Chapter I

INTRODUCTION

Elastomer blends are of great importance to the rubber industry. Almost all important rubber products in industry and transportation applications are used as blends. Moreover, the science and technology of elastomer blends are advancing at a rapid rate. One of the main advantages of elastomer blends is the great regulatable variability of their properties despite the limited number of initial components\(^1\)-\(^8\). The blending technology has long been widely used in rubber industry. Compounding with blends of two or more elastomers is an attractive method for attaining properties not available in a single elastomer. While elastomer blends are an integral part of polymer blends there are many factors unique to elastomer blends which decide their properties\(^9\)-\(^15\).

Polymer blends

In recent years, research and development activities in the field of polymer science and technology have been concentrated more on the modification of existing polymeric materials rather than on synthesising new polymers\(^16\)-\(^20\).
Polymer blends are prepared by

1. Mechanical mixing of polymers in extruders, compounders, internal mixers etc.

2. Dissolving the polymers in a common solvent.

3. Dissolving or dispersing one polymer in the monomer of another and polymerising.

In large volumes polymer blends and alloys are mainly prepared by the first method\textsuperscript{22-25}

All materials attract interest on the basis of their property-processing-cost-performance relationship. The most important concept in polymer blends is additivity of properties. By this we mean that when a polymer is mixed with another polymer, the resulting blend has a property which is the weighted average of the properties of the individual polymers. Modulus is one of such properties that is expected to obey some additivity relationship\textsuperscript{26}. For blends the weighing functions of the composition will be sensitive to the morphology. A very intriguing possibility, although less frequently observed, is synergism in property,
such as tensile strength, when the blend has a better property than those of the components. The success of a new material depends on several factors such as combination of properties and cost dilution. For example, when we blend a high thermal resistant polymer having poor processability with another polymer having good processability and poor thermal stability, the resulting blend may be useful for certain applications for which both the individual polymers are unsuitable. Similarly, when a costlier polymer is blended with a cheaper one it may reduce the properties to a level still acceptable for a particular application. At the same time it will bring the cost of the blend to a range which is competitive in the market. Thus blending is an attractive means to engineer a material so that the user does not have to pay for more than he needs. This is the most important driving force for developing products from polymer blends.

Since the driving force for development of polymer blends is generally some combination of economics and blend performance or properties, knowledge of the rules of mixtures for blend properties is of critical interest. These rules will again depend on the state of miscibility of the blend. The properties of miscible blends will follow
relationships that are functions of composition and to some extent the degree of interaction between the blend components\textsuperscript{27,28}. Immiscible blend properties will depend on the phase morphology and phase interaction as well as composition. There are many possible properties of interest such as mechanical, thermal, electrical and chemical.

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property, deciding the practical utility of a polymer blend\textsuperscript{29-37}. In polymer blends the property (P) depends on average properties of the constituents and can be described by the following equation:

\[ P = P_1C_1 + P_2C_2 + IP_1P_2 \]

where P is the property of the blend, P\textsubscript{1} and P\textsubscript{2} the properties of the isolated components and C\textsubscript{1} and C\textsubscript{2} the respective concentrations of the constituents. I is an interaction parameter which can be positive, zero or negative as shown in Fig.1.1. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is nonsynergistic.
Fig. 1.1: Variation of property with composition for a binary polymer blend.
The most important factor governing the ultimate properties of a polymer blend is intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor adhesion between the molecules at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialised, the applicability of such polymer blends is limited because of the inferior macroscopic properties. So successful blending of incompatible polymer systems is gaining increasing importance both in the academic and industrial field.

