ELASTOMER BLENDS

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ABSTRACT

Blending of elastomers is often used to enhance the performance characteristics of rubber products. This article reviews the thermodynamic principles underlying polymer-polymer miscibility, with special reference to elastomer blends. It discusses the distribution of fillers, additives, and curatives in different phases of the blend and its effect on the properties of the vulcanizate. It describes the different methods used in preparing elastomer blends, with special emphasis on compatibilization. Characterization of blends using optical and electron microscopy, solution properties, thermal and dynamic mechanical methods have been described along with results. The effect of blending on mechanical properties, hysteresis, adhesion and tack, transport properties and electrical conductivity has been discussed. Past attempts for property enhancement by blending elastomers have been reviewed, followed by a discussion of commercial application of elastomer blends.

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I. INTRODUCTION

Development of polymeric materials has largely been driven by the desire to make better products at minimum cost. Since developing new polymeric materials is cost intensive, polymers are often blended to provide a property portfolio required for successful performance of the product. Whereas blending of thermoplastics is of recent origin, elastomer blends have been used for a long time. This is because the rubber products have to meet a set of performance and process requirements, which could be contradictory in nature. For example, a tire compound has to be soft and elastic in order to conform to the road surface. At the same time, it has to be stiff and strong in order to bear load, and be abrasion resistant to provide long service life. Similarly, many mechanical goods, such as seals and ‘O’ rings, have to be soft and conform to the contour of the equipment; but at the same time, they have to undergo minimum compression set in order to perform under high stress over a long period of time. Since different elastomers have different types of responses to stress, blending of selected rubbers has been practiced to meet the need for contradicting sets of properties. Similar contradictory requirements are also required in some plastic products where rubber is added to plastics to provide toughness and prevent failure. Toughening of thermosets and thermoplastics have been practiced over a long period of time through blending of plastics with rubber. In fact, the recent development of thermoplastic elastomers (TPE) can be traced to this need for development of toughened plastics. Many TPEs, such as thermoplastic polyolefins (TPOs) and thermoplastic vulcanizates (TPVs) are special blends, made either in the reactor or in mixing equipment. Even TPEs produced by ionic and condensation polymerization can be construed as blends of different blocks of polymers, covalently bonded to each other. The need for strong interphase bonding is common to both TPEs and rubber blends.

Two prior discussions of rubber blends are included in Science and Technology of Rubber edited by Ehrich and Handbook of Elastomers edited by Bhomik and Stephens.\(^1\) Antony, De and Martin van Duin have reviewed blends of self crosslinking elastomers.\(^2\) However, there is substantial progress in the area of polymer blends, driven by new developments of thermoplastic blends, TPVs and rubber recycling, both fundamental and applied. In this chapter, different aspects of rubber blends will be discussed in a common framework of polymer/polymer miscibility; influence of rubber types on distribution of additives, curatives, and crosslink density; preparation, properties, and characterization of rubber blends. This will be followed by compatibilization, an overview of past work along with some notable applications. The discussion will be limited to blends of elastomers commonly used in the industry and will not include thermoplastic and ionic elastomers. Abbreviations for different rubbers and some accelerators, as noted below, will be often used in place of their full names.

Abbreviations: Natural Rubber (NR), Poly-butadiene Rubber (BR), Synthetic Poly-isoprene (IR), Styrene Butadiene Rubber (SBR), Butyl Rubber (IIR), Chloro-butyl rubber (CIIR), Bromo-butyl Rubber (BIIR), Chloroprene Rubber (CR),
Acrylonitrile-butadiene rubber (NBR), Ethylene Propylene Rubber (EPR), Ethylene-Propylene Diene-Rubber (EPDM), Polyvinyl Chloride (PVC), Tetramethyl Thiuram Disulfide (TMTD), Dibenzothiazyl Disulfide (MBTS).

II. POLYMER—POLYMER MISCIBILITY

The thermodynamic relations involved in mixing polymers in organic solvents, has been successfully derived and used to predict miscibility with reasonable accuracy. Prediction of miscibility of polymer pairs, however, is considerably complicated because the polymer molecules in general are associated with large molecular weight, of the order of hundreds of thousands and because the segments (which are the interacting entities and are connected at each end) are constrained by their neighboring segments. As a result, they cannot be moved to fill any available site in a lattice model, often used for estimating thermodynamic parameters. This is only one example of the complicating differences between polymer molecules and small molecules that must be worked out in achieving successful prediction of polymer—polymer miscibility. The other factors include the small entropy change on mixing, the volume change for mixing, the polydispersity of molecular weight, the heterogeneity in molecular composition (both in homo- and co-polymers) ,the complex morphology ,the slow relaxation of stress and strain and the influence of processing parameters on miscibility.

However, the increasing commercial value of polymer blends has fueled the search for a predictive model for polymer—polymer miscibility. The general understanding of the important factors influencing the miscibility of polymers has improved substantially. Although a generally applicable predictive scheme has not yet been developed, modeling efforts have identified trends and parameters that have provided qualitative judgments on the miscibility under a given set of molecular and processing conditions. In this section, simple thermodynamic models for polymer—polymer miscibility will be discussed with particular reference to elastomer blends.

A. THERMODYNAMIC MODEL AND PREDICTION OF MISCIBILITY

In general, two components (solid, liquid or gas) mix with each other because in the process of mixing, the Gibbs free energy is decreased. However, the change in free energy of a binary mixture (ΔGm) can vary with composition (Figure 1). Complete miscibility requires that ΔGm, the free energy change on mixing is either zero or negative. At the same time, the second differential of ΔG with respect to 0, the volume fraction of component one is less than zero.

![Figure 1](image_url)

**FIG. 1.** — Possible free energy of mixing diagrams for binary mixtures.

In Figure 1, the curve OBP satisfies both conditions for all 0 values and represents a completely miscible binary system. The compositions OD and PE of the curve OCP, satisfy both the
conditions, but the compositions DCE, although satisfying the first condition, fails to satisfy the second. Hence, they represent immiscible states and separate into two phases having different compositions with different volume fractions of components A and B. The system represented by curve OAP is immiscible for all compositions because \( \Delta G_m > 0 \). Temperature and pressure have, of course, substantial effects on Gibbs free energy. Hence, change in these parameters will have significant effect on free energy change. As a result, immiscibility and phase separation do occur either by lowering or by increasing the temperature of a miscible system.

It follows from statistical thermodynamics that change in entropy, \( \Delta S_m \), is directly proportional to the number of distinct configurations or combinations that one can make out of an assembly of \( n_1 \) and \( n_2 \) molecules.

\[
\Delta S_m = k \ln \left( \frac{n_1 + n_2}{n_1! n_2!} \right)
\]

(1)

This is very small for a polymer blend due to the existence of constraints on segmental movement as discussed earlier and as shown in Figure 2. Another contribution to \( \Delta S_m \) is a change in volume on mixing, \( \Delta V_m \). Contraction in volume (negative \( \Delta V_m \)) results in a negative \( \Delta S_m \) and expansion leads to a positive \( \Delta S_m \). This magnitude of \( \Delta S_m \) due to volume change is however very small. The change in enthalpy \( \Delta H_m \), on the other hand, can be viewed as the change in the interaction energy due to substitution of some 1-1 and 2-2 intermolecular interactions for 1-2 interactions in the process of mixing components 1 and 2. These interaction energies arise due to several interaction forces existing between molecules. Conventionally, these are described by the following terms:

- Dispersion forces (non-bonded Van der Waals interactions)
- Dipole-dipole interaction or dipole-induced dipole interaction
- Hydrogen bonding
- Acid-base interaction
- Coulombic interaction.

For a mixture of small molecules, \( \Delta S_m \) is large and can compensate for positive \( \Delta H_m \), leading to zero or negative \( \Delta G_m \), there by, facilitating solubility of one component in another. In considering mixtures of large molecules, such as a polymer, with small molecules (solvent), \( \Delta S_m \) is smaller and may be inadequate to compensate for positive \( \Delta H_m \), leading in many cases to immiscibility of a polymer in a solvent. For polymer—polymer mixtures, where the molecular weights of both components are large, \( \Delta S_m \) becomes even smaller, lowering the potential of offsetting a positive \( \Delta H_m \). Immiscibility then becomes much more likely than miscibility.

Flory and Huggins independently developed the lattice model and derived thermodynamic expressions for the entropy change and enthalpy change accompanying the mixing of a polymer.
with a solvent. The Hildebrand Solubility Parameter concept, widely used for solvent—solvent miscibility, has also been used for polymer—solvent studies because it gives a simple clue for predicting the potential for miscibility of polymers with solvents and swelling of vulcanized rubbers in organic liquids. Flory's lattice model does not adequately describe the miscibility of polymer blends, in part, because it does not take into account the volume change that often accompanies polymer blending. Toward the end of the sixties, Flory modified Prigogine's equation-of-state concept for polymer blends and put forth a new model, usually known as the Flory-Prigogine model. A number of modifications have been offered to improve this model for describing polymer—polymer miscibility, and the phase separation behavior of polymer blends. Where as detailed discussion of these models are beyond the scope of this review, some of the important features will be noted where necessary. Only Flory Huggins model and Hildebrand's solubility parameter model are discussed briefly to provide basic understanding of polymer—polymer miscibility.

B. FLORY-HUGGINS LATTICE MODEL

A basic assumption in the Flory-Huggins lattice model is that a polymer chain consists of a number of equivalent or interchangeable segments. Further, assuming that a polymer solution consists of a three-dimensional lattice and each lattice site is occupied either by a polymer segment or by a solvent molecule, Flory and Huggins calculated the entropy change of mixing as

$$\Delta S_m = -k\left(n_1 \ln n - n_2 \ln n_2\right)$$

where $k$ is Boltzman's constant; $n_1$ and $n_2$ are the number of molecules of polymer and solvent, respectively; and $\varnothing_1$ and $\varnothing_2$ are volume fractions. They also estimated the enthalpy change on mixing, taking into account the change in near neighbor interactions and computed the free energy change on mixing $\Delta G_m$.

$$\frac{\Delta G_m}{V} = kT\left[\frac{\varnothing_1}{V_1} \ln \varnothing_1 + \frac{\varnothing_2}{V_2} \ln \varnothing_2 + \frac{z\Delta W_{12}\varnothing_1\varnothing_2}{V/kT}\right]$$

In this equation, $V$ is the total volume of the solution, and $V_1$ and $V_2$ are molar volumes of solvent and polymer segment, respectively. The term $z\Delta W/kt$ is usually called $\chi$ (chi), the Flory Interaction Parameter. Although $\chi$ is written as a reduced enthalpy term, in practice, $\chi$ is used as a reduced free energy term, dependent on factors such as temperature, composition, and molecular weight distribution, and includes entropy change associated with volume change on mixing as well as inestimable entropy terms arising from the estimation of $\Delta S_m$ based on the lattice model.

For a polymer—polymer blend, one may introduce $\chi_{12}$ for $\chi$ when polymer 1 and polymer 2 are blend components. The equation for free energy change of mixing polymer a with polymer b is given by

$$\frac{\Delta G_{ab}}{V} = kT\left[\left(\frac{\varnothing_1}{V_1} \ln \varnothing_1 + \frac{\varnothing_2}{V_2} \ln \varnothing_2\right) + \frac{\chi_{12}\varnothing_1\varnothing_2}{V_S}\right]$$

Since both $V_1$ and $V_2$ (polymer molar volumes) are very large, $\Delta S_m$, the combinatorial entropy change on mixing, the term in parentheses in Equation 4, is very small. Hence, the sign and the magnitude of $\Delta G_{ab}$ largely depends on $\Delta H_m$ represented by the last term in Equation 4. $V_s$, the statistical average volume of the interacting polymer segment, is much larger in a polymer blend than in a polymer solution, because the connectivity of polymer chains leads to the exclusion of neighboring polymer segments from the domain of others, unless considerable
organization (specific interaction) exists to force them into close configuration. Hence, ΔH_m in a polymer blend is smaller, leading to a smaller value of χ.

The Flory-Huggins model does not provide a priori, a method for predicting the value of χ. In working with polymer solutions, χ is experimentally determined by measuring the free energy change as a function of temperature and composition by osmotic pressure, light scattering, and viscosity measurements. A large database for χ is available for polymer-solvent systems. χ for polymer blends are obtained from the study of phase separation; and some analytical techniques including small angle neutron scattering and inverse gas liquid chromatography. Very limited data is available for polymer-polymer interaction parameters. Tables I and II present some χ values both for polymer-solvent and polymer-polymer systems to illustrate the magnitude and dependence on structural factors of the interaction parameters. It may be noted that χ for miscible polymer-polymer systems is five to ten times smaller than for polymer-solvent systems.

**Table I**

**Polymer-Solvent Interaction Parameters**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Interaction Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Cyclohexane</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.40</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>Chloroform</td>
<td>0.38</td>
</tr>
<tr>
<td>Polyvinyl acetate</td>
<td>Methyl ethyl ketone</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Dioxane</td>
<td>0.41</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>Tetrahydrofuran</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>Methyl ethyl ketone</td>
<td>0.40</td>
</tr>
<tr>
<td>Polydimethyl siloxane</td>
<td>Cyclohexane</td>
<td>0.40</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Acetone</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Dioxane</td>
<td>0.38</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>Benzene</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Carbon tetrachloride</td>
<td>0.38</td>
</tr>
<tr>
<td>Polyoxyethylene</td>
<td>Water</td>
<td>0.45</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>Benzene</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Table II**

**Polymer-Polymer Interaction Parameters**

<table>
<thead>
<tr>
<th>Polymer I</th>
<th>Polymer II</th>
<th>Interaction Parameter</th>
<th>Method of Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Polymethyl methacrylate</td>
<td>0.014</td>
<td>Second virial coefficient</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>0.01</td>
<td>Phase separation</td>
</tr>
<tr>
<td>Polyphenylene oxide</td>
<td>Polystyrene</td>
<td>-0.1</td>
<td>Phase separation</td>
</tr>
<tr>
<td>Polyphenylene oxide</td>
<td>Poly (o-chlorostyrene)</td>
<td>0.03</td>
<td>Phase separation</td>
</tr>
</tbody>
</table>
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Polyphenylene oxide Poly (o-fluorostyrene) 0.09 Phase separation

Deuterated polystyrene Polyphenylene oxide -0.275 Neutron scattering

Chlorinated polyethylene Polymethyl methacrylate 0.07 Phase separation

C. SOLUBILITY PARAMETER AND INTERACTION PARAMETER

Earlier, Hildebrand and Scott\(^5\) had developed a theoretical expression for regular solutions of nonelectrolytes. A regular solution is defined as one where \(\Delta V_m = 0\), \(\Delta H_m\) is positive and \(\Delta S_m = n_1 \ln X_1 + n_2 \ln X_2\) (i.e., only combinatorial entropy). Assuming that a solution process involves replacing similar molecules with dissimilar ones, they developed a relationship, between \(\Delta H_m\) and the square root of the energy of vaporization, usually known as the solubility parameter \(\delta\). This is given by the following equation

\[
\Delta H_m / V_1 = K (\delta_1 - \delta_2)^2 \Omega_1 \Omega_2
\]

(5)

In this equation, \(V_1\) is the average molar volume of the two solvents, \(K\) is a constant close to 1, \(\delta_1, \Omega_1\), and \(\delta_2, \Omega_2\) are solubility parameter and volume fraction of component 1 and 2, respectively. This term is quite similar to the last term in Equation 4 that represent \(\Delta H_m\). Both are energy terms. As a result of this similarity, there have been frequent attempts in the past to replace \(kT\delta^2\) with a function of \((\delta_1 - \delta_2)^2\) and to estimate \(\Delta H_m\) from a knowledge of the solubility parameters of polymers and solvents, but with limited success. However, there are some advantages in using solubility parameter concept in predicting polymer, solvent and polymer, polymer miscibility namely:

- For most organic liquids, \(\delta\) can be estimated from an accessible source such as energy of vaporization, boiling point, refractive index, surface tension, etc.
- For most polymers, \(\delta\) has been estimated by measuring solubility, swelling, or viscosity in a number of solvents
- And for most solvents and polymers, \(\delta\) can be estimated by a group contribution approach from the knowledge of the chemical structure and molar volume for the molecules (in case of a liquid) or repeating unit (in case of a polymer) and existing empirical data on group contributions.\(^14\)

Although the solubility parameter of the polymer can be estimated by measuring solubility or swelling in a series of solvents, the correlation is not unequivocal and often breaks down unless the solvents are chosen carefully. Mangaraj et al.\(^15\) found that the solubility parameter correlation holds well only if the solvents being considered belong to a homologous series, having chemical structures similar to the polymer. Hansen et al.\(^16\) have further elaborated the concept and have shown that \(\delta\) can be described in terms of three components: \(\delta_d\), the contribution from dispersion interaction; \(\delta_p\), the contribution from polarity; and \(\delta_h\), the contribution from hydrogen bonding and the total solubility parameter \(\delta_t\) is the root mean square of the three components.

\[
\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2
\]

(6)

\[
(\delta_1 - \delta_2)^2 = \frac{1}{3} (\delta_{d_1} - \delta_{d_2})^2 + \frac{1}{3} (\delta_{p_1} - \delta_{p_2})^2 + \frac{1}{3} (\delta_{h_1} - \delta_{h_2})^2
\]

(7)

The attempt to obtain the three components of \(\delta\) and to apply them for determining polymer-solvent and polymers—polymer miscibility has met limited success. It may be stated that the
solubility parameters concept is limited and can never predict a negative $\Delta H_m$, and it does not predict the very small positive $\Delta H_m$ accurately, often associated with miscible polymer system. However, in spite of this limitation, the solubility parameter concept provides a simple capability for estimating approximate values of $\Delta H_m$, which can assist in understanding polymer—polymer miscibility and predicting the same with very limited accuracy. Managaraj, Allen and Gee et al. have shown that internal pressure ($\delta E/\delta V$)$_p$, a thermodynamic quantity similar to CED, can be measured directly for most polymers and can be used in place of $\delta$.

