CHAPTER VI - EFFECT OF BLEND RATIO AND SILICA CONTENT ON

(A) MECHANICAL PROPERTIES AND DEGRADATION
(B) DYNAMIC MECHANICAL PROPERTIES

OF NR-EVA BLENDS.

The results of the above study have been accepted for publication in (1) Kautschuk Gummi Kunststoffe and communicated for publication to (2) Journal of Materials Science.
The reinforcing action of fillers on elastomers depends on factors such as particle size, structure and physico-chemical interaction of filler with the polymer. However, in blends of elastomers, the reinforcing activity also depends on distribution and dispersion of the filler in each phase of the blend. In this chapter, the effects of precipitated silica on the mechanical, dynamic mechanical and degradation resistance of NR-EVA blends have been evaluated. Blend ratios selected for the evaluation are 100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and 0:100, NR:EVA. The crosslinking system used in the present evaluation is a mixed one, consisting of sulphur and dicumyl peroxide, since it was found to yield better technological properties for the blends (Chapter III). Effects of silica in protecting NR:EVA blends against the action of heat, ozone and γ-radiation were assessed. The results obtained are discussed under two headings.

Part A discusses the effect of precipitated silica on mechanical properties and degradation of NR-EVA blends.

Part B discusses the dynamic mechanical properties of silica filled NR-EVA blends with special reference to the effect of blend ratio and silica content on storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) at different temperatures. The experimental techniques for determining the mechanical properties, degradation behaviour and dynamic mechanical measurements are given in Chapter II.
VI.A.1 EFFECT OF SILICA ON TENSILE AND TEAR STRENGTHS

Effect of loading of silica on the tensile strength of NR-EVA blends is shown in Figure VI.A.1. At 45 phr level, silica adversely affected the tensile strength of the blends. However, loading upto 30 phr did not seriously affect the tensile strength of those blends which contained a higher proportion of NR. But in EVA rich blends, silica reduced the tensile strength even at 15 phr loadings. From Figure VI.A.2, it is clear that tear strength increased with increase in proportion of EVA in the blend. Addition of silica increased the tear strength of those blends which had a higher proportion of NR. But in EVA rich blends, tear strength decreased with the addition of silica.

The above observations on tensile and tear strengths of silica filled NR-EVA blends can be explained based on the morphology of the blends and distribution of the filler in each phase of the blend. It is already seen that in NR-EVA blends, EVA also formed a continuous phase when its proportion was 40 per cent or more, due to its lower melt viscosity and that NR remained as dispersed particles when its percentage was 40 or below (Chapter III, Section III.A). It is also well known that silica has high affinity towards polar polymers and preferentially get distributed into the polar component of the blend119. Considering the above, it is possible that silica got distributed preferentially in the EVA phase of those
blends in which EVA also formed a continuous phase (blends E to J). \( V_{ro} \) and \( V_{rf} \) are the volume fractions of rubber in the unfilled and silica filled vulcanisates respectively, swollen in xylene to an equilibrium state. The weight fraction of filler in the vulcanisate is denoted as \( z \). From the nature of the \( V_{ro}/V_{rf} \) versus \( e^{-2} \) plots the reinforcing activity of the filler can be ascertained. Identical slopes of the straight lines obtained by plotting \( V_{ro}/V_{rf} \) against \( e^{-2} \) (Figure VI.A.3) for the silica filled EVA and NR compounds, especially in the region of higher silica loading, indicated that reinforcing activity of silica in both the polymers is almost same. But it is already established that strong physico-chemical interactions between filler and polymer can reduce the extent of crystallization of the polymer\(^{120}\). Hence the basic reason for the lower tensile and tear strengths of the silica filled EVA and blends containing higher proportion of EVA appears to be lower extent of crystallization of the EVA. For NR and NR rich blends, silica improved the tear strength and tensile strength due to reinforcement of the NR phase.