Elastomer blends

None of the commercially available elastomers satisfy the divergent requirements of various products. Hence in order to attain desirable technical compromise of properties, blending between two or more rubbers is widely practised. Pneumatic tires are examples of composite products in which the rubber compounds are made from blends of two or three elastomers as shown below.
One particular advantage of blending BR with NR is the effect of high curing temperatures on physical properties. This heat stability is conveyed by cis BR when blended with NR or SBR\textsuperscript{32}. Similar improvements in thermal reversion are claimed for blends of emulsion BR with NR. The addition of cis BR is said to decrease the tensile strength and modulus of NR vulcanizates but to increase elasticity and abrasion resistance\textsuperscript{33}. The poor processing properties of cis BR are improved by blending with liquid BR, and excellent properties for sulfur vulcanizates are claimed. Difficulties in the processing of some NR blends are claimed to be overcome by use of specific black and or blending with NR or SBR\textsuperscript{34,35}. Tread wear and wet skid
resistance of SBR are found to improve for NR/SBR elastomer blends. Enhanced heat resistance in black filled and mineral filled stocks of EPDM/butyl blends has been established\textsuperscript{36,37} Blending of high unsaturated rubbers with EPDM and EPM usually seeks to take advantage of the latter's ozone resistance\textsuperscript{38}. Blends of EPDM with NR, SBR, NBR and CR give compounds with good ozone and chemical resistance and good compression set characteristics\textsuperscript{39}. The difficulty experienced with covulcanization of butyl rubber with diene rubbers is alleviated by use of chlorobutyl and can be used for inner liner or tubeless tires, where impermeability and damping properties of butyl rubber is exploited\textsuperscript{40}. EPDM/NBR blends have also been considered for obtaining moderate resistance to oils and ozone, plus an acceptable level of general mechanical properties\textsuperscript{41}. A blend of silicone and fluorosilicone polymers bonds easily with fluorosilicone adhesives and has better physical properties, better processing and is cheaper than the unblended polymer\textsuperscript{42}. Comparison of mixing methods showed an advantage for directly compounding ingredients into the blend of elastomers, over mixing previously prepared master batches. Study of black loadings showed reinforcing furnace blacks generally to be the best type\textsuperscript{43}. The processing behaviour ie., mixing, extruding and calendering characteristics of
many stereo regular elastomers need modification to be technologically acceptable for factory operations. For example, in the case of polybutadiene, varies from very difficult to easy and may be improved by addition of oil, liquid polymers, or other broader distribution elastomers, such as NR or emulsion SBR.

Vulcanizate physical properties are affected by two major factors: vulcanization and filler distribution. In order to achieve a single Tg which controls blend properties such as resilience, some covalcanization between the different phases in the blend is needed. This explains the use of chlorobutyl in place of butyl rubber for blending with diene elastomers which give better general physical properties and the variation of the termonomer in EPDM influences physical properties of its blends with diene rubbers. This covalcanization (interphase crosslinking) is influenced by the type of curative system used, including its solubility in each phase and the response of the individual elastomers to the curatives. Filler disaggregation to an adequate level is needed for optimum properties but another potent factor appears to be distribution of the filler in the phases of the blend. This distribution is clearly influenced by the molecular weight of each phase.
Properties of elastomer blends

Mechanical properties of elastomer blends may not often approach the level of average properties of the individual components which is due to the incompatibility on the molecular scale and exist in the form of two separate phases. A heterogenous blend usually results when two chemically dissimilar rubbers are mixed 46-50. Several investigators have tried to correlate between the morphology as revealed by electron microscopic studies and the mechanical properties of the blends. It is convenient to divide the variables of a blend system into two categories direct and indirect variables 51. The direct variables can be further subdivided into those which are important because the pure component properties depend on them and those that are unique to the blend systems. The direct variables are the fundamental ones and can be controlled by the indirect or processing variables.

The first three fundamental variables are those that also affect the pure components. They are the glass transition temperature ($T_g$), the molecular weight and crosslink density of the components. Among the rubbery materials, a higher $T_g$ or molecular weight generally increases toughness for a given crosslink density 52,
moreover the mechanical properties of elastomers depend very strongly on crosslink density. Specifically, the energy required to rupture an elastomer in simple tension generally passes through a maximum as a function of crosslink density.

The remaining four direct variables are unique to blends. The properties obviously depend on the properties of each component in the blend. In addition, morphology of the blend may be important. One rubber may form the continuous phase while the other is dispersed phase, or a cocontinuous structure when both phases are continuous may exist. Also, various sizes and shapes of the dispersed particles are possible.

The interfacial adhesion between the two phases may determine the path that a growing crack takes in a deformed rubber blend and also determines the extent to which stresses can be transferred between the matrix and particle phases. If the interfacial adhesion is sufficiently low, the small cavities may be opened up between the dispersed domains and the matrix when the blend is stressed. Thus the interfacial adhesion plays a key role in determining the mechanical properties. The relative stiffness between the two phases is a function of the molecular weight, \( T_g \), and rate of crosslinking (and scission) of the two rubber
phases. The micro deformation of the blend particle will depend in part on this property. It is found in many composites that the relative stiffness also affects the mechanical properties.