The basic thermodynamic conditions for phase separation have been discussed earlier. Applying these conditions to Equation 4 (equation for $\Delta G_m$ of a polymer—polymer mixture), it has been shown that two polymers having the same number of repeating units and molecular weights of approximately $10^6$, will exhibit an upper critical solution temperature of 400 K (127 °C) provided $\delta_1$ differs from $\delta_2$ by no more than 0.04 units. Further, it has been shown that for $\delta_2 - \delta_1 = 1 \text{ (cal/cc)}$, the critical molecular weight for immiscibility, $M_c$, at 25 °C is 1,200 and for $\delta_2 - \delta_1 = 0.1$, $M_c$ should be less than 120,000.

Thus, molecular weight plays an important role in polymer—polymer mixing for systems with slightly endothermic mixing. In predicting miscibility, the best that can be done is to match the $\delta$'s of the candidate polymers as closely as possible. A difference of 0.1 or more in $\delta$ values of the polymer pair, can lead to immiscibility.

For polar polymer pairs, chemical moieties in the main chain or side groups interact with each other, providing exothermic heat of mixing and driving force for miscibility. Paul attributes the existence of a number of miscible polymer pairs to exothermic interaction (negative $\Delta H_m$). Exothermic interactions are often referred to as "specific interactions". Specific interactions, in simple terms, evaluates the type of dissimilarities of the two components in polymer blends, as compared to similarity criteria used in solubility parameter approach. In some cases, this interactive dissimilarity is the driving force for miscibility. The term "complementary dissimilarity" is often used in reference to the specific interactions that lead to miscibility. These are "attractive" interactions such as hydrogen bonding, $\pi-\pi$ complexing, and $n-\pi$ complexing. Miscibility of polymer pairs such as PVC/ NBR, Poly(methyl Methacrylate) (PMMA)/ Polyvinyl Fluoride (PVDF), Polystyrene (PS)/ Polyvinyl methyl ether (PVME), EVA/ CR and Styrene Acrylonitrile Copolymer (SAN)/ Polycaprolactone (PCL) is ascribed to the existence of specific interaction and negative enthalpy of mixing. Recently, Karasz and McKnight have developed a model based on segmental interaction parameters in co-polymers. Each segment in a co-polymer is associated with an entropic term, which is configurational and an enthalpic term due to chemical interaction. Depending on the magnitude of these interactions, a pair of co-polymers can be miscible or immiscible, or can act as a compatibilizer for an immiscible blend. Paul and Barlow have suggested that a net mixing exotherm may exist in a blend due to dilution of more unfavorable interactions, where at least one component in the blend is a co-polymer.

In the late 50's Prigogine and Mahet developed a statistical mechanical molecular theory of solutions for simple molecules based on PVT relations, Flory extended this theory to polymer solutions in terms of reduced temperature, pressure and volume concepts. This approach usually known as Flory Prigogine Model is similar to that used for describing an equation of state for miscibility and phase separation phenomena for small molecules and polymer solution. Flory Prigogine model has been expounded by McMaster and later by Patterson et al. to describe polymer—polymer miscibility and phase separation as a function of temperature and pressure. They have emphasized on the role of free volume and volume change on mixing. Another model which take into account poly-dispersity in molecular weight, heterogeneity in chemical composition, stiffness of the main chain, and free volume change arising from vacancies in lattice model, has been developed by Koningsveld. Sanchez modified Flory Huggins model to include negative heat and volume change on mixing. These theoretical approaches have been discussed in detail.
by many authors including Paul,\textsuperscript{20} Walsh\textsuperscript{21} and Mangaraj.\textsuperscript{13}

In summary, it may be stated that for a pair of polymers, where the difference in solubility parameter is small (\(\leq 0.1\)), or where specific interaction exists, there is a potential for miscibility. Otherwise, most polymer blends are immiscible, except at very extreme compositions. Elastomers, which are polymers with low glass transition temperatures and high molecular weight also follow the above rule. The solubility parameters of typical elastomers\textsuperscript{12} are given in Table III. Although some of the diene elastomers are miscible with each other, miscibility of diene rubbers with highly polar rubbers such as nitrile, carboxylated nitrile, and neoprene is questionable.

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Solubility Parameter</th>
<th>Total</th>
<th>Hansen Solubility Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile butadiene (NBR)</td>
<td>18.0</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>Copolymer -18%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-25%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-39%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.0</td>
<td>10.4</td>
<td>18.6</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>16.3</td>
<td>8.0</td>
<td>16.0</td>
</tr>
<tr>
<td>-isoprene (IIR) co-polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polychloroprene (CR)</td>
<td>18.7</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.9</td>
<td>9.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene</td>
<td>16.0</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>Polydimethyl</td>
<td>15</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>Siloxane elastomer (SR)</td>
<td>16.4</td>
<td>8.1</td>
<td>16</td>
</tr>
<tr>
<td>Styrene - butadiene co-polymer</td>
<td>17.0</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.1</td>
<td>8.9</td>
<td>17.4</td>
</tr>
<tr>
<td>Polyethyl acrylate</td>
<td>18.6</td>
<td>9.2</td>
<td>16.4</td>
</tr>
<tr>
<td>Ethylene - propylene-co-polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene propylene–diene (norbornene) terpolymer</td>
<td>17.1</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Ethylene–vinyl acetate</td>
<td>16.5</td>
<td>8.1</td>
<td>14.5</td>
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<tr>
<td>Polyisobutylene</td>
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<td>8.2</td>
<td>16.6</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>16.9</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Natural rubber</td>
<td>21</td>
<td>16.2</td>
<td>10.8</td>
</tr>
</tbody>
</table>

One of the predominant effect of polymer—polymer immiscibility is phase separation, i.e. when the two polymers exist in discrete domains both in the liquid and solid phases. Figure 3a illustrates phase diagram of a polymer blend as a function of temperature.\textsuperscript{20} The diagram on the right hand side represents a miscible polymer blend, having single glass transition temperature. As the temperature is increased, the two polymers which are immiscible at lower temperature, become miscible. The temperature for complete miscibility, the upper critical solution tempera-
ture (UCST) is lower for blend composition at both ends than in the middle. The dark line represents upper critical solution temperature. As the temperature is raised further, one often finds themiscible polymer blends turn cloudy, indicating the existence of lower critical solution temperature (LCST). In other words, above this temperature, miscible blends of certain composition become immiscible and separate into two phases. It has been suggested that most polymer pairs, which are miscible due to negative enthalpy change on mixing, become immiscible at higher temperatures, possibly due to a change in the nature of ΔHm. Other factors which may contribute to the existence of LCST are negative volume change on mixing and positive excess heat capacities. Further, it has been observed that LCST behavior is not affected by molecular weight above a certain critical molecular weight for each polymer pair. This confirms that entropic contribution to LCST behavior is minimal. Paul et al. have shown that cloud temperature for a series of polyvinylidene fluoride blends is directly proportional to the magnitude of the negative heat of mixing.

The significance of phase separation is quite important to elastomer blends. Most elastomers in their commercial form are high molecular weight polymers. They are masticated in a Banbury or open roll mixer so that their molecular weights are sufficiently lowered to provide good mixing due to enhanced entropy change. In the case of elastomer blends, the state of miscibility is stabilized by crosslinking at higher temperatures. However, if the temperature of vulcanization is either greater than LCST or lower than UCST, the uniform dispersion of the two elastomers will be hampered, giving an inhomogeneous blend.

![Liquid-Liquid Phase Diagram and Solid-Liquid Transition Behavior](image)

**FIG. 3(a,b).** Possible phase and transition behavior in polymer blends.

The dissimilarity in polarity which leads to immiscibility of elastomer blends also affects other aspects of elastomer technology, particularly the distribution of compounding ingredients prior to vulcanization and the crosslink density, once the compound is vulcanized.

Recently Schuster, Issel and Peterseim obtained accurate solubility parameters of four elastomers, namely NR, IIR, EPDM and CisBR, using inverse gas liquid chromatography. The δ values agree with δ values obtained by other methods and empirical calculation using group contributions. It is claimed that the experimental δ values are accurate up to the second place of decimal and can be used to estimate the critical molecular weight (Mc) above which phase separation takes place. The estimated Mc values for all rubbers are far below the molecular weights of the commonly used rubber grades used in the industry. Further, the interfacial tension, $\Gamma \sim \chi^{1/2}$, $= (\delta_1 - \delta_3)^2 RT$ calculated from solubility parameter values (δ1, δ3) is high for most blends. The
dispersion of the minor component in the matrix should be coarse. This has been confirmed by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The results of this study also show that the critical of difference for good miscibility of a polymer blend = 0.2 (cal/cc)? which translates to an $\chi$ value of approximately 0.04 at room temperature.

Due to partial shielding of the double bonds and higher polarizability as well as easier accessibility of cis 1,4 butadiene segments in SBR, $\delta$ increases with increase in styrene content and decreases with BR content. Analysis of temperature dependence of $\delta$, shows that where as for EPDM, NR, BR and emulsion SBR, the $\delta$ versus temperature curves are parallel with each other. Those for NR and vinyl BR intersect, indicating the potential for phase separation. Since the two elastomers were fairly similar to each other, including their rheological characteristics, the domain size of the minor component 'd' should be proportional to $\Delta \delta$, the difference in solubility parameters of the component rubbers. Domain size 'd' for NR blends with BR, Vinyl BR, E-SBR. Solution SBR and EPDM are given by a relation, $d = 1260(\Delta \delta - 0.204)$. For NR/SBR blends with different styrene content, $\Delta \delta$ changes and the distribution of the domains become heterogeneous, finally breaking into binary distribution. Further, the aspect ratio 'AR', of the domains in the blend (given by equation below) is increased if the degree of compatibility is decreased.

$$AR = 0.671 + 0.178 \Delta \delta$$

The authors have extended this correlation to partitioning of fillers between two elastomers in a blend. If the filler surface is associated with an energy density $\delta_a$ corresponding to an interfacial tension, then the distribution of the filler through adsorption on the filler surface should be proportional to $[\delta_a - \delta_2] - (\delta_a - \delta_1) = (\delta_2 - \delta_1)$, the solubility parameter difference. Based on this hypothesis, the affinity sequence of carbon black for rubber (at constant chain length) would follow the priority rule.

$$\text{SBR} > \text{cis 1,4BR} > \text{cis 1.4 IR} = \text{NR}$$

Earlier, Banaccai P Li used inverse gas chromatography to estimate $\chi$ and $\delta$ for a number of elastomer with limited accuracy. He was able to explain the contribution of microstructures, such as vinyl content in BR and styrene content in SBR, towards $\delta$ and the consequences of $\Delta \delta$ on miscibility and morphology of binary blends containing NR, SBR, BR and EPDM. He also measured the temperature dependence of $\delta$ for different rubbers and used them to predict LCST and UCST, as well as domain size and size distribution in phase inversion region.

### III. DISTRIBUTION OF COMPOUNDING INGREDIENTS IN ELASTOMER BLENDS

A variety of ingredients including fillers, plasticizers, processing aid, vulcanizing agents, promoters and antioxidants are mixed with a rubber to carry out effective vulcanization and to provide the required physical properties. In contrast, a thermoplastic is often processed with a few ingredients such as fillers, stabilizers and processing aid. Besides, where as most thermoplastics are processed much above their melting point or glass transition temperature at comparatively low viscosity, rubber compounds are mixed in highly viscous state. It is, therefore, much more difficult to get fair distribution of ingredients in a rubber compound than in a thermoplastic compound. This situation is further complicated for elastomer blends because there may be partition or preferential distribution of one or more ingredients in one component compared to the other, depending on the polarity or surface characteristics of the additive. This may influence the morphology and physical properties of the vulcanized rubber blend appreciably. It is, therefore, important to discuss the potential of uneven distribution of compounding ingredients in elastomer blends and its net effect on physical properties of the compound.

The compounding ingredients fall into two general categories, namely, reactive and inert. Vulcanizing ingredients such as sulfur, accelerators, ultra-accelerators and promoters take part in the curing reaction. Their distribution in the different elastomers in a rubber component is influ-
enced not only by mechanical mixing, but also by their migration to potential active sites. The latter is also controlled by the reactivity of the additives with rubber. In other words, the negative free energy of chemical reaction largely overwhelm the small free energy of physical mixing. Since rubber vulcanization is carried over a long period, four to six minutes, compared to less than a minute in thermoplastic processing, it is likely that the reactive ingredients will be able to migrate on an as-needed basis in the rubber compound. However, when the processing time is small, for example, in injection molding, the likelihood of uneven distribution and uneven cure may exist.

The non-reactive ingredients include fillers, plasticizers, processing aids and antioxidants. The last two are added in small quantities, much below their saturation level. Hence, their distribution ordinarily does not pose any problem. Plasticizers are often liquid. Hence, it is likely that they get a fair opportunity to mix well in the rubber compound. There may be some degree of partitioning of these compounds in the different components of the blends, but the effect of uneven distribution will be minimal.

A. DISTRIBUTION OF FILLERS

Fillers, such as carbon black, silica, talc, calcium carbonate and clay are used in large quantity in a rubber compound. Whereas the last three act mainly as extenders for reducing the cost, carbon black and silica act as reinforcing fillers. In fact, the physical properties of many rubber compounds are very low without an adequate level of such reinforcing fillers. The effect of carbon black loading on physical performance of rubbers has been discussed by Corrish and Palmer26 and by Bulgin and Walker.27 They have found that different rubbers have different responses to filler loading with respect to certain properties. Hence, their fair distribution among the different components in an elastomer blend is very important for successful performance of the rubber compound.

