation at break, tear strength and surface hardness in the case of each of silica filled and HAF black filled rubber vulcanizates on addition of different amounts of UPR. In general HAF black filled compounds show better properties in conformity with the known fact that carbon black is a better reinforcement than silica for NR. The effect of increasing amounts of UPR is not very noticeable although 300% modulus and tear strength increase in value upto 4% of resin.

In the case of tear strength the percentage increase on addition of 4% resin is about 20% for black filled compound. Silica filled compounds show less sensitivity to resin content with the exception of tensile strength which shows a decreasing tendency on addition of more and more resin. Hence filled compounds are less influenced by the resin than gum compounds. The surface activity of the filler particle can possibly account for this. The surface absorption of the resin or its curatives by the filler material cannot be ruled out.

![Graph showing variation of tensile strength with resin content](image)

**Fig.5.22** Variation of tensile strength with resin content
Modification using unsaturated polyester resin

Fig. 5.23 Variation of 300% modulus with resin content

Fig. 5.24 Variation of elongation at break with resin content
Fig. 5.25 Variation of tear strength with resin content

Fig. 5.26 Variation of hardness with resin content
Modification using unsaturated polyester resin

Fig. 5.27 shows the effect of the resin on the mass of oil absorbed by filled NR. There is a slight reduction in oil absorption.

Fig. 5.28 shows the retention of tensile strength with resin content after ageing at 70°C for 72 hours. The loss of tensile strength is moderate in filled compounds even in the absence of UPR. The retention of tensile strength shows a slight increase on addition of more of resin.

Fig. 5.29 shows the effect of resin content on tear strength after ageing of filled NR. The increase in retention of tear strength with resin content is very much noticeable. Since the presence of resin is not conducive to increased crystallinity some other phenomenon is responsible for this. It is possible that the resin molecule (or crosslinked particles) might be acting as crack stoppers after initiation of the crack. The ageing process can lead to complete curing of the resin which cannot be taken for granted in the case of the unaged materials.

![Graph showing variation of mass of oil absorbed with resin content](image)

**Fig. 5.27** Variation of mass of oil absorbed with resin content
d) Effect of IUPR on the properties of gum and filled NR vulcanizate

Cure characteristics are shown in Table 5.5. Fig.5.30 shows the variation of cure time with IUPR content. Cure time increases with resin content. This indicates that IUPR also does not activate the curing reaction.
### Table 5.5 Cure characteristics of NR vulcanizate containing IUPR

<table>
<thead>
<tr>
<th>Resin content (%)</th>
<th>Scorch time (min)</th>
<th>Cure time (min)</th>
<th>Maximum Torque (dNm)</th>
<th>Cure rate index (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.62</td>
<td>5.62</td>
<td>2.69</td>
<td>33.33</td>
</tr>
<tr>
<td>2</td>
<td>2.59</td>
<td>5.56</td>
<td>2.49</td>
<td>33.67</td>
</tr>
<tr>
<td>4</td>
<td>2.87</td>
<td>5.51</td>
<td>2.37</td>
<td>37.88</td>
</tr>
<tr>
<td>6</td>
<td>2.96</td>
<td>5.72</td>
<td>2.28</td>
<td>36.23</td>
</tr>
<tr>
<td>8</td>
<td>3.13</td>
<td>6.39</td>
<td>2.12</td>
<td>30.67</td>
</tr>
<tr>
<td>Silica filled</td>
<td>0</td>
<td>1.73</td>
<td>3.73</td>
<td>2.74</td>
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<td></td>
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<td>2.16</td>
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<td>5.22</td>
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<td>3.77</td>
<td>4.62</td>
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<td>2</td>
<td>1.98</td>
<td>3.92</td>
<td>4.34</td>
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<td>4.19</td>
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<td>2.54</td>
<td>4.96</td>
<td>4.08</td>
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<td></td>
<td>8</td>
<td>2.64</td>
<td>6.36</td>
<td>3.98</td>
</tr>
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![Graph](attachment:image.png)

**Fig.5.30** Variation of cure time with resin content
Fig.5.31 shows the variation of tensile strength of gum and filled NR when various amounts of IUPR are added. Only a small increase in tensile strength is noticed on addition of resin. A similar trend is noticed in the case of 300% modulus, elongation at break, tear strength and surface hardness (Figs.5.32 to 5.35). A total lack of chemical interaction between the resin and rubber and the adsorption effects of the filler on the resin are possible reasons for this.
Fig. 5.33 Variation of elongation at break with resin content

Fig. 5.34 Variation of tear strength with resin content
Fig. 5.35 Variation of hardness with resin content

Fig. 5.34 Variation of mass of oil absorbed with resin content
Modification using unsaturated polyester resin

The mass of oil absorbed falls steeply (Fig. 5.36) with resin content in the case of gum rubber mixed with IUPR. This is similar to the behavior of UPR. The presence of the resin probably acts as a polar barrier for absorption of the oil by the rubber. The presence of the filler particles on the other hand apparently interferes with this process. Hence the lack of sensitivity to resin content in the case of silica and HAF filled compounds.