The morphology of a blend depends upon the condition under which the rubbers are mixed. Two methods have been used (1) solutions of rubbers stirred together, then dried or precipitated. (2) The bulk rubbers are comasticated in a Brabender plasticorder, or similar high shearing mixer. With this technique, the mixing time, temperature, and/or speed can be varied to obtain different morphologies. Annealing after mixing is another method of changing the morphology which can cause an increase in dispersed particle size or phase inversion.

Distribution of insoluble compounding ingredients

A general question which comes up in the case of elastomer blends is regarding the distribution of filler particles between the separate zones and how are performance characteristic affected.\textsuperscript{54}

Fillers are broadly defined as reinforcing and non-reinforcing. Carbon black and silica are included in
the first class, while clays and whiting are examples of the second category.

Based on a series of investigations on blend homogeneity of natural rubber with some of the principal synthetic elastomers the following conclusions have been arrived at.

Filler distribution between separate polymer phases is strongly influenced by molecular features and processing variations. In 50/50 preblend with NR, the commonly used commercial types of SBR show a strong affinity for carbon black, when added to the blend at relatively high loadings (eg., 40 phr) similar to NR/BR blend containing carbon black. In unmilled solution or latex black masterbatch of NR and SBR no preferential distribution of black was observed. Studies on 50/50 preblends of IR/BR and NR/BR containing precipitated silica showed that there was a strong tendency for the silica particles to locate preferentially in the isoprene phase. Similar results were also obtained with NR/SBR blends. Under high shear mixing conditions carbon black will migrate from a NR masterbatch to polybutadiene. High transfer was favoured by a relatively high black loading and low heat history for the NR black masterbatch. With a NR silica masterbatch, little or no transfer to polybutadiene was observed.
The effect of an appreciable volume loading of filler on the properties of cured elastomeric vulcanizates depends on whether the elastomer is stress-crystallising or not. Dinsmore\textsuperscript{54} reported that the ratio of the tensile strength, of black filled to that of gum vulcanizates is 1 to 1.5 for NR vulcanizates and 5 to 10 for vulcanizates of SBR and similar elastomers. Thus appreciable improvements in strength properties may be obtained for non stress crystallising rubbers by incorporation of carbon black. Certain elastomers have optimum filler loading for particular properties such as wear and tear resistance\textsuperscript{54}. In a 50/50 NR/BR preblend, carbon black normally locate preferentially in the BR component and this distribution results in optimum vulcanizate performance\textsuperscript{57,58}. The incorporation of carbon black into 50/50 elastomer preblends indicated that black affinity decreased in the order BR, SBR, CR, NBR, NR, EPDM, IIR\textsuperscript{59}. In addition, black transfer during blending was observed from a mechanically mixed IIR masterbatch to a high unsaturation gum rubber but not from a NR masterbatch. Transfer, thus, appears to be confined to those situations in which the adsorptive capacity of the filler has not been fully realised. This may occur if the polymer filler masterbatch has minimum thermal or mechanical history or involves low molecular weight or low unsaturation elastomers, situation in which bound rubber...
formation is minimized\textsuperscript{60-62}.

It is apparent that the surface polarity of carbon black influences its distribution in elastomer blends, and also that the behaviour of inorganic filler is disparate eg. in cis BR-NR blends, silica tends to accumulate in the NR phase. Filler distribution is also influenced by the point of addition of filler, the viscosity levels of the elastomers, and the blending methods. The ability of rubbers to accept black and other filler is said to be an important factor in attaining good dispersion which in turn affects reinforcement and ultimate performance properties. The reinforcing ability of a filler in an elastomer can be assessed by bound rubber determination\textsuperscript{66}.

Distribution of fillers can profoundly influence the modulus in elastomer blends. At lower strains where the carbon black network structure dominates the stiffness properties, an increase in the nonuniformity of this filler distribution results in a lower stock modulus. This indicates that the transfer of a portion of the carbon black from one phase would lower its modulus proportionally more than the increase in modulus of the phase with the higher carbon black concentration. The effect of carbon black distribution on modulus is thus related to the nonlinear
dependence of rubber modulus on carbon black loading\textsuperscript{66,67} Blending of elastomers with different affinities for black provides an opportunity to control the state of aggregation and connectivity of the carbon black and thereby influence the electrical conductivity. Conductivities can be achieved in the blends which exceed those of the pure components. This is due to increased agglomeration of carbon black in the immiscible blends. Carbon black tends to redistribute when mixed into blends, particularly where it has a low affinity for one of the phases. This results in an accumulation of carbon black at the interface\textsuperscript{68,69} and consequently higher electrical conductivity. Blends of rubber with similar affinity for carbon black do not exhibit this synergism (eg. SBR/NR).