Carbon black is usually prepared by burning hydrocarbons in an oxygen poor environment. The black produced in the continuous process known as channel black is somewhat different from furnace black produced in the batch process. The difference is manifested not only in size, surface area and morphology, but also in the type and concentration of functional groups such as \(-\text{OH}, -\text{COOH}, -\text{SH}, \text{carbonyl} \) etc., on the carbon black surfaces. Hence, the nature and intensity of interaction depends both on the chemical composition of the elastomer as well as on the type and nature of carbon black. Wolf has provided an in depth discussion of the chemical nature of carbon black and its interaction with different rubber types before and after mixing and vulcanization.28

Ayala, Hess et al. have studied carbon black—elastomer interaction for four elastomers, namely styrene butadiene rubber (SBR), natural rubber (NR), butyl rubber (IIR) and nitrile rubber (NBR).29 They also subjected the carbon black to high temperature to study the effect of graphitization on mixing. They used a variety of techniques to study carbon black, including surface area by nitrogen adsorption, (ASTM D3037), dibutyl phthalate absorption (DBPA) by ASTM D2414, moisture absorption and adsorption of model hydrocarbons using inverse gas chromatography (IGC). They compounded 45 phr of five different carbon blacks (N121, N231, N330, N650 and N472) with the four different rubbers, and measured bound rubber content for each compound. They also obtained SIMS spectra of both the carbon blacks and the compounded rubbers. They observed the existence of readily ionizable hydrocarbon fragments such as \(\text{CH}_3^+, \text{C}_2\text{H}_5^+, \text{C}_3\text{H}_5^+ \) and \(\text{C}_4\text{H}_5^+\) at the edge of graphite-like layers that compose carbon black's reactive surface and the subsequent interaction of polymers with the charged species. In addition, they also found \(\text{OH}^-, \text{C}_2\text{H}_4^-, \text{O}^-, \text{CH}^+\) and \(\text{C}^-\) on the surface, which decrease significantly on heat treatment at 1100 °C.

They found a direct correlation between the concentration of the ionized species and bound
rubber content. Further, they observed both these quantities decreased with the increase in heat treatment temperature for carbon black. Subsequently, they measured both static and dynamic properties of the vulcanized compounds and obtained a parameter $\sigma/\eta$, which is a measure of the interaction between carbon black and rubber. $\sigma$ is a measure of the slope of stress—strain curve in the initial linear range (100 to 300% strain) and is largely determined by the strength of the adhesion between rubber and filler. The $\eta$ term is a ratio of dynamic modulus $G'$ at 1% and 25% strain amplitude and measures the intensity of filler—filler interaction or filler networking. The ratio, therefore, gives a relative measure of the intensity of rubber black interaction vis-a-vis filler—filler interaction. Table IV presents $\sigma/\eta$ values for the four rubber compounds containing untreated and heat-treated carbon black. It is evident that the interaction is the highest for SBR followed by NBR, NR and IIR. The interaction with heat-treated blacks is lower than virgin blacks, but follow the same order.

Bound rubber contents (BRC) in different elastomers are presented in Table V. Where as BRC in SBR, NR and NBR are comparable, that in IIR is very small. However, BRC also follows the same relative order as $\sigma/\eta$. Thus, conclusions based on phenomenological studies such as stress—strain behavior confirms the conclusions made from molecular (spectral) studies and bound rubber content. Moisture adsorption and heat of adsorption measurements also showed excellent agreement with $\delta/\eta$ results, correlating within grade but not across the grades. The higher interaction between carbon black and SBR also explains the large increase in tensile strength and modulus as the gum SBR is filled with carbon black. The difference in the degree of interaction between carbon black and different rubbers may lead to non-uniform distribution of carbon black in elastomer blends and the resulting change in their mechanical behavior.

### Table IV

<table>
<thead>
<tr>
<th>Carbon Black</th>
<th>SBR</th>
<th>IIR</th>
<th>NR</th>
<th>NBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.97</td>
<td>1.23</td>
<td>2.15</td>
<td>2.56</td>
</tr>
<tr>
<td>1000 °C</td>
<td>2.78</td>
<td>1.13</td>
<td>1.84</td>
<td>2.37</td>
</tr>
<tr>
<td>1100 °C</td>
<td>2.27</td>
<td>.87</td>
<td>1.69</td>
<td>2.05</td>
</tr>
<tr>
<td>1500 °C</td>
<td>1.10</td>
<td>.29</td>
<td>.64</td>
<td>.86</td>
</tr>
</tbody>
</table>

### Table V

<table>
<thead>
<tr>
<th>Carbon Black</th>
<th>SBR</th>
<th>IIR</th>
<th>NR</th>
<th>NBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>20.4</td>
<td>8.2</td>
<td>26.2</td>
<td>30.2</td>
</tr>
<tr>
<td>HT 1000 °C</td>
<td>18.9</td>
<td>7.4</td>
<td>21.9</td>
<td>29.2</td>
</tr>
<tr>
<td>HT 1100 °C</td>
<td>16.9</td>
<td>0.9</td>
<td>20.3</td>
<td>30.1</td>
</tr>
<tr>
<td>HT 1500 °C</td>
<td>8.3</td>
<td>0</td>
<td>16.2</td>
<td>23.1</td>
</tr>
</tbody>
</table>

Table VI presents the effect of two blacks on the physical properties of a rubber. It is evident that bound rubber content decreases with graphitization and both tensile strength and abrasion resistance decrease with a decrease in BRC. Elongation at break however, changes in the opposite way.

Cullen and coworkers studied the distribution of carbon black in 50/50 blends of different rubbers and found that the black affinity decreases in the order of BR, SBR, CR, NBR, NR, EPDM and IIR. Transfer of black takes place from saturated rubber master batches to those of unsaturated rubbers. These conclusions are in agreement with the findings of Marsh et al. and Sircar and Lamond. Vonwinkel has demonstrated that carbon black accumulates in the BR
phase of NR/BR blend.\textsuperscript{32}

The point of addition of filler, the viscosity of elastomers and the blending method also influence carbon black distribution. Fillers, particularly carbon black, can be preferentially localized in a certain phase by using chemical and thermal manipulation. Smith and coworker have demonstrated that the ability to accept black also depends on the wetting characteristics of the rubber, which can be changed by using suitable surfactant.\textsuperscript{33} Ashida found that when HAF black was added to a preblend of BR/IR, the black concentration was initially greater in the IR phase, but with time of mixing, it gradually decreased to a level lower than that in BR.\textsuperscript{34} When IR was added to a BR master batch containing carbon black, the latter stayed mostly in the BR phase, even after extended time of mixing.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Carbon black A</th>
<th></th>
<th>Carbon black B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Graphitized</td>
<td>Original</td>
<td>Graphitized</td>
</tr>
<tr>
<td>Specific surface area\textsuperscript{b}</td>
<td>M\textsuperscript{2}/g</td>
<td>116</td>
<td>86</td>
<td>108</td>
</tr>
<tr>
<td>Vehicle demand\textsuperscript{c}</td>
<td>Cm\textsuperscript{2}/g</td>
<td>1.72</td>
<td>1.78</td>
<td>1.33</td>
</tr>
<tr>
<td>Bound rubber</td>
<td>%</td>
<td>34.4</td>
<td>5.6</td>
<td>30.6</td>
</tr>
<tr>
<td>Modulus (300%)</td>
<td>Mpa</td>
<td>14.4</td>
<td>3.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Mpa</td>
<td>26.2</td>
<td>23.4</td>
<td>27.6</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>450</td>
<td>730</td>
<td>630</td>
</tr>
<tr>
<td>Hysteresis\textsuperscript{d}, \tan \delta</td>
<td>0.204</td>
<td>0.297</td>
<td>0.238</td>
<td>0.315</td>
</tr>
<tr>
<td>Relative abrasion</td>
<td>%</td>
<td>100</td>
<td>34</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From G. Kraus, "Science and Technology of Rubber," ch. 8, p. 346.
\textsuperscript{b}By N\textsubscript{2} adsorption
\textsuperscript{c}Linseed oil
\textsuperscript{d}Method not specified
\textsuperscript{e}Laboratory test

Bound rubber, which contributes to the physical properties of vulcanizates, is a hard filamentous carbon-rubber phase of restricted mobility and acts like macro-fibers. This causes greater strain amplification in the under-loaded softer phase, thereby increasing molecular slippage and alignments at the phase boundaries. Bound rubber content in a black filled rubber vulcanizate depends on the polarity and mechano-chemical stability of the rubbers. Elastomers which are polar, and which undergo mechano-chemical chain scission more easily during mixing, contains large amounts of bound rubber. BRC increases with increase in filler loading. However, the rate of increase of BRC with filler loading reaches a threshold which is different for different elastomers. BRC also increases with increase in the surface area of the black, which indicates that bound rubber is mainly a manifestation of strong adsorption of rubber on the black surface. However, BRC may be influenced by formation of covalent and pseudo-covalent (hydrogen bonding) between the active groups on carbon black surfaces and those on elastomers.

Like carbon black, amorphous silica is also a reinforcing filler and a part of the rubber is bound to silica during processing. The surface chemistry of both carbon black and silica is illustrated in Figure 4.\textsuperscript{28}
GOODYEAR MEDAL ADDRESS

SURFACE CHEMISTRY

<table>
<thead>
<tr>
<th>Carbon black</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphitic basal planes</strong></td>
<td><strong>Siloxane</strong></td>
</tr>
<tr>
<td><strong>Functional groups:</strong></td>
<td><strong>Silanols:</strong></td>
</tr>
<tr>
<td>* Phenol</td>
<td>* Isolated</td>
</tr>
<tr>
<td>* Ketone</td>
<td>* Geminal</td>
</tr>
<tr>
<td>* Carboxyl</td>
<td>* Pyrone</td>
</tr>
<tr>
<td>* Lactol</td>
<td>* Vicinal</td>
</tr>
<tr>
<td>* Quinone</td>
<td>* Lactone</td>
</tr>
</tbody>
</table>

![Diagram of surface chemistry of carbon blacks and silicas.](image)

FIG. 4. — Surface chemistry of carbon blacks and silicas.

Unlike carbon black, the silica does not have a variety of functional and ionizable groups. Hence, the interaction is largely adsorptive and breaks down easily in ammonia atmosphere. As a result the BRC drops from approximately 20% to about 3%, whereas furnace black-bound rubber content is hardly affected (Table VII). Hence, silica fillers are often treated with silane coupling agent to make them reactive and bond intimately to rubber. A variety of silane coupling agents are available with non polar to polar and reactive functionality. It may be necessary to select the coupling agent to match the polarity of the elastomer. The reactivity of the silane largely depends on the attached alkoxy group. Triethoxy silane appears to be the most promising as a coupling agent amongst the silanes. The reaction between ethoxy groups and rubber takes place in two steps. In the first step, the ethoxy groups react with silanol groups of the filler, followed by crosslinking reaction between the neighboring molecules by forming siloxane bonds. Since all these reactions occur in the rubber matrix containing more than one rubber, the degree of interaction between filler and rubber can be different. The methoxy silanes are also reactive because of less steric hindrance. The distribution of carbon black and silica in the two different components of an elastomer blend has not been investigated in detail. This is possibly because the domain size is very small compared to the size of a filler particle and the filler networks penetrate between several bound rubber gels.

<table>
<thead>
<tr>
<th>Table VII</th>
<th>EFFECT OF AMMONIA TREATMENT ON BRC FOR SBR FILLED WITH CARBON BLACK AND SILICA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler</td>
<td>Treatment</td>
</tr>
<tr>
<td>Carbon black N330</td>
<td>—</td>
</tr>
<tr>
<td>Carbon black N330</td>
<td>ammonia</td>
</tr>
<tr>
<td>Silica (134 m²/g BET)</td>
<td>—</td>
</tr>
<tr>
<td>Silica (134 m²/g BET)</td>
<td>ammonia</td>
</tr>
</tbody>
</table>

Manno, Tripathy and De have carried out in-depth study of carbon black/rubber interaction, particularly using polar rubbers, such as epoxidized natural rubber (ENR) and oxidized carbon black. They suggest that both primary covalent bond and secondary bonds (hydrogen bonding, dipole dipole interaction and dispersion type Vander Wal bonds) exist between carbon black and rubber, which breakdown under dynamic stress. The strong interaction between oxidized carbon black and ENR leads to an eighteen fold increase in B, the molecular interaction parameter in the
Guth Gold relation $E' = E'_o (1 + \alpha V'_f + B\nu^2)$. For non-oxidized carbon black and ENR, the increase in B is six fold. This explains the driving force for the greater portion of carbon black to the polar phase as compared to the non-polar or less polar phase of an elastomer blend.

Klupel, Schuster and Schafer have analyzed carbon black distribution in elastomer blends by measuring the increase in loss modulus maxima in the glass transition region. They found that in an EPDM/BR/N550 compound, carbon black is preferably located in BR phase. In NR/SBR (40% styrene)/N530 blends, the carbon black concentration is higher in the SBR phase.

B. DISTRIBUTION OF CURATIVES

Differential distribution of vulcanizing agents such as sulfur, accelerator and ultra accelerator in sulfur cure system and peroxide as well as co-agent in a peroxide cure system is possible in elastomer blends, particularly when the two elastomers differ in the concentration of reaction sites such as degree of unsaturation and polarity. This is because sulfur, peroxide, and most accelerators are polar in nature and are likely to partition preferentially into the polar phase.

It was observed by Gardiner that curatives such as sulfur, TMTD, MBTS and DOTG migrate from compounded rubber to uncompounded ones and between compounded rubbers from those with low unsaturation to the ones with high unsaturation even if the initial concentrations are equal. It has been demonstrated that whereas sulfur distribution from NR to SBR is gradual, that from NR to Butyl is sharp at the interface. This is due to large differences of sulfur solubility in NR and IIR compared to that between NR and SBR. MBTS diffusion follows the same trend. However, the difference in distribution is smaller because of the smaller rate of diffusion, contributed by its larger molecular size. This imbalance in sulfur and accelerator concentration leads to over and under cure, which can be avoided to some extent by selecting a proper mixing schedule, master batching or by using curatives where the rate of diffusion is independent of rubber polarity. Amidon and Gencarelli have found that that the use of long chain dithiocarbamates provides more uniform crosslinking in the blends of EPDM and unsaturated rubbers. Similar observations have recently been made for long chain thiram disulfides for co-vulcanization of rubbers of low and high polarity.

Co-vulcanization at the phase interface of a rubber blend is important to provide mechanical compatibility and improved performance. This is best achieved if the cure rates are similar in both phases. Co-vulcanization is difficult in blends of EPDM with high diene elastomers. It is better achieved by using fast accelerators such as thiram di- and tetrasulfides. The interfacial bonds are largely monosulfidic at the initial stage, maturing to polysulfidic as the vulcanization progresses. Yasimura and Fujimoto and later Corrish showed that separate dynamic mechanical peaks observed at the initial stage, merge on continued vulcanization to give a single peak, characteristic of compatible blend. Baranwal and Son have shown that grafting accelerators to component elastomers prior to blending provides improved properties for NR/EPDM blends.