Fig. 5.37 shows the variation of retention of tensile strength with resin content on ageing at 70°C for 72 hours. As in the case of UPR only the gum compound benefits from the addition of IUPR. At 4% resin content the increase in retention of tensile strength is about 80% over samples containing no resin. Filled compounds on the other hand are not much affected by the resin content.

As in the case of UPR there is a general increase in retention of tear strength on ageing on addition of IUPR (Fig.5.38). This effect is more noticeable in gum compounds where at 6% resin the increase in retention of tear strength is about 40-45%.
Fig.5.38 Retention of tear strength on ageing at 70°C for 72 hrs

Fig.5.39, 5.40 and 5.41 show the thermograms of samples of NR, NR+UPR, and NR+IUPR respectively. The onset point of degradation is slightly higher for NR modified with UPR and IUPR. The residue content is also slightly higher. The thermal data are given in Table 5.7 and 5.8. Thermal stability of the modified compounds is comparable to the unmodified sample. Thermal stability is not affected by changing the MA/PA ratio.
Modification using unsaturated polyester resin

Fig.5.39 Thermogram of NR vulcanizate

Fig.5.40 Thermogram of 4% UPR loaded NR vulcanizate
Fig. 5.41 Thermogram of 4% IUPR loaded NR vulcanizate

Table 5.7 Thermal data of vulcanized NR with and without resin

<table>
<thead>
<tr>
<th>Property</th>
<th>NR</th>
<th>NR+4% UPR</th>
<th>NR+4% IUPR</th>
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</thead>
<tbody>
<tr>
<td>Onset of degradation (°C)</td>
<td>312.72</td>
<td>317.47</td>
<td>317.53</td>
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<tr>
<td>Temperature of 50% degradation (°C)</td>
<td>388.99</td>
<td>385</td>
<td>385.17</td>
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<tr>
<td>Maximum degradation temperature (°C)</td>
<td>384.23</td>
<td>382.37</td>
<td>381.68</td>
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<tr>
<td>Maximum rate of degradation (%/°C)</td>
<td>1.556</td>
<td>1.583</td>
<td>1.586</td>
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<tr>
<td>Residue (%)</td>
<td>4.297</td>
<td>4.811</td>
<td>4.492</td>
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</table>
Table 5.8 Thermal data of vulcanized NR with 4% of synthesized UPR

<table>
<thead>
<tr>
<th>Property</th>
<th>NR+UPR 1</th>
<th>NR+UPR 2</th>
<th>NR+UPR 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of degradation (°C)</td>
<td>293.94</td>
<td>300.47</td>
<td>301.62</td>
</tr>
<tr>
<td>Temperature of 50% degradation (°C)</td>
<td>391.32</td>
<td>391.54</td>
<td>391.15</td>
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<tr>
<td>Maximum degradation temperature (°C)</td>
<td>388.12</td>
<td>387.08</td>
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</tr>
<tr>
<td>Maximum rate of degradation (%/°C)</td>
<td>1.567</td>
<td>1.553</td>
<td>1.528</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>5.09</td>
<td>5.21</td>
<td>5.497</td>
</tr>
</tbody>
</table>

Fig. 5.42 SEM micrographs (a) NR  (b) NR+UPR 4%

Fig. 5.42 shows the micrographs of gum NR and NR modified by commercial UPR respectively. The dispersion of the resin is not very uniform. This can be judged from the size of the resin particles. The short gel time of the resin after addition of catalyst and accelerator is partly responsible for this. Because the improvement in mechanical properties of the rubber is very modest it is likely that most of the UPR remains distributed as discrete particle without much chemical interaction with the rubber chains.

5.4 Conclusion

The properties of the modified rubber are somewhat negatively influenced by the extent of unsaturation in the UPR. Only a moderate improvement in tensile
strength is obtained on addition of UPR to NR at the optimal concentration of 4%. The tensile strength is more or less unchanged in most cases. Commercial UPR shows a slight superiority over the synthesized samples at 4%. A high MA:PA ratio is found to affect the tensile strength value negatively. The retention of tensile and tear strength after ageing at 70°C for 72 hours shows an increasing trend as the resin content goes up. Not much improvement in tensile strength is noticed on addition of IUPR resin. Some improvement in ageing resistance is noticeable. The presence of fillers blunts the effect of the resin for most properties.

The addition of the resin (both UPR and IUPR) leads to reduced oil absorption in all cases, filled and unfilled. Hence UPR modification has improved the oil resistance of NR.

References