The hysteresis of a blend is often found to be lower than the weighted average of the components, particularly in filled system with a nonuniform carbon black distribution. The phase with the lower carbon black loading will have both reduced modulus and hysteresis particularly when the softer phase is the continuous phase where a low blend hysteresis\textsuperscript{70} may result. Most of the hysteresis reduction accompanying a non-uniform distribution of carbon black can be attributed to the nonlinear relationship
between hysteresis and carbon black loading particularly at very high loading.  

Homogenity of blends

Homogenous or miscible blends are characterised by one value of any physical parameters whereas immiscible or heterogenous blends are characterised by several values of the same parameter. A homogeneous polymer blend has one glass transition temperature in between those of the two polymers. In a highly phase separated polymer blend, the transitional behaviour of the individual components will be unchanged while in a miscible blend a single and unique transition will appear.

Microscopy is unique for detailed characterisation of the phase morphology in blends. Optical (visible light) contrast can arise from a number of sources such as colour, opacity, refractive index, orientation, absorption etc. With transmission electron microscope (TEM), electron scattering differences are the primary source of contrast. Scanning electron microscope on the other hand, depends primarily on surface texture for contrast. Scattering methods depend on the principle that stable homogenous mixture is transparent whereas unstable non-homogenous mixture is turbid unless the components of the mixture have
identical refractive indices\textsuperscript{3}. The utility of polymer blends obviously does not require achieving miscibility. Most of the multicomponent polymer system commercially utilised are two phase blends.

In heterogenous or phase separated blends, interfacial adhesion between the respective phases governs the ultimate mechanical properties. For polymeric constituents having limited affinity for each other, the interface represents a flaw yielding ultimate mechanical properties significantly lower than expected from constituent values. If indeed polymers are miscible excellent adhesion is expected, provided sufficient temperature and pressure are employed to allow for molecular mixing.

The primary advantage of a miscible blend compared to immiscible blend counterparts is the assurance of mechanical compatibility. The simplified average of ultimate mechanical properties is not always the observed or expected case, due to the importance of the position of the glass transition temperature (T\textsubscript{g}) and or brittle ductile behaviour.
Blend compatibility

Although the great majority of elastomer blends are heterogeneous some technically advantageous combination or compromise of properties can be realised from the blends. However in most heterogenious rubber mixtures the mechanical properties are found to be inferior to those of the components. This is due to three types of incompatibilities generally met within these type of blends, namely thermodynamic incompatibility, viscosity mismatch and cure rate mismatch.

Viscosity considerations

Tokita and Avegeropolous have thoroughly investigated the mixing parameters required for the optimum blending of elastomers. In a blend of EPDM/NR it was concluded that smaller domain size was achieved through a higher stress field during mixing, lower interfacial tension between the phases, and diminishing concentration of the disperse phase (less coalescence). Higher mixing temperature appeared to reduced domain size by diminishing the interfacial tension. Since the temperature normally goes up during mixing, the high shear blending of polymers with similar viscosities will give the most homogenous mixtures. Further studies in EPDM/BR blends indicated that the driving force for blend homogeneity was related to a
similarity in the viscosities of the two phases under the specific condition of mixing. Because of the large difference in $T_g$ between EPDM and BR it was possible to vary their relative viscosities simply by changing the shear rate and or mixing temperature, the domain size of the disperse phase (or the size of the cocontinuous phases) could thus be altered for the same blend. It was also possible to shift the disperse phase from one polymer to another even though that polymer was the minor component (25%). In this instance, the low viscosity phase actually encapsulate, the high viscosity component, and then becomes continuous. The shape of the domains is more nearly spherical when the high viscosity component is the disperse phase. A softer disperse phase typically gives elongated domains. Extremely large domain size of the BR phase in NR/BR and SBR/BR blends were related to significantly higher viscosity for the BR phase.\textsuperscript{77} Thus incompatibility due to viscosity mismatch which prevents or greatly delays the formation of intimate mixture can be overcome by improving the blending process either by adjusting oil or filler concentration in the two elastomers and by adjusting the individual raw polymer viscosities so that, through much of the process, the effective viscosities of the phases will no longer be mismatched.\textsuperscript{78,79}
Thermodynamic considerations

Thermodynamic incompatibility prevents mixing on a molecular scale. Thermodynamic incompatibility of polymer blends is governed by the well-known Gibbs free energy relation

$$\Delta G = \Delta H - T\Delta S$$

where $\Delta G$ is the change in free energy of mixing, $\Delta H$ the change in enthalpy of mixing, $\Delta S$ the change in entropy of mixing and $T$ the absolute temperature.