C. DISTRIBUTION OF CROSSLINK DENSITY (CLD)

A variety of analytical techniques has been used to estimate crosslink density in different phases of an elastomer blend. This includes sol-gel analysis, dynamic mechanical thermal analysis (DMA), differential scanning calorimetry, stress-strain measurements, swollen-state NMR spectroscopy, network visualization microscopy, and isopotential swelling. Swollen state NMR spectroscopy provides the best unequivocal estimate of crosslink densities in different phases. The basis of the technique depends on the fact that signals of NMR spectra of polymers are broader than those of simple molecules and the signal width is increased as the polymer is crosslinked due to reduction in chain mobility. Swelling of the vulcanizates permits observation of spectra with sufficient resolution. Figure 5 provides NMR spectra of swollen natural rubber
vulcanizates with different crosslink density. The effect of crosslink density (CLD) on signal width is quantified through the study of signal width as a function of CLD. Since hydrogen atoms of different elastomers are in different environment, the widening of each signal width can be analyzed to give a measure of the crosslink density in different phases of an elastomer blend. This is accomplished by a sophisticated deconvolution process and by the use higher frequency 300 MHz FT spectrometer. Addition of Trimethoxy Silane (TMS) marker in the swelling solvent helps in proper identification of each peak. In case of black filled vulcanizates suitable calibration procedure is used to eliminate the effect of carbon black on the widening of signal width.

![Chemical shift ppm graph](image)

**Fig. 5.** — 300MHz NMR spectra of swollen NR, low and high CLD.

Blends of natural rubber (NR) and nitrile rubber (NBR) with 18% acrylonitrile were first to be investigated in respect of crosslink distribution. When 0.6 phr TMTM accelerator was used, along with 1.5 phr of sulfur for crosslinking at 150 °C, the NR phase had much smaller crosslink density (CLD) than NBR phase. The degree of maldistribution of CLD decreased with decrease in acrylonitrile content (Figure 6). Replacement of sulfur with a sulfur donor bis-alkylto-phenol disulfide (BAPO, 4.5 phr) reduced the maldistribution, but could not eliminate. Similar behavior was observed when TMTD was used as an accelerator in place of TMTM. However, when NN	extsuperscript{1} diocyledyl NN	extsuperscript{1} di-isopropyl thiuram disulfide (ODIP) was used as an accelerator, crosslinking of NR phase increased substantially. It has been suggested that sulfur, TMTD and TMTM being polar are retained in a much higher concentration in polar NBR phase than in NR phase. Further phase sizes being smaller at low acrylonitrile content also allow the diffusion of the curatives following their differential solubility in the two phases. ODIP, on the other hand, is less polar. As a result, the NR phase retains a higher concentration of ODIP, resulting in higher CLD. The solubility parameter δ of ODIP is between the δ's of NR and NBR (16.7 and 21.3 MPa	extsuperscript{1/2}). With a NBR with 41% acrylonitrile, most ODIP is retained in NR phase, and the CLD of NBR phase is very small. The dramatic decrease in CLD is also caused by greater phase sizes, which inhibits migration of curatives during the crosslinking process. When NBR (41% acrylonitrile) and NR blends are vulcanized with sulphenamides, such as CBS, MBS and TBBS at equimolar level, the CLD distribution is more uniform, albeit, small difference. However, if a small amount of either TMTD or ODIP is added to sulphenamides, the distribution becomes unsymmetrical (Figure 7). It has been further demonstrated that the physical properties of the
blend vulcanizates are much higher when CLD is uniformly distributed in both phases instead of being unevenly distributed, even for blends with high nitrile content (Table VIII). In other words, whereas interphase bondings are strong in spite of differences in polarity, the difference in CLD between the phases weakens the system as a whole. It has also been demonstrated that the use of carbon black as filler, does not alter the situation appreciably. The asymmetrically crosslinked blends continue to be weaker than the uniformly crosslinked blend, in spite of carbon black content.

![Graph](image)

**Fig. 6.** Dependence of crosslink density in the NR (Σ) and NBR (χ) phases of gum NR/NBR (18% acrylonitrile) blends on NBR content.

![Graph](image)

**Fig. 7.** Crosslink distribution in gum vulcanizates of 50:50 NR: NBR blends distribution of crosslink density.

Similar maldistribution is also observed in elastomer blends differing in the degree of unsaturation. When a 50 : 50 NR/EPDM blend was crosslinked with sulfur and mercaptobenzothiazole (MBT), the CLD in NR phase was found to commensurate with 85% of the curatives. This was due to preferential migration of curatives into NR phase because of the greater rate of consumption of sulfur (higher degree of unsaturation) in the NR phase. With very small phase size, approximately 1μm, the rate of diffusion was very high. When 60 : 40 blends of NR/EPDM with two different norbornene content (1.1% and 10.5%) were vulcanized, the EPDM phase for the first blend (low NB) was hardly crosslinked. The CLD in the second EPDM phase was higher compared to the first one, but lower than the CLD in NR phase. When curing was prolonged, no additional vulcanization took place in EPDM phase, but CLD decreased in NR phase due to reversion.

Numerous efforts have been made to improve CLD of EPDM phase in elastomer blends. Coran found that the use of maleic anhydride grafted EPDM when blended with NR provides higher modulus and tensile strength than ungrafted EPDM/ NR blends and he attributed this to the formation of ionic crosslinks formed by ZnO with maleic anhydride. Later on, it has been found that maleic anhydride modification also increases CLD in EPDM phase, possibly because
of greater polarity leading to favorable distribution of curatives. When EPDM was modified with a small amount (5-milimole phr) of N chlorothio-N Methyl p-toluene sulfonamide, the crosslink density in EPDM increased from 4 to 20 mole/m³ and the tensile strength of the blend increased significantly. It was suggested that MBT (2-mercapro benzothiazole) displaces N methyl p-toluene sulfonamide forming a crosslink precursor, which helps in establishing crosslinks in the EPDM phases. Similar crosslink precursors have been formed by the modification EPDM by sulfur donors such as thiodimorpholine, dithiodicaprolactam and BAPD, which help in enhancing CLD in EPDM phase. Small increases in crosslink density, about 0.3 wt. %, to 20-25 mole/m³, are sufficient to provide adequate tensile strength to the blend. Recently, Ravishankar et al. have shown that the rate of peroxide crosslinking of EPDM is increased by replacing norborne with vinyl norborne due to increase in unsaturation.

CLD maldistribution is observed even in blends of comparable unsaturation and polarity. A blend of NR/BR when cured with 1 phr dicumyl peroxide gives a CLD ratio 0.77. It decreases to 0.4 at 3 phr peroxide. However, when the same blend was cured with sulfur/ TMTD system, CLD ratio with 0.33, which was increased to 0.5 by the addition of 0.5 phr MBTS. These differences are attributed to the difference in the efficiency of crosslinking at the double bond in the two polymers. In fact, the CLD in BR phase was close to the CLD in pure BR for the same level of peroxide. Similarly, in sulfur cure system, the higher CLD in BR phase was attributed to more efficient conversion of the sulfur to crosslinks by TMTD. The disparity in CLD appeared to increase with increasing curative level and with increasing BR content of the blend (Table VIII). An extensive investigation of blends of synthetic polyisoprene (IR) with BR along with a variety of sulfur cure systems, shows that the disparity in CLD is the greatest in S/TMTD/MBT and S/CBS cure systems. Although overall CLD decreased with increased BR content, the ratio remained the same. In the initial phase, crosslink formation occurred in the NR phase, but final CLD was higher in the BR phase. Tensile strength was higher for cure systems where CLD ratio was close to unity (Table VIII). In a NR/BR blend with s/sulphenamide (CBS, MBS, TBBS), it was found that the BR phase is more crosslinked at the early stage. Subsequently the crosslink formation was more rapid in NR phase, leading to higher ratio of CLD (approaching 1 only in the case of S/TBBS). However, cure reversion takes place for NR and the ratio decreases again at longer curing.

Incorporation of all the curatives in the IR phase in IR/NR blend, prior to blending prevented maldistribution of CLD and contributed to higher strength for the blend.

**Table VIII**

<table>
<thead>
<tr>
<th>Accelerator(s)*, phr</th>
<th>Crosslink distribution ( n_{\text{NR}} : n_{\text{BR}} )</th>
<th>Tensile strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBBS, 1.17</td>
<td>1.01</td>
<td>25.8</td>
</tr>
<tr>
<td>TBBS, 1.17/TMTD, 0.1</td>
<td>0.67</td>
<td>17.8</td>
</tr>
<tr>
<td>TBBS, 1.17/ODIP, 0.37</td>
<td>1.75</td>
<td>19.8</td>
</tr>
</tbody>
</table>

* With 1.3 phr sulfur.
TABLE IX
CROSSLINK DISTRIBUTION IN NR/cis-BR (94% cis-1,4) BLENDS VULCANIZED WITH 1 : 1 S : MBS

<table>
<thead>
<tr>
<th>NR:BR</th>
<th>Sulfur, phr</th>
<th>( \eta_{\text{phys}} ), mol/m^3</th>
<th>Ratio ( \eta_{\text{phys}}^{\text{NR}} : \eta_{\text{phys}}^{\text{BR}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>0.6</td>
<td>41.3</td>
<td>44.0</td>
</tr>
<tr>
<td>2:1</td>
<td>0.9</td>
<td>46.0</td>
<td>45.3</td>
</tr>
<tr>
<td>2:1</td>
<td>1.4</td>
<td>64.3</td>
<td>70.3</td>
</tr>
<tr>
<td>2:1</td>
<td>1.9</td>
<td>66.7</td>
<td>75.7</td>
</tr>
<tr>
<td>1:1</td>
<td>0.6</td>
<td>22.4</td>
<td>50.0</td>
</tr>
<tr>
<td>1:1</td>
<td>0.9</td>
<td>52.4</td>
<td>59.2</td>
</tr>
<tr>
<td>1:1</td>
<td>1.4</td>
<td>65.0</td>
<td>75.1</td>
</tr>
<tr>
<td>1:1</td>
<td>1.9</td>
<td>&gt;79</td>
<td>&gt;92</td>
</tr>
<tr>
<td>1:2</td>
<td>0.6</td>
<td>36.9</td>
<td>36.4</td>
</tr>
<tr>
<td>1:2</td>
<td>0.9</td>
<td>53.0</td>
<td>62.7</td>
</tr>
<tr>
<td>1:2</td>
<td>1.4</td>
<td>60.3</td>
<td>76.7</td>
</tr>
<tr>
<td>1:2</td>
<td>1.9</td>
<td>&gt;79</td>
<td>&gt;92</td>
</tr>
</tbody>
</table>

Fig. 8. — Dependence of CLD in NR/BR blends as a function of cure time.

D. DISTRIBUTION OF OTHER NON-REACTIVE INGREDIENTS

Diffusion of plasticizers and processing oil depend largely on solubility parameters of the elastomers. The relative solubility and diffusivity can be estimated, at least approximately using empirical models, given by Mangaraj et al.\textsuperscript{42} This may help in selecting plasticizers and processing aids for a rubber blend. Distribution of antioxidants and antiozonants probably follows the same trend as plasticizers. It has been shown by Lewis et al. that antioxidants such as NN’ diphenyl p-phenylene diamine migrate from EPDM to NR and SBR phases during vulcanization.\textsuperscript{43} It may be useful to select less polar antioxidants for rubber blends with different levels of unsaturation.

Goonetilleke and Billingham have measured solubility and diffusivity of a series of phenolic antioxidants (AO) in NR and polyethylene.\textsuperscript{44} They found that where as solubility depends largely on the additive size ,polymer—AO interaction and melting point of the AO, diffusivity depends largely on the size of the additive molecule and its polarity. The polar AOs diffuse faster than non-polar ones. Greater polarity and smaller size give higher diffusivity.
E. CONCLUSION

In conclusion, all the elastomer blend systems studied so far show a tendency to have an uneven distribution of CLD between the phases. The factors contributing to uneven distribution are differences in polarity, unsaturation and reactivity at the crosslink site. Ease of diffusion of curatives from one phase to the other, which depends on the domain size and diffusivity, D, in each phase also controls the CLD distribution. Different curatives, depending on their polarity (solubility parameter), and reactivity affect the distribution differently. Uniform distribution of CLD helps in improving physical properties of the blend. Hence, judicious choice of curatives can bring about even distribution and improved physicals for the blend. The same can be achieved by minor modification of one of the blend component or by using a special processing step. In a recent article, Vanden and Noordermee have discussed various approaches including sequence of carbon black addition, mixing procedure and selection of proper curative to achieve uniform crosslinking in a blend.50

IV. PREPARATION OF ELASTOMER BLENDS

Elastomer blends are prepared by three different techniques, namely latex, solution, and dry blending. The following provides brief description of blending technology.

A. LATEX BLENDING

The technique has the potential for fine dispersion of the components, because the particles in the latex are very fine and they are dispersed well with the help of surfactants (soap). Coagulation is carried out by decreasing the soap concentration. Angrove has reviewed latex blending, with particular attention to processing, properties and economics.51 Blackley and Charnock have investigated latex blending of NR/BR. Japan Synthetic Rubber, JSR, has a patent which claims that BR blends with SBR or NR, when prepared by latex blending, gives a homogeneous dispersion of carbon black.51 However, latex blending does not provide any cost advantage, since coagulation, removal of water and drying are cost intensive processes.

B. SOLUTION BLENDING

This technique gives coarser particles because the low solution viscosity promotes rapid coalescence. Keyte and Walters observed this phenomenon in NR/SBR blends,52 when they found a coarse mixture of layers of SBR encapsulated with NR when the two rubbers were solution blended. This situation is comparable to that found in the preliminary stage of mill blending. Even rapid precipitating with a non-solvent gave the same type of macro heterogeneity. This may be due to different saturation limits of the two components in the non-solvent. Shunda et al. prepared a satisfactory blend of NR/BR by precipitating with methanol from solution.53 Blending during solution polymerization provides better dispersion than solution blending, because the polymer molecules are formed in situ, thereby providing a chance for blending at molecular level. The process also helps the incorporation of black into the master batch. Rapid evaporation of the solvent is necessary to prevent coagulation. However the drying process needs adequate amount of energy, approximately 15J/cc which makes solution blending costly.

Combination of solution and latex blending is also used for master-batching. In the Columbian hydro-dispersion process, the elastomer blend is kept in solution and the lack is dispersed in water. The black transfers into the solution quite rapidly and produces a master batch. In the reverse process, the black dispersed in a solvent is blended with latex. This also provides a good dispersion.
C. DRY BLENDING

Most elastomer blends are prepared by dry blending in a mill, Banbury or extruder. This is because the process is economical and facilitates the incorporation of compounding ingredients in one operation. Further blending is facilitated by mastication, which not only reduces viscosity but under proper condition provides opportunity for reaction (block or graft polymerization) and co-vulcanization. Better dispersion is achieved when the viscosity of the two components are close. Masterbatching is necessary when the two components cure at different rates. Evans and Patridge however suggest that incorporation of all the ingredients in one step is desirable. Shunda, who prepared the same blend both in Banbury and open roll mill suggests that the mill provides better dispersion. Mechano-chemical blending, where reactive monomers are added to one or both components provide better blends due to in-situ formation of graft or block copolymers that act as compatibilizer. Angier and Watson have shown that inter-polymerization takes place in blends of NR, CR, NBR, SBR and BR when mastication is carried out in nitrogen atmosphere.

V. CHARACTERIZATION OF ELASTOMER BLENDS

Characterization of elastomer includes identification of the component elastomers as well as their miscibility, compatibility and morphology. A variety of methods including solubility, spectroscopy, microscopy, thermo-analytical techniques and dynamic mechanical and electrical measurements have been used to characterize elastomer blends. Hess, Herd and Vegavari have made an excellent review of the techniques used for characterization of elastomer blends, including the description of each technique and their application in evaluating a large number of blends.