VI.A.2 MODULUS, HARDNESS AND ABRASION LOSS

The modulus and the hardness values shown in Figures VI.A.4 and VI.A.5, respectively, increased with loading of silica and this effect was more pronounced in blends A to F in which NR remained as a continuous phase. The increase in modulus and hardness is due to reduced elasticity of the filled blends. For NR (compound A)
abrasion loss reduced with loading of silica due to its reinforcing effect, but in blends as well as in pure EVA (B to I and J) addition of silica increased abrasion loss (Figure VI.A.6). This observation again pointed out the fact that the expected property increase due to reinforcement of the EVA phase was offset by the reverse effect caused by the decrease in the extent of crystallization of the EVA phase. This is further supported by the compression set behaviour of the silica filled NR-EVA blends.

VI.A.3 EFFECT ON COMPRESSION SET

Figure VI.A.7 shows the compression set behaviour of silica filled NR-EVA blends. Compression set of NR (compound A) increased with loading of silica filler, which is typical for compounds containing high reinforcing filler. However, this tendency was reversed from blend E onwards in which EVA also showed phase continuity. In these cases, compression set was lower for the blends when filler loading was increased. For crystallizing elastomers, it is reported that compression set values decreased when the crystallizing tendency was reduced. In the present case also, strong physico-chemical interaction between EVA and silica might have adversely affected the extent of crystallization of the EVA phase, which resulted in lower compression set values of the blends, as the filler loading was increased.
VI.A.4 EFFECT ON RADIATION RESISTANCE

Retention of tensile strength of silica filled NR-EVA blends, after exposing the test samples to 20 Mrad of $\gamma$-radiation, from a $^{60}$Co source, is presented in Figure VI.A.8. As the EVA content increased, resistance to degradation by $\gamma$-radiation also increased as evidenced by higher retention of tensile strength. This effect was found to be more pronounced in blends E to I in which EVA formed a continuous phase. Silica enhanced the resistance to degradation by radiation and this effect increased with loading of silica. During irradiation by $\gamma$-rays, two types of reactions take place, i.e., degradation and crosslinking of the polymer chains. When the former reaction predominates, the strength of the material is decreased. Precipitated silica is found to favour the second type of reaction, as shown by better tensile retention of silica filled NR, EVA and their blends.

VI.A.5 EFFECT ON OZONE RESISTANCE

Figure VI.A.9 is the photograph of samples exposed to ozonised air for 8 h (top) and 85 h (bottom) respectively. In the unfilled blend (C$_{3}$S$_{0}$) small cracks were initiated after 8 h of exposure. This sample developed deep cracks as seen in the photograph after 85 h of exposure. On the other hand, samples C$_{3}$S$_{15}$, C$_{3}$S$_{30}$ and C$_{3}$S$_{45}$ which contained 15, 30 and 45 phr precipitated silica respectively, did not develop any crack during this period. Addition
of silica increased the modulus of the blend and reduced its elongation. Hence the stress required to produce the critical strain, necessary for the ozone attack to take place, might be much higher in silica filled blends.

VI.B.1 DYNAMIC MECHANICAL PROPERTIES OF SILICA FILLED NR-EVA BLENDS

The tan δ values of the unfilled blends as a function of temperature are shown in Figure VI.B.1. It is seen that the tan δ values of pure EVA increased sharply above 75°C and reached a plateau value beyond 95°C. The sharp increase in the tan δ value in this temperature range is associated with the melting of the crystalline segments of the EVA phase. The results on the thermal behaviour of NR-EVA blends described in Chapter IV, Section 1 indicate that the EVA phase has a sharp melting point of 86.7°C. The damping curve of EVA has three distinct zones: (a) a rubbery plateau, (b) a melt transition and (c) a viscous plateau. The damping curves of the blends also show a similar trend as that of EVA, although the intensity of transition is lower. This is associated with the decrease in crystallinity of the samples. The damping curve of natural rubber is different from that of EVA and their blends. In this case the curve is almost in parallel to the temperature axis. This is associated with the amorphous nature of the NR phase. The damping curves of systems containing 45 parts of silica filler is shown in
Figure VI.B.2. It is seen that addition of silica decreased the tan $\delta$ values substantially except that of natural rubber where a marginal increase in tan $\delta$ values can be observed at high temperatures. The sharp decrease in tan $\delta$ values of EVA blends is associated with the decrease in the crystallinity of the EVA phase due to the presence of filler. Silica filler has high affinity towards the EVA phase due to its polar nature. Therefore, the crystallinity of EVA is impaired. It can also be noticed that the crystalline transition zone become broader as a result of the addition of filler.