Polymer blends exhibit a wide range of morphological states from coarse to fine ones. In addition to the usual possibilities of obtaining separate phases, with various size, shape and geometrical arrangement of inclusions, more complex structures are possible especially in crystalline polymer blends. For such systems specific properties can be expected e.g., for gradient polymers which contain crystalline elements. One of the main aspect of study on polymer blends is the dependence of the mechanical properties on composition. This is due to the fact that these complex systems exhibit a behaviour which does not simply follow the sum of the properties of the components.
It seems interesting to note that until quite recently, relatively very little attention has been given to the interaction of the components in terms of the thermal stability of the composition.  

Polymers can be blended to form a wide variety of random or structural systems with desirable combination of properties but in practice, these theoretically expected properties are not achieved because adhesion of the phases are not created. The most pertinent dynamic properties pertaining to elastomer blends are homogenity of mixing (phase morphology) and cure compatibility.  

The complete miscibility of polymers requires that the free energy of mixing be negative, which can only be achieved by exothermic mixing or a large entropy of mixing. Therefore, most of the blends of elastomers are immiscible because mixing is endothermic and entropic contribution is small, because of the high molecular weights. Hence an almost insignificant positive free energy of interaction is enough to overcome this small entropy of mixing. Thus two polymers do not have to be very dissimilar before they are insoluble in each other and lead to the existence of discrete zones of heterogeneity.
upon mixing. Fortunately miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance but some degree of micro heterogeneity is usually desirable to preserve the individual properties of the respective polymer component. Based on microscopic studies, almost all bulk mixes of elastomer blends are microheterogenous to varying degrees.\textsuperscript{83}

Miscibility implies that a lower free energy is associated with molecular dispersion of the components than with a phase separated morphology. The free energy change (excess free energy) accompanying formation of a strictly random two component mixture can be expressed as\textsuperscript{82,84}

\[
\Delta G_{m} = \frac{V}{K T} \left[ \left( \frac{\phi_i}{V_i N_i} \right) \ln \phi_i + \left( \frac{\phi_j}{V_j N_j} \right) \ln \phi_j + \phi_i \phi_j \frac{x}{V_r} \right]
\]

where \( V \) is the total volume, and \( V_i, N_i \) and \( \phi_i \) the molar volume, degree of polymerisation and the volume fraction of the \( i \)th component respectively. \( V_r \) is an arbitrary reference volume that can be conventionally taken to be equal to the root mean square of the respective molar volumes of the component chain units. The first two terms on the right hand side of the above equation correspond to the ideal, or random mixing entropy. The third term
represents the excess enthalpy. This mixing enthalpy is zero for an ideal mixture, that is, a mixture of molecules that have the same size, shape and in which the intermolecular forces between pairs of like segments of each type, as well as between unlike segments, are all equivalent. Such ideality is not expected in practice, and the excess enthalpy due to mixing is described by the Flory Huggins interaction parameter $X$.

In strictly van der Waals mixtures, phase separation can be induced by increases in one molar mass of the constituents, since the miscibility is of entropic origin. For high polymers, this combinatorial entropy makes a sufficiently small contribution to the free energy such that miscibility is always limited to mixtures in which the components chemically interact and thereby effect a negative excess enthalpy. When such specific interactions are present increases in molecular weight can still effect phase separation. Blends with high exothermic mixing enthalpies, on the other hand, can be expected to remain miscible at the highest of molecular weights.

Cure compatibility

While true miscibility may not be required for good rubber properties, adhesion between the polymer phases
is necessary and the respective interfacial energies are important in this respect.