A. MICROSCOPY

1. Optical Microscopy. — Phase contrast optical microscopy is used to differentiate components in gum and lightly colored blends. However, most elastomer compounds contain large volume of carbon black. Hence they are mostly characterized by electron microscopy. A variety of methods, including swelling, etching and freezing are used to improve contrast between different phases. Marsh et al. immersed the blend in a selected solvent such that one of the components swells much more than the other. The swollen specimen was stretched and the solvent was evaporated. The swollen phase got more thinned after solvent evaporation and provided the necessary contrast. Hess and Chirico used differential pyrolysis to selectively remove one of the components, making its domains more transmissive than the domains of more stable component. Staining by Osmium tetroxide has been extensively used to improve phase contrast for blends containing unsaturated elastomers, since it stains only the rubbers with double bond. Moore; Keskuka and Traylor have used this technique to study the morphology of rubber toughened polystyrene and Miyamoto et al. to study that of styrene-butadiene—styrene block co-polymers. Smith and Andries have used two new techniques to help microtoming thin sections, namely the ebonite technology where the rubber is cured and hardened by a mixture of sulfur, sulfenamide and zinc stearate and the cryogenic technique where the specimens are frozen below their glass transition temperature before microtoming.

2. Electron Microscopy. — Whereas, scanning electron microscopy (SEM) is used to characterize surface, transmission electron microscopy (TEM) is used to examine morphological features in the bulk. TEM scan of SMR/ SBR blends (Figure 9) reveals that the boundaries between the two phases (matrix and dispersion) are quite distinct and the carbon black is mainly confined to NR phase. In similar scans of NR/BIR blend, the white inclusions are not as distinct as in the
previous case, indicating some extent of mixing of the two polymers. TEM micrograph for 130°C cured NR/BIIR/IIR blend shows the presence of large butyl domains with small bromobutyl inclusions. Again, carbon black is mainly confined to NR phase. The micrograph for 170 °C cured specimen shows that carbon black is confined to NR phase and well separated from butyl inclusions. This indicates that at high temperature, butyl dispersion coalesces into uniform and distinct domains, and is incompatible, with both NR and BIIR.

![TEM image of SMR/SBR blends](image)

**FIG. 9.** — TEM image of SMR/SBR blends: (a) neat (b) 10 phr black.

Sax and Ottino have used digital image analysis, where the scanning electron micrograph is converted into an array, in which each element represents the optical density of a small section of the image with a spatial resolution as small as 10 microns. The computer reads the particle size and particle size distribution of the dispersed phase for each element and provides a quantitative description of the morphology.

3. Elastic Scattering. — Elastic scattering which includes light, X-ray and small angle neutron scattering have been used to monitor both solution behavior and blend morphology. In homogeneous system, the thermal fluctuation in density and composition generates light, X-ray and neutron scattering, which can be used to characterize blend composition. Extrapolated zero angle scattering provides a measure of polymer interaction parameters. In multiphase polymer blends, the size and spatial distribution of phases can be estimated from the angle distribution of scattering. Glatter and Kratky as well as Higgins and Stein have developed special methods to use scattering techniques to study the morphology of multiphase rubber blends. Lewis and Price have used X-ray scattering to study the morphology of styrene butadiene styrene (SBS) block copolymers and Douy and Gallot have used the same to study the organized structure of butadiene styrene butadiene (BSB) co-polymers.

Atomic Force Microscopy, initially developed by Binning and coworkers, is currently being used to image both conducting and insulating surfaces of elastomers and their blends. It acts like a miniature surface profilometer with high resolution and provides topographical information in micro scale. Hence they are capable of analyzing morphological features, of both blends and composites. AFM images of 50/50 NR/EPDM blend shows EPDM phase is lighter in contrast to NR because of its greater height from the surface. The advantages of AFM include higher resolution, simplicity of specimen preparation and greater versatility in operation.

Light scattering is mainly used for studying polymer solution and to study polymer configuration in dilute solution. It has also been used to study the morphology of block co-polymers and to monitor the broadening of interface in BR-SBR blends. Small angle X-ray scattering which measures fluctuations in electron density has been used to measure particle size and particle size distribution in BR/CR blend. Small angle neutron scattering, in which neutrons in the
range 2 to 20 Å are used, measures the scattering contrast associated with short range nucleus-neutron interaction. This technique can be used to measure thermodynamic interaction parameters, domain size as well as the dimensions of the polymer chain. Kirste and Lehnen measured the increase in the coil size of blends of high molecular weight and low molecular weight silicone resins. Coalescence of BR domains in CR matrix has been followed by neutron scattering. This technique can also be used to study crystallization in polymer blends.

Infrared (IR) spectroscopy has also been used to characterize elastomer blends. Clark and Scott used IR spectroscopy along with chemical analysis to characterize sulfur-cured blends. Yamagi et al. used aliquots from carbon disulfide digestion of a NR, SBR and BR blend and characterized the composition using standard blends of known composition. Recently, De, Bhownik and coworkers have used IR spectroscopy extensively to characterize reactive and non reactive elastomer blends.

B. SOLUTION BEHAVIOR

As mentioned earlier, the solubility of polymers are limited to solvents, which have interaction parameter χ is less than 0.4 and two polymers are not miscible unless the differences in their interaction parameter in the same solvent is less than 0.05. Hence, if two polymers are not soluble in a common solvent, then they are immiscible. This criteria is used to test the potential for a miscible blend. Usually attempts are made to make 10% solution of the two components in a selected solvent at room temperature and study the clarity. Voyutsky used this technique to test compatibility of two rubbers and Britenbach and Wolf studied the effect of molecular weight on miscibility. Braun and Rehag however found that where as a mixture of BR and polypentenamer is miscible in toluene, electron micrographs clearly indicated heterogeneity in films cast from dilute solution.

Feldman and Rusu used dilute solution viscosity measurement to study the compatibility of PVC with other polymers and Menin and Roux used gel permeation chromatography to determine the composition of a blend of BR with IIR.

Solubility parameters of elastomers have been estimated, from the knowledge of their solubility and swelling (in case of vulcanized rubber), phase separation and intrinsic viscosity in a number of solvents. This knowledge can be used to infer the composition of the blends. Alternately, the interaction parameters can be estimated using gas liquid chromatography. Miscibility of the two polymers may be predicted if the interaction parameter is less than 0.05. However it may be pointed out that any inference made from solution behavior can not be extrapolated to predict the behavior accurately. It has been found that many blends of NR, BR and SBR do not follow the prediction based on the results of their solution studies.

C. THERMAL TECHNIQUES

Thermo-analytical techniques such as Differential Scanning Calorimetry (DSC) and Differential Thermogravimetry (TGA) have been used for analysis of polymer blends, including elastomer blends. Whereas DSC measures changes in specific heat of the system as a function of temperature, TGA measures weight loss at different temperatures. The specific heat of different polymers is different. Being a second degree derivative, it undergoes appreciable change as the polymer undergoes phase transition from solid to leathery state or liquid state. Hence, changes in the slope of Cp versus T (absolute temperature), provides a measure of glass transition (Tg) and melting transition (Tm) temperatures. In case of a blend, if the two components of a blend are miscible, then it will have a single Tg or Tm. An immiscible blend will have two Tg s, which may be the same or slightly different from the Tg of the individual components. Compatible blends, on the other-hand, may have a broad Tg, indicating some interaction between the two
polymers. Further for a pair of miscible polymers, the specific heat changes should be additive, i.e. $\Delta C_{pb} = w_1 C_{p1} + w_2 C_{p2}$, where $C_{pb}$ denotes specific heat of the blend; $C_{p1}$ and $w_1$ denote specific heat change and weight fraction of polymer 1; and $C_{p2}$ and $w_2$ denote the same of polymer 2. Hence $C_p$ changes can be used to estimate weight fraction of each component in a miscible polymer blend. The estimation can also be used to identify immiscible blends.

Ng and Chee measured specific heat changes for blends of natural rubber (SMR) and epoxidized natural rubber (ENR) and blends of ENRs with different degrees of epoxidation\textsuperscript{79} (Figure 10). Their results follow Fox equation, which gives $T_g$ of the co-polymer $T_g^{-1} = T_g^{-1} + (T_g^{-1} - T_g^{-1}) W_c$; where $T_g$ is the transition temperature of epoxidized rubber co-polymer. And $T_g$ and $T_g r$ are the transition temperatures for pure epoxidized and unepoxidized rubber, respectively; and $W_c$ is the weight fraction of the epoxidized component in the blend. Each ENR has a characteristic $T_g$ that increases with increasing degree of epoxidation. Further, each ENR blend with NR show two transition temperatures, close to the $T_g$ of individual components. Similar behavior is shown by blends of Standard Malaysian Rubber (SMR) with ENR. Even NR is not miscible with ENR, where the rubber has been epoxidized by only ten percent. The authors have used “mean field theory” principles for phase separation, which gives polymer polymer interaction parameter $\chi_{ab}$ for a blend of two random co-polymers designated $A \times B_1-x$ and $AyB_1-y$, $\chi_{bc} = (x-y)^2 \chi_{ab}$; where $x$ and $y$ are volume fractions of each component; and $\chi_{ab}$ is segment—segment interaction parameters. The critical $\chi_{ab}$, for which phase separation takes place is controlled by the degrees of polymerization of each co-polymer. The latter for both polymers was approximately $4.4 \times 10^3$ and $\chi_{ab} 0.05$, which is close to the value of 0.078 obtained by Kallitisis and Kaltoglu.\textsuperscript{80}

![DSC scans of SMR, ENR and their blends (scan rate 20 °C/min).](image)

Amaree, Katbab and Ahafarajolla\textsuperscript{81} have used differential thermo-gravimetric analysis (TGA) to study SBR/BR blends commonly used for tire tread compound.\textsuperscript{81} Figure 11 presents the TGA scan of SBR and SBR/BR 50:50 blend, measured at low heating rates, 20 °C/minute. They are almost the same and, hence, it is impossible to distinguish between the pure component and the blend. However, at a higher heating rates (80 °C/minute), BR degrades in two distinct weight loss steps (Fig. 11). The first is almost exclusively due to volatile depolymerization prod-
ucts and the second is due to the degradation of a residue resulting from cyclized and crosslinked BR. The occurrence of cyclization and cis-trans isomerization of polybutadiene has been confirmed by NMR and IR studies.\textsuperscript{82} Figure 12 gives the TGA thermogram of different BR/SBR blends containing 60% carbon black, taken at a heating rate of 80 °C/minute. They have two distinct peaks and each peak is characterized by a peak height, namely $h_1$ and $h_2$. The ratio between the two peak heights is used as a criteria for analyzing BR in SBR/BR blends. The ratio approaches 1 as BR content in the blend approaches zero, and increases above 1 as BR content increases. However, other factors, such as the carbon black content and uniformity of mixing, also affect this ratio. The ratio $h_1 / h_2$ increases as carbon black content decreases. Comparison of the experimental values of BR content with those estimated from peak height ratio gave a fairly good agreement. It is, therefore, apparent that DTA can be used to study thermal degradation of elastomers and elastomer blends, particularly if the two base resins thermally degrade following two different mechanisms. This will also provide a means of characterizing blend composition.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig11.png}
\caption{DTG curve of BR, SBR and NBR.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig12.png}
\caption{DTG curve of BR/SBR blend.}
\end{figure}

Sircar, Galaska et al. has recently reviewed the application of thermal techniques, such as DSC, TGA, DMA, DEA and TMA (thermomechanical analyzer), for determining Tg of elastomers and their blends.\textsuperscript{83} They have shown that the change in the derivative of DSC curves (\textit{d}Cp/\textit{d}T) provides a better measure of not only Tg but also various secondary transitions and multiple transitions as seen in a heterogeneous blend. Figure 13 gives the DSC trace and the derivative trace as a function of temperature for a SBR/BR blend before and after vulcanization. Where as the DSC curves do not clearly show the melting transition (-108 °C) of BR in the
unvulcanized blend, the derivative curve clearly indicates the same. Presence of carbon black and large SBR fraction is blamed for this suppression. However, the Tg of SBR is seen both in DSC and derivative traces. After vulcanization, the blend exhibits only one Tg in DSC trace around -83°C, close to the value calculated from Fox equation. However, two distinct peaks are observed in the derivative trace, at -92 and -82°C indicating limited heterogeneity even in the vulcanized state. This is in agreement with earlier findings. The reduction in domain size leads to a broadening of the Tg peak giving a single intermediate Tg. Thus analysis of derivative curve provides better information on the morphology of rubber blends, as well as a mutual interaction between the two rubbers. However, the high amplification required for resolution of overlying peaks causes considerable amount of machine noise. Table X presents glass transition temperatures of a number of common elastomers obtained by thermal techniques. Landi had used thermal analysis to study the phase stability in heterogeneous compositions of NBR.84 Roland and Lee had also used DSC to analyze the morphology of polyurethane block co-polymers.85

Fig. 13. — DSC and derivative traces of 60/40 uncured SBR/BR blends.

Fig. 14. — DSC and derivative traces of cured SBR/BR blends.

It may be mentioned that the difference between actual Tg and the one estimated by Fox equation can be used as a measure of incompatibility in a rubber blend. Presence of carbon black
and co-vulcanization may change the Tg by a few degrees.

In addition to DSC and TGA, other thermo-analytical methods such as Thermo Mechanical Analysis (TMA) and Thermal Simulated Current (TSC) have been used to measure Tg of elastomer blends. Where as the former measures change in coefficient of thermal expansion, the latter measures the depolarization current associated with the relaxation of trapped molecular motions. Both the techniques have been discussed by Sircar and Galaska and Tg measured by different methods have been compared.83

In conclusion, it may be mentioned that thermal techniques are powerful tools to study heterogeneity in elastomer blends, but appearance of single Tg cannot be accepted as unambiguous evidence of miscibility. DSC is incapable of distinguishing two peaks if they are within 10 °C from each other, particularly when the domain sizes are very small and when the two rubbers in the blend are very similar in chemical composition such as NR/BR or BR/SBR. A small change in Tg is essentially mechanical and cannot be construed as evidence of heterogeneity.

**Table X**

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Uncured Tg, Onset</th>
<th>1/2 height</th>
<th>DSC peak (Deriv.), Onset</th>
<th>Cured Tg, Onset</th>
<th>1/2 height</th>
<th>DSC peak (Deriv.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR (SMR 5)</td>
<td>-61.4</td>
<td>-59.5</td>
<td>-59.5</td>
<td>-58.5</td>
<td>-55.6</td>
<td>-55.6</td>
</tr>
<tr>
<td>IR (Natsyn 2200)</td>
<td>-60.7</td>
<td>-58.0</td>
<td>-58.2</td>
<td>-60.1</td>
<td>-57.8</td>
<td>-57.8</td>
</tr>
<tr>
<td>SBR 1500</td>
<td>-52.2</td>
<td>-48.8</td>
<td>-50.4</td>
<td>-46.6</td>
<td>-42.7</td>
<td>-43.7</td>
</tr>
<tr>
<td>BR, budene 1207</td>
<td>-103</td>
<td>-98.1</td>
<td>-98.9</td>
<td>-100.0</td>
<td>-96.3</td>
<td>-96.6</td>
</tr>
<tr>
<td>NBR nipol 1042</td>
<td>-34.3</td>
<td>-24.3</td>
<td>-26.8</td>
<td>-26.6</td>
<td>-18.9</td>
<td>-21.6</td>
</tr>
<tr>
<td>II, butyl 077</td>
<td>-62.8</td>
<td>-59.4</td>
<td>-59.4</td>
<td>-62.8</td>
<td>-58.5</td>
<td>-58.8</td>
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<tr>
<td>CR, neoprene GN</td>
<td>-38.3</td>
<td>-35.9</td>
<td>-36.0</td>
<td>-35.8</td>
<td>-33.0</td>
<td>-33.3</td>
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<tr>
<td>EPDM</td>
<td>-65.4</td>
<td>-62.2</td>
<td>-62.4</td>
<td>-63.3</td>
<td>-59.9</td>
<td>-59.6</td>
</tr>
</tbody>
</table>

(Nordel 1040)

*Heating rate, 20 °C/min; annealed at 100 °C for 10 min in nitrogen. quench cooled to -120 °C, held for 10 minutes before ramping.