The storage modulus values of unfilled blends are given in Figure VI.B.3. In the case of EVA and the blends, the storage modulus curves have three distinct regions namely, rubbery, transition and viscous regions. It is seen that the storage modulus of high EVA blends decreased sharply with temperature in the rubbery and the transition zone and it levels off in the viscous region. The storage modulus of NR is almost unaffected by temperature. The effect of addition of silica filler on the storage modulus of the blends as a function of temperature is given in Figure VI.B.4. In all cases, addition of silica increased the storage modulus of the blends considerably. The storage modulus of filled NR shows a marginal decrease with increasing temperature. Although the general trend of filled EVA and the blends are similar to that of unfilled systems, the transition region is less predominant than unfilled systems due to the decrease in the crystallinity of the samples.
The loss modulus of the unfilled and filled systems are given in Figures VI.B.5 and VI.B.6, respectively. In the case of unfilled systems, the loss modulus of NR and high NR blend (80:20 NR:EVA) is almost unaffected by temperature. However, the loss modulus of pure EVA and high EVA blends decreased sharply with temperature before they undergo melting. In the viscous region, the loss modulus values are unaffected by temperature. Addition of silica increased the storage modulus of the systems considerably. In the case of EVA and high EVA blends the storage modulus decreased with temperature and the decrease is more sharp in the rubbery region.

The storage modulus of the filled and unfilled blends at a temperature of 30°C as a function of EVA content is presented in Figure VI.B.7. It is seen that the storage modulus increased with the increase of EVA content in all cases. Addition of 15 parts of silica marginally increased the storage modulus. However, at 45 parts of silica loading the storage modulus of the systems showed a very high increase. This is an expected trend in the silica filled systems since silica imparts high stiffness to the polymer matrix. The loss modulus of the blends as a function EVA content is given in Figure VI.B.8. Addition of 15 parts of silica showed a marginal change in loss modulus. There was considerable increase in loss modulus at higher loading of silica for the NR rich blends.
Figure VI.A.1
Change of tensile strength with blend ratio and silica content.
Figure VI.A.2
Change of tear strength with blend ratio and silica content.
Figure VI.A.3
Plots of $V_{ro}/V_{rf}$ against $e^{-z}$
Figure VI.A.4
Change of modulus 300% with blend ratio and silica content.
Figure VI.A.5
Change of hardness (Shore A) with blend ratio and silica content.
Figure VI.A.6
Change of Din abrasion loss with blend ratio and silica content.
Figure VI.A.7
Change of compression set with blend ratio and silica content.
Figure VI.A.8
Change of retention of tensile strength with blend ratio and silica content.
Figure VI.A.9
Photograph of blend C (80:20 NR:EVA) having different silica content after 8 h and 85 h of exposure to ozonised air.
Figure VI.B.1
Effect of temperature on loss tangent of unfilled NR-EVA blends.
Figure VI.B.2
Effect of temperature on loss tangent of silica filled NR-EVA blends.
Figure VI.B.3
Effect of temperature on storage modulus of unfilled NR-EVA blends.
Figure VI.B.4
Effect of temperature on storage modulus of silica filled NR-EVA blends.
Figure VI.B.5
Effect of temperature on loss modulus of unfilled NR-EVA blends.
Figure VI.B.6
Effect of temperature on loss modulus of silica filled NR-EVA blends.
Figure VI.B.7
Effect of EVA content and silica on storage modulus at 30°C.
Figure VI.B.8
Effect of EVA content and silica on loss modulus at 30°C.