Covulcanization\textsuperscript{85} was defined in terms of a single network structure including crosslinked macromolecules of both polymers. They should be vulcanized to similar levels with crosslinking across the microdomain interfaces. The nature of the polymer (e.g., unsaturation, polarity) determines curative reactivity which is also influenced by solubility. Vulcanizates with components having similar curative reactivity generally give better properties than those whose components have large difference in this respect\textsuperscript{86,87}

\textbf{Curative diffusion}

Curative diffusion\textsuperscript{88-91} between the domain of an elastomer blend takes place during vulcanization. This process may deplete curatives from one side of the polymer-polymer interface and actually speed up cure on the other side. Thus, there is an interfacial layer of rubber with a different state of cure than the bulk. The net result can be a weaker layer of a rubber at the interface which may reduce adhesion.
Gardiner measured a diffusion gradient \((D)\), which represents the concentration changes as a function of distance and time. His measurements for the diffusion of accelerator (tellurium diethyldithio carbamate) and sulfur from IIR to other elastomers are shown below:

<table>
<thead>
<tr>
<th>Curative</th>
<th>From</th>
<th>To</th>
<th>(D \times 10^7 \text{cm}^2/\text{S})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator (TDDC)</td>
<td>IIR</td>
<td>BR</td>
<td>12.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EPDM</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CR</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBR</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NR</td>
<td>0.70</td>
</tr>
<tr>
<td>Sulfur</td>
<td>IIR</td>
<td>SBR</td>
<td>4.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBR &amp; 50 PHR N700 CB</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NR</td>
<td>2.82</td>
</tr>
</tbody>
</table>

Gardiner emphasised that curative migration is related to diffusion during curing and not transfer during mixing. Curative diffusion was controlled through selective (phase) mixing of curatives into the individual
polymers using specific curative combinations. Cure rate mismatch occurs due to solubility differences and curative migration of ingredients in elastomer blends. Solubilities of curatives in various rubbers at 153°C are shown below.\textsuperscript{85,93,94}

<table>
<thead>
<tr>
<th>Curatives</th>
<th>SBR</th>
<th>EPDM</th>
<th>BR</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>17.3</td>
<td>10.7</td>
<td>16.8</td>
</tr>
<tr>
<td>MBT</td>
<td>5.2</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>TMTD</td>
<td>14.3</td>
<td>5.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

The solubility of the common curatives is greater in highly unsaturated elastomers than in less unsaturated elastomers and migration from the latter to the former may be inevitable even when concentrations are equal initially.\textsuperscript{89} Such migration will be accentuated by higher curative reaction rates in the high diene elastomers, causing excess material to be drawn from the adjacent phase and associated with over and undercure.\textsuperscript{90,57} In such circumstances vulcanizate properties may not approach the level attainable by either of the elastomers alone and will be well below the additive line in terms of their properties.
Blending procedures

The general mixing methods for preparing elastomer blends include, latex, solution, solution and latex, mechanical, mechanochemical and powdered rubber. These methods may be further divided into two general categories of preblending and phase mixing. In the first case, the compounding ingredients are generally added to the premixed polymers in a manner similar to the mixing of a single elastomer. In a phase mix, an attempt is made to control the specific location of filler and or extender oil and curing agents. This is generally accomplished by the preparation of separate masterbatches which are then blended mechanically.

Preblending

This procedure is probably the one most commonly used for mixing of polymer blends in a Banbury. One of the polymers, may first be masticated to improve mixing behaviour and reduce viscosity difference. Evans and Partridge showed that a single stage preblending procedure was a most cost effective method for preparing blends of NBR and halobutyl (CIIR). NBR has been compounded with 25% of the carbon black and two third of the extender oil. This masterbatch was then blended with the CIIR and the remaining carbon black and oil prior to
adding curatives on a mill. It was found that rubber properties are not significantly different for the two compounding procedures. For best results, the polymer components of a blend are usually mixed for a short amount of time prior to addition of the filler and other compounding ingredients. Bristow compared the properties of NR/BR as a function of preblending: addition of ingredients with no preblending, and the blending of separate masterbatch which contained proportionate amounts of the compounding ingredients. No major differences in final compound properties were indicated within comparison. However, no studies were carried out with uneven proportions of compounding ingredients added to the separate masterbatches.

Solution and latex mixing

Latex and solution mixing have both been employed for the preparation of elastomer blends. These methods offer distinct advantages of mixing smaller particle size carbon black in conjunction with cleanliness of operation and better utilisation of mixing facilities. However, the advantages in blend uniformity, if any, would appear to be small. Comparison of latex and solution masterbatches to mixes made in Banbury or on a two roll
mill showed that former gave uniform blends, but roll mixing\textsuperscript{101} was found to be the most effective means of blending masterbatches. The mill mixes were very uniform and indicated lower die swell in comparison to latex blending. However, most rubber properties were found to reflect the overall blend ratios of the polymers and there were no major trends associated with the mixing procedure.