**D. DYNAMIC MECHANICAL ANALYSIS (DMA)**

When a polymeric material is subjected to dynamic mechanical stress, the stress—strain curve is not reversible, because a part of the energy is lost due to internal friction. The energy loss is appreciable for most elastomeric material and is used for controlling fatigue and vibration isolation. Hence, the dynamic modulus is expressed as a complex G, consisting of two components, storage modulus G' and the loss modulus G". The storage modulus represents the energy stored to cause subsequent deformation and the loss modulus represents the energy lost due to hysteresis. The ratio of the two G'/G" is called loss factor or tan δ and represents internal friction or damping. When a polymer undergoes a primary or secondary transition, internal motions are set up and both loss modulus as well as loss factor undergoes appreciable change. Hence, DMA provides information on change in internal damping as well as glass transition temperature of polymeric materials and their blends. Dynamic mechanical analyzers operate both as a function of temperature and frequency to provide information on subtle molecular motions in polymers that causes change in G' and tan δ. Figure 15 presents typical DMA curves for carbon black loaded elastomer compounds Thermal scans to estimate Tg etc. are carried out at low frequency, usually at 1 Hz.

Lavalle and Samus et al. have made an in-depth analysis of the miscibility of PVC and
polyurethane (PU) elastomer. Two types of PU were used, one containing polyether soft segment and the other based on polyester. DMA was used along with other techniques to measure miscibility. They found that area under loss modulus curve and tanδ curve, both good measures of damping, are maximum at the composition corresponding to phase inversion where the blend develops co-continuous morphology. Further it was observed that where as the polyester PU/ PVC blend exhibits such synergistic improvement on damping, the polyether PU blend did not do so. This shows the two components in the second blend are not miscible or compatible. The PV containing more polar polyester soft segment is miscible with PVC.87

Roland has examined the miscibility of poly-isoprene with syndiotactic poly vinyl methyl ether (PVE). He has used DMA to examine their miscibility. The dynamic loss tangent measured in tension shows two distinct peaks, at −58 °C and the other at −10 °C, showing that the two polymers are not miscible. This is in contrast to the blend of IR with atactic PVE, which is miscible. This has been explained on the basis that the particular stereo-chemical arrangement of the pendant ether groups prohibit Vanderwaals interaction needed for thermal mixing. The frequency dependence of loss modulus has been related to inter-chain friction and its effect on misciblity.88

![Typical DMA scan showing changes in E', E'' and tanδ for carbon black filled BR.](image)

Mazich and Samus, et al., have used DMA, along with transmission/ electron microscopy to study the blend of natural rubber (NR) with polyisobutene (IIR) and bromobutyl (BIIR) rubber, as well as their carbon black filled versions.88 The DMA scan of 80/20/20 blend of NR/BIIR/IIR with 25 parts carbon black from −90 to 20 °C at 0.1 and 10 Hz., showed that the temperatures corresponding to high frequency peak is greater than the low frequency peak as expected. Whereas, the low frequency peak appears to have a single point of inflexion, the high frequency peak has a broad shoulder indicating a multiphase structure. Comparison with DMA of individual polymers showed that the -45° peak corresponds to the modified Tg of NR and the shoulder corresponds to the behavior of the two butyls.

They also found that in the DMA scans of NR and binary blends of NR with bromobutyl rubber with 25% carbon black, the NR peak for NR/ BIIR blend matches the peak for pure NR and the higher shoulder region indicates the presence of butyl rubber. Replacement of IR with BIIR provides similar DMA scan with smaller NR peak and slightly higher shoulder. The large reduction in the NR peak is due to larger phase size in the incompatible blend. The DMA scan of the tertiary blend at three different temperatures shows that whereas the scans for 130 °C and
150 °C cured blends are super-imposable, the 120 °C cured blend appear different. This difference was attributed to different morphological changes taking place due to curing at different temperatures.

VI. COMPATIBILIZATION OF RUBBER BLENDS

Since most polymers, including elastomers, are immiscible with each other, their blends undergo phase separation with poor adhesion between the matrix and dispersed phase. The properties of such blends are often poorer than the individual components. At the same time, it is often desired to combine the performance characteristics of two or more polymers, to develop high performance products. This is accomplished by compatibilizing the blend, either by adding a third component, called compatibilizer, or by enhancing the interaction of the two component polymers, chemically or mechanically. The role of the compatibilizer is to:
- Reduce interfacial energy and improve adhesion between phases
- Achieve finer dispersion during mixing and
- Stabilize the fine dispersion against agglomeration during processing and through out the service life.

The ultimate objective is to land on a morphology that will allow smooth stress transfer from one phase to the other and allow the product to resist failure under multiple stress. In case of elastomer blends, compatibilization may be necessary to aid uniform distribution of fillers, curatives and plasticizers to obtain a morphologically and mechanically sound product.90

A. COMPATIBILIZATION AND THE BLENDING PROCESS

The first step in blend development is mixing the components. Whereas extruders, particularly twin screw extruders are used for blending thermoplastics in their melt phase, or leathery phase, elastomers, as mentioned earlier, are blended by Banbury or open roll mixers. In both cases, the materials are exposed to shearing stress. The size of the dispersed phase is determined by the balance between drop break up and coalescence process, which, in turn, is governed by the type and severity of the stress, interfacial tension between the two phases and the rheological characteristics of the components.91 The shape of the dispersed phase may be deformed from spheres to platelets following a smearing action of the shear field (Figure 16). The need for reducing potential energy initiates agglomeration process which is less severe if the interfacial tension is small. Addition of a small amount of compatibilizer acts like a solid emulsifier and stabilizes the droplets, thereby reducing the dispersed phase size. The component with major surface acts as matrix. In case of equimolar blends, the one with lower viscosity try to encapsulate the one with higher viscosity. It has been observed and theoretically established that better dispersion is achieved when both phases have similar viscosity. The essential condition for forming co-continuous phase is

\[ \eta_1 \phi_1 / \eta_2 \phi_2 = 1 \]

where \( \eta_1, \eta_2 \) and \( \phi_1, \phi_2 \) are the viscosity and weight fraction of each component in the blend.92 Co-continuous phase provides the special morphology, where the two phases behave in tandem and the blend exhibits the best properties of the two components. On the other hand, if the viscosity of the minor phase is high, it does not get broken down into small dispersed particles. Mangaraj and Heggs et al. have shown that the component with high viscosity can be better dispersed, if it is premixed with a plasticizer to bring the viscosity closer to that of the low viscosity component.93 They obtained a fine dispersion of Nylon 66 in its blend with high molecular weight polycarbonate by plasticizing the latter with polycaprolactone. The cooling rate of the blend also influences the particle size. Whereas rapid cooling provides smaller particles, slower cooling allows ripening (agglomeration) and generates large particles.94
In case of elastomers, the initial molecular weights are very high. The molecular weight is lowered by mechanochemical chain scission, by using sharp cutting edges of a kneader mixer, such as Banbury or the knife cutting in open roll mixer. The molecular weight degradation is aided by using peptizers, which probably end caps the degraded chains. Plasticizers are added to reduce the viscosity and processing aid to improve flow, but in spite of that, many elastomer blends separate into different phases after the mixing is completed, possibly due to re-agglomeration. Hence, compatibilization is essential to reduce the size of the dispersed phase, and to provide a blend with co-continuous phase.

Fig. 16. — Proposed mechanism for initial morphology development in polymer blends.

B. METHODS OF COMPATIBILIZATION

Compatibilization is carried out in non-reactive and reactive mode.\textsuperscript{95} In nonreactive mode, an external polymeric material is added, such as a co-polymer, preferably a block co-polymer. Diblock co-polymers are favored, although in many instances triblock co-polymers, such as styrene-ethylene-butylene-styrene triblock co-polymer, have been used. Random and graft co-polymers have also been used to that effect. The essential function of a compatibilizer is to wet the interface between the two phases. Block and graft co-polymers achieve this by spreading at the interface and mixing with both phases through their component parts, which are similar to one phase or the other. In reactive mode, block and graft polymers are formed in situ, during mixing of the two components.

1. Non-ReactiveCompatibilization. — Block and graft co-polymers, available commercially or prepared prior to blending are often used for compatibilization. Asaletha and Thomas have made an in-depth study of compatibilization of natural rubber (NR) and polystyrene (PS) blends, using a graft co-polymer of styrene unto natural rubber.\textsuperscript{96} The latter was prepared by mixing an emulsion of styrene monomer and NR latex, and exposing the solution to γ radiation from cobalt 60 source. They monitored the effect of molecular weight of the homopolymer and graft co-polymer, concentration of graft co-polymer, and the sequence of addition on compatibilization efficiency. Films were prepared by casting from solution in different solvents and their morphology as well as the stress—strain behavior, were used as criteria of compatibilization. The dispersed phase size was found to decrease with increasing amounts of co-polymer compatibilizer (Figure
17). The mechanical properties, such as tensile strength and modulus also increased (Table XI) with addition of compatibilizer. Both the decrease in domain size and improvement in physical properties leveled off at a critical co-polymer volume fraction, $\phi_c$, which is sufficient to saturate the interphase surfaces. The authors used Noolandi and Herg's thermodynamic model\textsuperscript{97} to calculate the critical volume fraction, $\phi_c$, of the compatibilizer for different blend ratios. Figure 18 plots the experimental values of particle size reduction against volume fraction of compatibilizer $\phi_c$.\textsuperscript{97} It shows that the critical volume fraction is close to 0.005 to 0.02%. They also used Taylor's equation, which provides critical Weber number, (We), where particles are unable to undergo any further deformation.

**FIG. 17.** — Optical photographs of 60/40 NR/PS films cast from CCl$_4$ and CHCl$_3$, containing variable amounts of graft co-polymer: (a) 0% graft from CHCl$_3$; (b) 1.2% graft from CHCl$_3$; (c) 0% graft from CCl$_4$; (d) 1.2% graft from CCl$_4$.

### TABLE XI
**MECHANICAL PROPERTIES OF 50/50 NR/PS BLENDS**

<table>
<thead>
<tr>
<th>Wt. % graft polymer</th>
<th>Stress at % elongation (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile impact strength (J/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15%</td>
<td>30%</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.24</td>
<td>1.78</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.54</td>
<td>1.82</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.96</td>
<td>2.05</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>1.99</td>
<td>2.28</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.56</td>
<td>2.78</td>
<td>3.24</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>3.20</td>
<td>3.47</td>
<td>3.88</td>
<td></td>
</tr>
</tbody>
</table>
They used We and experimental data on the size of dispersed particles to calculate the critical surface area $\Sigma_c$ and the critical mass, $m_c$, of the co-polymer required to saturate the interface. They found $\Sigma_c$ has some important features, namely:

- $\Sigma_c$ increases as the molecular weight of the homopolymer decreases
- $\Sigma_c$ depends on the mode of addition of the co-polymer. It is higher for a two step process, where the co-polymer is preblended with the dispersed phase than when it is mixed with both components in one step
- $\Sigma_c$ is greater for higher co-polymer molecular weight.

In addition, $\Sigma_c$ also depends on the solvent from which the blend film is cast, good solvent providing greater $\Sigma_c$ compared to poor solvent. As mentioned earlier, the co-polymer could conform on the phase interface in three different configurations and each conformation will lead to a particular surface area occupied by the compatibilizer molecule. Comparison of the experimental $\Sigma_c$ with theoretical $\Sigma_c$ for the three conformations, showed that the actual conformation is one, in which a portion of the co-polymer remains at the interface and the rest penetrates into corresponding homopolymer phases. As the molecular weight of the co-polymer increases, chain entanglement does not allow the molecule to penetrate further into the homopolymer phases, resulting in an increase of interfacial thickness and reduction of interfacial tension $\gamma_{12}$. Thus, as the compatibilizer molecular weight increases, better compatibilization takes place. However, chemical structures of the blocks, also play an important role. Hence, optimization of molecular weight and chemical composition is desirable for developing sound commercial blend.

In earlier work, Reiss and co-workers had shown that for polyisoprene polystyrene blend, block co-polymers provide better compatibilization than graft co-polymers and solubilization of compatibilizer by phases takes place when the molecular weight of the blend components are comparable or smaller than the molecular weight of corresponding block in the compatibilizer. Teysie and coworkers had examined the compatibilizing action of many co-polymers, concluded that the structure and the molecular weight of the co-polymer control the efficiency of compatibilization and tapered block co-polymers are more effective as compatibilizer than linear block co-polymers. Gailard and coworkers found that addition of styrene-butadiene block co-polymers reduced the interfacial tension in PS/BR blends. Coran and Patel, during their inves-
tigation on thermoplastic elastomers based on blending of polypropylene with several elastomers, found that parameters such as critical surface tension for wetting the interface, critical entanglement spacing, crystallinity and tensile strength of the hard phase, determine the mechanical properties of the blends.\textsuperscript{100} Leibler, Noolandi and Herg, who have developed the thermodynamic basis for co-polymer compatibilization, suggest that reduction of interfacial tension takes place due to adsorption of the co-polymer at the interface and an asymmetric co-polymer is less efficient than a symmetric one.\textsuperscript{101} It may, however, be noted that block and graft co-polymers are costly, and compatibilization based on their use adds to the cost of the blend.

2. Reactive Compatibilization. — Compatibilization, which is carried out during the blending process by adding a reactive material, either as a blend component or as a reactive third component, is classified as reactive compatibilization. The classical example of reactive compatibilization is DuPont’s production of super tough nylon by blending nylon with MA-g-EPDM, maleic anhydride grafted EPDM.\textsuperscript{102} The maleic anhydride reacts with amine end groups forming a co-polymer of nylon-EPDM, which compatibilizes the two phases.

Blending of nylon with functionalized elastomers has been carried out by several authors. Ide and Hasegawa blended MA grafted PP and styrene-methacrylic acid co-polymer to nylon\textsuperscript{103} for making nylon PP and nylon/polystyrene blends. Han et al. studied the blending of nylon 6 with a series of functionalized rubbers, particularly the effect of blending on morphology, rheology and physical properties.\textsuperscript{104} Cimino et al. studied the blends of nylon 6 with EP rubbers and MA functionalized EP rubbers.\textsuperscript{105} McKnight et al. studied the morphology of blends of nylon 6 with ethylene methacrylic acid co-polymers.\textsuperscript{106} Recently, Scott and Macosko have carried out an in-depth investigation of MA-grafted EPDM/ nylon 6 blend.\textsuperscript{107} The MA-g-EPDM used for this investigation contained 0.7 wt. % MA and 76 wt. % ethylene. Zytel 330, a polyamide with amine end groups was blended with MA-g-EPDM in a Haake Rheomix 600 with Haake System 90 drive, at 200 °C and 50 RPM. After seven minutes of mixing, the material was taken out and molded into 3.2mm slabs for subsequent characterization by DTA and SEM. Similar experiments were carried with EPDM/nylon system to provide a control. Figures 19 and 20 present the torque and temperature versus time for mixing of the two compounds. The higher torque and temperature for the reactive blend indicates the existence of coupling reaction leading to higher molecular weight, greater viscosity and heat buildup. Reaction exotherm contributes less than five percent of the total temperature build up. The rest is due to exotherm of the coupling reaction. The temperature rise during mixing also affects the torque readings and morphology. The latter was examined by SEM for both nonreactive and reactive blends using samples microtomed at −100 °C with a diamond knife followed by removal of rubber by exposing the fractured samples to hot xylene. The authors calculated the diameters of the dispersion particles from the knowledge of Torque, viscosity ratio $\gamma$ and temperature during blending.
Figure 21 presents SEM micrographs for non-reactive blends and Figure 22 represents those for reactive blends with 20 and 50 percent (w/w) EPDM. The reduction in the particle size is evident for the reactive blends, with 25 and 50 percent rubber. The morphology is co-continuous. The particle diameters at different rubber loading are reported in Table XII. Scott and Macosko used experimental values of shear stress, temperature, torque and viscosity ratio to calculate the ratio \( d_1/d_2 \), where \( d_1 \) is the average diameter of the particles in the reactive blend; and \( d_2 \) that of the non-reactive blend. The experimental values are compared with calculated values in Table XII. The smaller values for experimental \( d_1/d_2 \) illustrates the effect of interfacial tension reduction and particle coalescence rate, which was not taken into account in theoretical calculation. In addition to reducing particle size, the increase in concentration of the reactive functionality narrows the distribution of particle size, contributing to greater homogeneity.