Phase mixing

Separate masterbatches are employed with this type of mixing in order to locate specific types and amounts of curing agents\textsuperscript{85,90,92,102} or filler\textsuperscript{58,59,70,103} in the separate polymer phases. In one of the first studies of this type\textsuperscript{58} solution mixing\textsuperscript{104} was used to prepare NR and BR masterbatches at different carbon black loading. This is a convenient method for difficult-to-mix polymers such as cis 1,4 BR. The masterbatches were subsequently blended in a Banbury to produce tread compounds with variation in carbon black phase distributions. The phase mixing procedure assumes that the carbon black (or other ingredients) will remain in the polymer to which it has been added. But this is not always true since there are specific conditions under which carbon black has been observed to migrate from one polymer to another during mixing.
Covulcanization of elastomer blends\textsuperscript{110}

Several investigators have tried to improve covulcanization of elastomer blends and thereby improve the properties of the blends closely along the additive line with respect to the properties of the two individual elastomers. Improved covulcanization of EPDM/NR blends\textsuperscript{93} was achieved by Woods and Davidson by using a TETD accelerator–lead oxide activator combination. The lead salts of TETD are insoluble in both polar and nonpolar materials, which eliminates the thermodynamic driving force for curative diffusion\textsuperscript{105}. Coran achieved better cure compatibility for EPDM/NR blends by modifying the EPDM with maleic anhydride which permits EPDM to be crosslinked independently with zinc oxide in the accelerated sulfur vulcanizing system. An ionic crosslink network is produced in the EPDM phase. This type of crosslinking is not competitive with the accelerated sulfur system which reacts rapidly with NR compared to conventional NR/EPDM blends, those with the modified EPDM exhibited higher tensile strength and fatigue life along with reduced hysteresis and permanent set, all of which reflect better covulcanization. The maleic anhydride treatment has also been applied to IIR and EPDM by Suma\textsuperscript{106} and coworkers for
improved blending with NR. Elastomer blends can be described in terms of three types of systems.

1. Unvulcanized domains of polymer A in an unvulcanized matrix of polymer B (plastic behaviour).

2. Unvulcanized domains of polymer A in a vulcanized matrix of polymer B (rubber like elasticity but diluted by the A phase).


Zapp obtained interfacial bonding in the CIIR/SBR and CIIR/BR blends through the use of very active thiuram and thiuram tetrasulfide curative systems, and also with bis alkyl phenol polysulfide as sulfur donors. Interfacial bonds were associated with a preponderance of monosulfidic crosslinks. Reinforcing carbon blacks indicated only a minimal effect on the sulfur bond chemistry or in the interfacial bonding. However, covulcanized carbon black loaded blends using a sulfur donor cure system displayed tensile strength and rupture energies which were significantly higher than systems cured with elemental sulfur.
Special mixing techniques

A number of mixing schemes have been developed to control more precisely the different aspects of the overall homogeneity, phase morphology, filler distribution and interfacial interaction of the different components of elastomer blends. Controlled heterogeneity in elastomer blends has been used to improve the green strength of blends of NR with the other elastomers accomplished by blending of separately mixed major and minor components of the blend.

a) Dynamic vulcanization

The concept of dynamic curing was originally developed by Gessler for blends of CIIR and polypropylene. With this mixing technique, the elastomer phase was crosslinked to provide a vulcanizate within a thermoplastic matrix. Dynamically vulcanized blends have been defined as elastomeric alloys (EA) which represents a synergistic combination of an elastomer and thermoplastic. The resultant properties are above those that would be expected for a simple blend of the component polymers. Alloying is primarily chemical in nature with strong interaction between the elastomer and the thermoplastic. Dynamic vulcanization technique has been applied by Coran\textsuperscript{24,105} and
coworkers \textsuperscript{107,108} to enhance properties of elastomer blends. They dynamically vulcanized EPDM/NR blends in which the EPDM was vulcanized into small domains through the use of an EPDM polymer modified with maleic anhydride. Partial dynamic precrosslinking or precuring is one of the recent technique used for NR/IIR blend homogenisation.