Reactive compatibilization is also carried out by adding a reactive monomer or compound, which in the presence of a catalyst, can react with one or both phases providing a graft co-polymer in situ that act as a compatibilizer. Beaty and coworkers added methylmethacrylate and peroxide to waste plastics (containing PE, PP, PS and PET) which homogenized the blend very effectively.\textsuperscript{108}

Reactive processing has been frequently used to bring about compatibilization of immisci-
ble blends. Recently, Lambla and Seadan have compatibilized a blend of nylon and polyethylene by interfacial grafting and simultaneous crosslinking. Two monomers, namely maleic anhydride and 1-undecenal, were used along with a variety of peroxides. The blends were initially carried out with Haake rheocord and subsequently in a twin screw extruder. The blends were characterized by IR, DMA and stress—strain measurements. Physical properties improved substantially and the improvement was greater the higher the peroxide content.\textsuperscript{109}

![Fig. 21. SEM of fracture surface: (a) PA/EP nonreactive blend with 20 wt.-\% rubber; (b) PA/EP nonreactive blend with 50 wt.-\% rubber.](image)

![Fig. 22. SEM of fracture surface: (a) PA/EP reactive blend with 20 wt.-\% rubber; (b) after extraction with xylene of PA/EP-MA reactive blend with 20 wt.-\% rubber; (c) PA/EP-MA reactive blend with 50 wt.-\% rubber.](image)

<table>
<thead>
<tr>
<th>Table XII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis of Dispersed Phase Size in Blends with 20 wt.-% Rubber for the Functionality Concentration Study</td>
</tr>
<tr>
<td>EP-MA in rubber (wt. fraction)</td>
</tr>
<tr>
<td>0.00</td>
</tr>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>0.03</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>1.00</td>
</tr>
</tbody>
</table>

Reactive compatibilization has also been used in the development of thermoplastic elastomers. Coran and Patel studied the use of polyolefins modified by phenolic, triethylene tetramine and chlorine as reactive compatibilizer in polyolefin-nitrile rubber blend.\textsuperscript{110} The polyolefin-rubber block co-polymer, which was formed in situ, acted as compatibilizer for the immiscible blend of polyolefins and nitrile rubber.

Impact modification of thermoset composites, based on the use of carboxy terminated
polybutadiene (CTBN) and amine-terminated polybutadiene (ATBN) can be classified as reactive compatibilization. This route is preferred over external compatibilizer because it is low cost and more efficient. However, one has to select the reactive component so that it is fully reacted during mixing cycle, reacts within processing window and does not produce any liquid or volatile byproducts, which are difficult to remove.

3. *Compatibilization by Surface Activation*. — Chemical modification of particle surface aids compatibilization by inducing chemical and physical interaction between the two phases. This process is particularly important in scrap tire recycling. Cryogenically ground tire materials, when surface modified by exposure to reactive gases or chemicals, develop functional groups on the surface and can be blended with virgin plastics and rubber compounds to produce composites with good physical properties. Mangaraj has reviewed the use of surface activation in scrap tire recycling.\textsuperscript{111} Bauman et al. has demonstrated that surface treatment of plastics and rubber improves mechanical properties of their blends.\textsuperscript{112} Surface treatment can be carried out, either exposing the polymer to a reactive gas, vapor or liquid. When EPDM scrap was ground into fine powder and treated with a mixture of SO\textsubscript{2} (40%), fluorine (1%) and nitrogen (59%) at room temperature, and the powder was blended with thermoplastic polyurethane (PU), it provided significant improvement in physical properties over untreated EPDM/PU blend. Addition of 15% ground EPDM scrap, while reducing the cost, did not reduce the physicals appreciably. Similarly, when fillers, such as silica or carbon black are treated with functional silanes, they reduce interfacial tension and enhance the bonding with rubber and fillers. Bundopdebhuya and De et al. has shown that treatment of silica surface with 3-aminopropyl trimethoxy silane improves dispersion and rubber filler interaction.\textsuperscript{113} It may be mentioned that this route of compatibilization is cost-effective, but not very efficient. Better compatibilization is achieved using reactive compatibilizers. Table XIII lists some commercially available compatibilizers.\textsuperscript{114}

<table>
<thead>
<tr>
<th>Compatibilizer</th>
<th>Manufacturer</th>
<th>Trade Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ethylene Acrylic Acid Copolymer</td>
<td>DuPont</td>
<td>Surlyn 1652</td>
</tr>
<tr>
<td>2. Ethylene Acrylic Acid Copolymer</td>
<td>Dow Chemical</td>
<td>Primacor</td>
</tr>
<tr>
<td>3. Propylene Maleic Anhydride Copolymer</td>
<td>Uniroyal</td>
<td>Polybond</td>
</tr>
<tr>
<td>4. Propylene Maleic Anhydride Copolymer</td>
<td>Eastman Kodak</td>
<td>Epoline</td>
</tr>
<tr>
<td>5. EPDM, Maleic Anhydride Copolymer</td>
<td>DuPont</td>
<td>Fusabond and MF 274D</td>
</tr>
<tr>
<td>6. SEBS, Maleic Anhydride Copolymer</td>
<td>Shell Chemical</td>
<td>Kraton 1901X</td>
</tr>
<tr>
<td>7. EPDM, Maleic Anhydride Copolymer</td>
<td>Uniroyal</td>
<td>Royaltuf</td>
</tr>
<tr>
<td>8. EVA, grafted Maleic Anhydride</td>
<td>DuPont</td>
<td>Fusabond MG 423D</td>
</tr>
<tr>
<td>9. HOPE, grafted Maleic Anhydride</td>
<td>DuPont</td>
<td>Fusabond MB 100D</td>
</tr>
<tr>
<td>10. LLDPE, Grafted Maleic Anhydride</td>
<td>DuPont</td>
<td>Fusabond MB 110/MB 226D</td>
</tr>
<tr>
<td>11. Ethylene Octene Copolymer, Maleic Anhydride</td>
<td>DuPont</td>
<td>Fusabond MN 493D</td>
</tr>
</tbody>
</table>

4. *Compatibilization by Crosslinking*. — Although most elastomer blends exhibit phase separation, depending on their difference in polarity, there is evidence that co-curing may lead to the obliteration of phase boundary. For example, when cis polybutadiene is blended with SBR (23.5% styrene), it exhibits two glass transition temperature, but after co-vulcanization, the blend exhibit only one Tg. Covulcanization may take place in two steps, namely:
• Location of the curing agent at the phase interface and generation of a block or graft co-polymer during vulcanization, and
• Compatibilization of the components by thickening of the interface.

However, this can only happen if the temperature of co-vulcanization is above the order-disorder transition and is between upper and lower critical solution temperature of the blend. Substantial amount of work has been done on self-crosslinking rubber blends where two elastomers with opposite ionic charges interact with each other and form crosslinks and in the process provide high level of compatibility.\textsuperscript{115}

Dynamic vulcanization, which was originally suggested by Gessler has been used to prepare thermoplastic vulcanizes.\textsuperscript{116} The rubber is mixed above the melting point of the thermoplastic and vulcanizing agents are added in the course of mixing, which preferentially migrate into the rubber phase. After the latter is vulcanized, an elastomeric thermoplastic is obtained where the interphase is thickened due to low level of crosslinking. Dynamic vulcanization provides reduced compression set, improved mechanical properties, greater stability of the melt phase morphology (during fabrication), greater melt strength and long term reliability.

Compatibilization of blends of IR with BR was studied by Inoue as a function of vinyl content in BR.\textsuperscript{117} It was found that miscibility increases with increasing vinyl content and blends containing more than 50\% BR had lower critical solution temperature close to 200 °C. Increase in vinyl content of SBR also helps to improve its miscibility with IR and NR. Maier et al. found that SBR/BR blends followed Flory Huggin's model in their phase separation behavior when BR was treated as co-polymer containing 1,2 and 1,4 linkages and SBR as a terpolymer containing styrene, 1,4 and 1,2 butadiene.\textsuperscript{118} Measmer and Mc Elarth have found that blending of NR with BIMS, improves the heat aging resistance rubber compounds used for engine mounts,\textsuperscript{119} possibly due to con-vulcanization. Hence, attention to the microstructure of BR and SBR is important in blending these rubbers with others.

Contrary to expectation, many elastomer blends are immiscible, particularly before vulcanization. However, they develop mechanical homogeneity after vulcanization, possibly due to formation of a block co-polymer in situ. Zanzig et al. found that a co-polymer, polyisopreno-polybutadiene (BIR) improves the compatibility in a blend of NR with cisBR.\textsuperscript{120} Tensile strength, elongation at break and abrasion resistance increased when appropriate amount of BIR was added to the blend. Woods and Mass have discussed the occurrence of co-vulcanization at phase interface of rubber blends and its beneficial effect.\textsuperscript{121} They suggested that lack of co-vulcanization in some blends could be due to difference in diffusivity and solubility of the curatives, I and difference in reactivity, in different phases. They found that use of lead salt of TETM, which is equally soluble in both phases, provides better co-vulcanization than the zinc salt, in NBR/EPDM blend.

The co-vulcanized system may rightly be described as interpenetrating network (IPN). Substantial work has been carried out on IPN by Sperling and coworkers\textsuperscript{122} and Klepner.\textsuperscript{123} Bhowmik and De have made extensive investigation on the effect of cure temperature and time on co-vulcanization and have concluded that the tendency for co-vulcanization follows the trend, NR/BR > NR, SBR, BR > NR/SBR.\textsuperscript{124}

Kawazura and Karozoo have carried out a systematic investigation of the effect of diblock co-polymer addition on the compatibility of rubber blends of NR/SBR and IIR/BR.\textsuperscript{125} The diblock co-polymers were prepared using anionic polymerization with n-butyl lithium in cyclohexane as catalyst. The diblock co-polymers are designed so that only one block is miscible with component one while the second block was miscible with the other components. They found that for blend ratio ranging from 75 : 25 to 25 : 75 the SBR/NR blends are immiscible between 20 and 200 °C. Mechanical properties including abrasion resistance of the blends were poorer than the pure components. Addition of a small amount of di-block co-polymer not only produced a
finer morphology but increased tensile strength and abrasion resistance both for unfilled and black filled compounds. They measured phase structure index (PSI) by estimating the average numbers of dark zones 10μm long in the direction of long axis and across the vertical lines of the TEM micrographs. Addition of diblock co-polymers improved PSI by a factor of 3 or more. Further, it was found that temperature dependence of tan δ was not affected by the addition of block co-polymers, which is very desirable for tire tread compound. The peel strength of each component adhered to the block co-polymer, were found to be greater than the two components adhered to each other, indicating that the diblock co-polymer reinforces the interface between the matrix and dispersed phase in the blend. They also found that reinforcement by carbon black increases with increase in molecular weight of the diblock co-polymer and lumps of diblock co-polymer are encapsulated by small molecules of the matrix through diffusion and solubilization. Balancing of 1.4 unit in both blocks of the compatibilizer is essential for providing co-vulcanization, which stabilizes the interface reinforcement and provides compatibilization of the blend. This was also confirmed by the observation that PSI increases as the ratio of 1.4 unit content in both blocks approaches unity (Figure 23).

In summary, it may be stated that compatibilization is important between component phases in plastics and rubber blends. It can be achieved by adding an external compatibilizer such as a block or graft co-polymer or by using reactive compatibilization. The latter can be carried out by functionalizing one of the blend components or by reacting with a functional chemical during blending, by surface activation, and by using interphase crosslinking reaction. The best approach to compatibilization for a blend should take into account the potential reaction at the phase boundary, the blend composition, cost, processing window, and availability of suitable reactive additive.

![Graph showing phase structure index as a function of 1.4 unit ratio.](image)

**Fig. 23.** Phase structure index as a function of 1.4 unit ratio.

**VII. PROPERTIES OF ELASTOMER BLENDS**

Blending is often carried out to develop a specific property portfolio, required for a certain product. It is therefore important to review how some of the important properties are affected by blending.
A. RHEOLOGY

Rubber blends exhibit both higher and lower viscosity than their weighted mean of their component viscosities. Lipatov suggested that lower viscosity could be due to increase in fractional free volume. On the other hand, presence of dispersed hard particles, may also dissipate additional energy as the continuous phase undergoes shear; and this may lead to increase in viscosity. A number of equations have been suggested to predict blend viscosity from the composition and component viscosity. The simplest one is by Heitmiller, who suggested that the blend viscosity \( \eta_b \) is related to the viscosities and the weight fractions of each component \( \eta_1, W_1 \) and \( \eta_2, W_2 \) and is given by the relation

\[
\frac{1}{\eta_b} = \frac{1}{\eta_1} + \frac{1}{\eta_2} = \frac{W_1}{\eta_1} + \frac{W_2}{\eta_2}
\]

The entanglement molecular weight and the magnitude of the plateau modulus are both affected by blending. In addition, the miscible blends are often associated with nematic interactions where the orientation of the neighboring chains induce similar orientation of the chains participating in flow. In addition, the blend may undergo adjustment in morphology and dissipate some of the applied stress. All these contribute to the decrease in blend viscosity.

Further, the low viscosity component of the blend often goes to the region of high shear (such as the walls of a pipe) and the component with higher viscosity stays at the center, leading to a sheath core configuration and plug flow. This results in lower viscosity of the blend. Shih observed that addition of a few percent of a fluoro-polymer to EPDM, substantially reduced its viscosity and vice versa. Nguyen had made similar observation when silicone resin was blended with SBR.

In carbon black or silica filled saturated elastomer compounds, where the polymer filler interaction is small, the viscosity is reduced by the circulation of hard particles during flow. However, in unsaturated rubbers, the interaction of black and silica with rubber produces bound rubber and increases viscosity. If both components of the blend are unsaturated, the viscosity increase will take place irrespective of the location of the black in one phase or both. On the other hand, if the blend is made of saturated and unsaturated rubbers, the black goes to the latter increasing its viscosity and leads to a sheath core configuration and plug flow. Sircar et al. noted that die swell of a rubber blend during extrusion can be reduced if the black is located in the rubber component with lower level of interaction.