b) Compatibilization

The blending of highly incompatible elastomers sometimes be improved by the addition of small amounts of another polymer. Homogeneity \textsuperscript{109} of binary and ternary blends of CR, NBR and EPM. NBR/EPM and CR/EPDM blends much more rapidly when a small amount of chlorinated polyethylene (CM) is added to the mix. The CM can be considered to be a compatibilizing or emulsifying agent which appears to form a skin on the EPM particles. It helps the larger NBR chunks to adhere to them.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

The main objective of the present study is to develop covulcanized elastomer blends such as NR/IIR, NBR/IIR and NBR/EPDM so as to improve their mechanical properties for critical applications.

Natural rubber (NR) maintains its leading position for applications requiring a combination of properties
is poor in air/gas retention properties and its resistance to oxidation and ozone degradation. Butyl rubber has excellent ageing behaviour and resistance to ozone cracking combined with low permeability to air and other gases. Blending and co-curing of NR and IIR is practically impossible due to the large difference in unsaturation between these rubbers. But if these two rubbers can be cocrosslinked the blend may turn out to be a very useful one.

Nitrile rubber (NBR) has excellent oil resistance, but is subject to degradation at high temperature. The high temperature ageing resistance is important for this rubber because of its frequent use in extractive media which often leach out the antioxidants in the vulcanizate. A more practically useful approach to improve the ageing resistance of NBR is by blending it with rubbers such as butyl rubber or by blending it with ethylene propylene ter polymer (EPDM) which has excellent resistance to ozone, oxygen and weathering even without antioxidants and antiozonants without sacrificing nitrile's oil resistance.
The following methods are proposed to be investigated for attaining uniform crosslinking in both elastomer phases and hence improving the mechanical properties of NR/IIR, NBR/IIR and NBR/EPDM blends.

1) Use of a novel compounding sequence

Instead of blending the rubbers first and then adding the compounding ingredients for both the rubbers as is done conventionally, the slower curing rubber of the above blends is proposed to be compounded first with its curing agents and other ingredients.

2) Partial precuring of the slower curing rubber

In order to prevent migration of the curing agents from the slower curing rubber to the faster curing one the slower curing rubber is proposed to be precured or precrosslinked to an optimum level before blending with the faster curing rubber. This procedure may also help to bring down the viscosity mismatch between the constituent elastomers in a blend. The partial precuring is proposed to be done both statically (in an air oven) and dynamically (in an internal mixer) such as Brabender plasticorder or Shaw intermix.
3) Carboxylation of the slower curing rubber

In order to make the nonpolar rubber, polar carboxylation of the nonpolar elastomer is proposed. This may reduce the tendency for curative migration and cure rate imbalance between the two constituent elastomers.

4) Use of a compatibiliser

Use of a polar rubbery compatibiliser such as amine terminated liquid natural rubber (ATNR) is yet another way proposed for improving the mechanical properties of the blend.

5) Evaluation of the efficiency of the above novel methods

In addition to measuring the mechanical properties, the efficiency of the above proposed novel methods for preparing elastomer blends will be investigated by several other techniques such as observing the dispersion of fillers and other ingredients in the blends, by optical microscopy and photomicroscopy, morphology of the blends by SEM studies of the fracture surfaces, measuring the crosslink densities by equilibrium swelling and by measuring the electrical conductivity and permeability of the blends.
The thesis is divided into following chapters:

Chapter I  Introduction
Chapter II  Experimental techniques
Chapter III  
  Part I  Mechanical property improvement of NBR/IIR blends by partial precuring of IIR  
  Part II  Effect of acrylonitrile content on the mechanical properties of NBR/IIR blend
Chapter IV  
  Part I  Studies on NR/IIR blends: Effect of partial dynamic curing of butyl before blending  
  Part II  Use of amine terminated liquid natural rubber as a compatibiliser in NR/NBR blend
Chapter V  
  Part I  Studies on the covulcanization of NBR/EPDM blends  
  Part II  Morphology, permeability, dispersion and conductivity studies of NBR/IIR, NR/IIR and NBR/EPDM blends
Chapter VI  Summary and conclusions.
REFERENCES


42. Dow Corning Corporation Adhesives Age, 14(6), 33 (1971).

43. L. Evans and E.G. Partridge, Meeting ACS Division of Rubber Chemistry (May, 1963).

44. P.J. Corish, Unpublished Work.