B. MODULUS

Hardness and modulus of rubber compounds are important characteristics, for qualifying them for product development. The upper and lower limits of the modulus (E) is estimated by using parallel and series coupling and are given by the following equations:

\[
E = \phi_1 E_1 + \phi_2 E_2 \text{ (parallel coupling)}, \quad E = \frac{E_1}{\phi_1 + \phi_2} / \frac{E_2}{\phi_2} \text{ (series coupling)}
\]

Nelson and coworkers observed that the modulus of a series of electron beam cured EPDM/BR blend follow parallel coupling equation. Chen predicted that in most cases, the modulus for non-reactive blends will be intermediate between the values predicted by parallel and series coupling. Kleiner reported that blends where the continuous and dispersed phase interact with each other, the modulus is given by

\[
E = \phi_1 E_1 + \phi_2 E_2 + \xi E_1 E_2
\]

where \( E \) is the modulus of the blend, \( E_1 \) and \( E_2 \) are moduli of the components and \( \xi \) is an empirical interaction parameter. The increased modulus is attributed partly due to volume relaxation, leading to increase in chain density for unit cross section. For blends with heterogeneous morphology, the modulus does not depend on, which component acts as matrix and which as dispersed phase. This has been confirmed by Nelson et al. who studied the moduli of EPDM/BR blends. Similar behavior has been observed for NR/SBR and NR/BR blends. The particle size
in heterogeneous blends does not have much influence on modulus.\textsuperscript{135}

Carbon black loading increases modulus of most elastomers. In low strain region where carbon black networking dominates the stress—strain behavior, non-uniform filler distribution lowers modulus.\textsuperscript{136} This may be attributed to the fact, under stress some of the carbon black moves from one phase to the other and the increase in modulus in the second phase is less than the loss of modulus of the first phase. In other words, the effect of carbon black distribution on modulus is nonlinear and it can not be predicted for all cases.

\section*{C. FAILURE PROPERTIES}

Elastomers are often blended to improve tear strength, cut growth resistance, fatigue life and resistance to ozone cracking. Synergistic property enhancement takes place in miscible blends, due to increase in chain density per unit cross section. In immiscible blends, property enhancement takes place due to interface bonding, stress relaxation and increased potential for crazing. Interfacial bonding facilitates stress transfer from one phase to the other. In rubber toughened plastics, this translates to shear banding and crazing, leading to improvement in impact resistance. Lemieux and Killogar have shown that a 80/20/20 blend of NR/BIR/BIIR improved the fatigue life substantially. In this case, the BIIR contributes to improve fatigue life and BIR acts as a softening agent cum compatibilizer.\textsuperscript{137} Interfacial bonding increases fatigue life (as much as three times) for SBR/CIIR blend and tensile strength for EPDM/silicone blend.\textsuperscript{138} Hamed has shown that the weak interface in EPDM/BR blend deflects the direction of crack propagation and thereby increases tear strength. In case of strong interface, the crack proceeds through dispersed particles, leading to an intermediate tear strength.\textsuperscript{139} Buckler et al. found that in a blend of cis 1,4 and 1,2 BR, the phases interpenetrate into each other, resulting in higher strength.\textsuperscript{140} Phadke et al. found that the inclusion of carbon black in a scrap rubber/virgin rubber compound, increases strength properties, as black promotes interfacial bonding between the two phases.\textsuperscript{141}

The properties of the continuous phase often determines the strength properties of a blend. In general, stronger continuous phase gives stronger blends. In blends where component rubbers have different affinity for carbon black, better properties are obtained when the component with greater affinity forms the continuous phase. This has been observed for NR/BR and NR/SBR blends.\textsuperscript{142} On the other hand, in co-continuous NR blends, better properties are obtained when the black stays in the second phase.\textsuperscript{143} This allows NR phase to crystallize under strain and contribute to enhanced strength.

It has been shown that the modulus of a blend is generally intermediate, when measurements are carried out between the glass transition temperatures of the two rubbers. In this case, the strength is influenced by the glassy phase and the elongation by the rubbery phase. Similar behavior has been shown by the blends of an elastomer of high and low molecular weight. This is because the short chains act as non-extendable phase and the long chain as flexible units, provide extension. Llorente et al. have found this type of behavior for polydimethyl-siloxane blend of high and low molecular weight.\textsuperscript{144} Similarly improvement in flex life can be achieved by adjusting the viscosity of the continuous and dispersed phase. The lower viscosity component migrates to the surface and the high viscosity component stays close to the normal axis and undergoes minimal strain.\textsuperscript{145}

\section*{D. HYSTERESIS}

Hysteresis of rubber compounds can be reduced either by increasing crosslink density or by higher black loading. Both options are undesirable in most circumstances. Hence elastomers are often blended to reduce hysteresis loss.\textsuperscript{146} This is because the hysteresis loss for a blend is often lower than those of their components. Hess and Chirico have shown that both modulus and hys-
teresis loss is reduced when the continuous phase contains lower level of carbon black.\textsuperscript{142} Further non-uniform distribution of carbon black in NR/BR and NR/SBR blends provides high cut growth resistance.\textsuperscript{147} The effect is further enhanced if the reinforcing filler stays largely in continuous phase. Nguyen studied the effect of carbon black loading on hysteresis loss of elastomer blends and found a nonlinear relationship between hysteresis loss and carbon black loading.\textsuperscript{130}

Keller found that addition of a small amount of chlorobutyl rubber to NR/BR blend (tire tread compound) reduces rolling resistance.\textsuperscript{148} Ahagon et al. have patented a blend composition of three rubbers containing chlorobutyl rubber which reduces hysteresis without changing wet traction. The level of the chlorobutyl in the blend is high enough to have appropriate frequency dependence of energy loss, i.e., resilience at low rate of deformation and substantial hysteresis loss at high rate of deformation. The latter prevents skidding on wet road. Additional reduction in loss can be achieved by introducing a non-uniform distribution of carbon black.\textsuperscript{149}

E. ADHESION AND TACK

Synthetic rubbers such as SBR, BR and EPDM have poor tack and auto-adhesion. This is improved by blending with natural rubber and some synthetic co-polymers and terpolymers. Tack is largely a surface phenomenon\textsuperscript{150} and is controlled by surface characteristics. Hence a small amount of NR in the blend provides the necessary tack, provided it migrates to the interface. Morrissey measured tack of a series of blends of NR with many synthetic elastomers and found that tack is proportional to NR content.\textsuperscript{151} Hamed observed that auto-adhesion in NR/SBR blends increases with increase in NR content and reaches maximum at about 80% of NR. It has been suggested at this concentration, the blend has the maximum chain density per unit cross section of the interface as well as the NR potential for undergoing crystallization under strain. This provides higher rupture energy and higher tack.\textsuperscript{152}

The potential for fusing at the interface also contributes to tack. Roland and Bohm have found that when BR is blended with a graft co-polymer of butadiene and isopropyl azo-dicarboxylate, high level of auto adhesion is obtained at a small concentration of the latter.\textsuperscript{153} However, in some cases tack can be obtained even if none of the individual component exhibits tacky behavior. It was observed that when a small amount of a terpolymer of styrene, butadiene and 5% N-isopropoxy methacrylamide was added to a blend of NR/BR, tack increased significantly at very low NR content.\textsuperscript{154} The blend of BR/terpolymer, however, did not show much tack. It was suggested that the terpolymer undergoes condensation and crosslinking at cure temperature, thereby increasing the viscosity and throwing out the small amount of NR to the surface. Small amount of the latter coats the entire surface and provides auto-adhesion. Barager found that chloro-butyl rubber (CXR) when added to polychloroprene, improves tack.\textsuperscript{155} Similar improvement in tack was observed when 75% CBR is added to blends IR or BR and to the blends of IR and butyl rubber. A blend containing higher level of IR and lower level of CBR provided good adhesion to SBR.\textsuperscript{156} Barager also found that adhesion between epichlorohydrin rubber and unsaturated rubber can be improved by adding about 10% of polychloroprene. Bhowmik and Gent have shown that adhesion between two pure elastomers is determined by the number and length of the interphase strands.\textsuperscript{157}

F. TRANSPORT PROPERTIES

Permeation of gases and liquids is important, because very often rubber blends are used for improving air retention, perm-selectivity (membranes) and resistance to vapor ingress. In general the permeability of a rubber blend in non-Fickian region is given by
where Pb is the permeability of the blend and Ps and Pt are those for the components and Vs,Vt are the volume fractions of the components. Permeability is the product of Solubility S and Diffusivity D. The process involves absorption on the exposed side, diffusion in the matrix and desorption at unexposed surface. Where as miscible blends and some heterogeneous blends exhibit synergistic behavior, most rubber blends exhibit intermediate P values as given in the above equation. Modeling of P has been carried out using both parallel and series configuration. Parallel configuration works better, when the continuous phase is more permeable and the dispersed phase provides more tortuous path. The series model works in limiting cases when the dispersed phase is more permeable. Barrier and coworkers have done extensive work on transport properties of rubber blends. Some of their results are illustrated in Figure 24.

In absence of strong rubber-filler interaction, presence of filler in rubber compound is likely to increase permeability. However, in presence of strong rubber filler interaction, the permeability may be lowered because of increased tortuosity of the path. The use of nano-fillers will further accentuate this effect.

![Graph showing relative air permeability of elastomer blends. NR taken as 100.](image)

**G. ELECTRICAL CONDUCTIVITY**

Electrical conductivity is often similar to transport properties, since in this case electrons percolate in polymer matrix. Distribution of carbon black and connectivity in a rubber blend is controlled by selecting rubbers with different affinity for carbon black and blending them in right proportion. Sircar measured electrical conductivity of a number of black filled rubber blends based on Chlorobutyl rubber. The conductivity of the blends exceeds that of the base rubber compound. Further certain blend components provide higher conductivity than others. This is probably due to increase in the size of the black agglomeration. If both phases do not have affinity for black, then the black deposits at the interface and enhances conductivity. Dissimilar affinity of individual rubber components with carbon black will contribute to agglomeration. On the other hand lower, affinity by both phases will lead to interfacial conductive path.

**VIII. ELASTOMER BLENDS AND THEIR APPLICATIONS**

**A. ELASTOMER BLENDS**

Krege has recently reviewed thermoplastics elastomer blends based on polyolefins, partic-
ularly the relation between morphology and physical behavior.\textsuperscript{163} TPE based on a blend of PVC and nitrile rubber (NBR) is the simplest one, since the two polymers are miscible with each other leading to a homogeneous rubbery phase with single glass transition temperature, analogous to plasticized PVC. Blends of stereo-block polypropylene and poly-olefins are also miscible. The blends exhibit a two-phase morphology (fringe micelle type) at room temperature. In contrast TPEs based on insoluble blends are compatible in the melt (not soluble) and exhibit two-phase morphology at use temperatures. The phases could be co-continuous or discontinuous with a semicrystalline phase containing dispersed particles of the minor component (either crosslinked or uncrosslinked).

Ethylene-Propylene co-polymers (EPR) with high ethylene content behave as thermoplastic elastomer and their elastomeric properties are greatly enhanced by incorporating cure-site monomers, such as ethylene norborne or hexadiene. Blends of isotactic polypropylene and EPR with highly branched or partially cured EPR give property enhancement desired for many applications.\textsuperscript{165} Gessler, Ban, and Kresge have shown that when processing oil is added, it reduces melting point and melt viscosity, thereby improving processability, and on cooling the oil is largely retained by the rubbery phase, thereby improving low temperature properties. Both bi-continuous and disperse phase morphologies are exhibited. When polyethylene is added to EPDM, heat distortion temperature is reduced due to lower melting point of PE.\textsuperscript{166} Blends of iPP with styrene-ethylene-butene-styrene (SEBS) triblock co-polymer give a co-continuous crystalline and elastomeric phase over large compositional range due to miscibility of EB block with PP.\textsuperscript{167} Many metalloocene catalyzed PE co-polymers with high ethylene content also behave like TPEs because polyolefins with long branches such as Hexene and Octene polymers separate into an amorphous phase with very low Tg. Blends of iPP with EPDM also exhibit TPE behavior and continuous phase morphology over a wide composition range. Where as atactic PP blend shows a broadband glass transition, iPP blend shows both solid and melt phase characteristics. The iPP is nonspherulitic and the morphology is similar to that of a monoclinic blend. It has higher modulus and exhibits elastic properties due to open fiber like microstructure.\textsuperscript{167} Several hypotheses have been suggested for obtaining co-continuous morphology including the ones based on volume fraction and torque ratio, volume fraction and viscosity ratio. It has been suggested that the critical volume fraction of EPDM for co-continuous morphology is 0.156 for EPDM / iPP blend. Study of the mechanical behavior of polyolefin EPDM blends shows that good elastomeric properties are exhibited when high levels of EPDM is blended with polyolefins having high crystalinity.

Silicone elastomers are blended with other elastomers for enhanced bio-compatibility. Medical Research Associates have taken several patents on blends of SEBS block co-polymers of specified block size with silicone rubber for a variety of medical applications.\textsuperscript{167a} A patent on improved medical grade adhesive has been granted to Squibb and Sons, consisting of a blend of poly-isobutylene, IIR and a radial styrene block co-polymer.\textsuperscript{168}

When the elastomer phase is dynamically crosslinked, the elastomer performance increases to a large extent. These blends, called thermoplastic vulcanizates (TPV), have excellent physical properties. The best properties are exhibited when the particle size of the phases is small, in the range of 1 micron or smaller.\textsuperscript{169}

Lohse, Garner and Graessler et al. have made an in-depth analysis of thermodynamic principles underlying the blends of saturated hydrocarbon elastomers.\textsuperscript{170} Saturated hydrocarbons, having no specific interaction and having repeating units very similar to each other, should be miscible with each other. However, in recent years it has been observed that polyolefin blends with molecular weight and compositions of commercial interest are exhibiting phase separation, upper and lower critical solution temperature like polar polymer pairs. The authors have used results of small angle neutron scattering and PVT measurements to investigate a large number of
polyolefin blends including elastomers.

The scattering data provided a direct measure of thermodynamic interaction density $\chi$, which was used to calculate Hildebrand’s solubility parameter ($\delta$) and solubility parameter differences (\(\Delta\delta\)) between different polyolefins. Table XIV gives the values of the solubility parameter differences from a standard polymer, HPB 97 (hydrogenated polybutadiene), of different saturated polyolefins at three different temperatures. It is obvious that the difference varies from 0.2 to 1.60. Since the solubility parameter difference between many pairs is much greater than 0.1 to 0.2 (J/cm\(^3\))\(^{1/2}\), the critical difference for phase separation, many of their blends will exhibit phase separation and will have heterogeneous morphology. It has been suggested that the solubility parameter in case of polyolefins, not only depends on their chemical composition but also on their packing, which is largely determined by co-monomer such as butene, hexene, octene, etc and their frequency of occurrence in the main chain. Packing length, 'p' has been defined as the ratio of the volume occupied by a chain divided by the radius of gyration which can be derived from molecular weight. Solubility parameter is inversely proportional to p. The smaller the p, the greater the solubility parameter. It has been suggested that polymers with small p have large radius of gyration and as such they overlap more closely the neighboring polymers leading to greater interaction and larger enthalpy change. In other words, although non-bonded interactions are same for all polyolefins, the ones having small p or better packing will have higher cohesive energy density and greater solubility parameter. The difference in packing also contributes to departure from regular mixing, that is when mixing occurs without volume change and the interaction energy between two polymers are geometric mean of their individual interaction energy. It has been shown that some of the differences are positive and some negative, meaning that the blends, depending on their composition, will exhibit either upper and lower critical solution temperature.

<table>
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<tr>
<th>Blend</th>
<th>T(^{\circ})C</th>
<th>$\chi$, J/cm(^3)</th>
<th>((\delta_1-\delta_2))^2 J/cm(^3)</th>
<th>$\chi_{irr}$, J/cm(^3)</th>
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<tr>
<td>PP/HPB 78</td>
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<td>0.0643</td>
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<td></td>
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<td></td>
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<td>167</td>
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<td>0.0256</td>
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<tr>
<td>PP/HPB97</td>
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<td>0.0484</td>
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Sample key: HPBx = Hydrogenated Poly-butadiene, model ethylene-butene co-polymer. PEP = hydrogenated polyisoprene, model alternate ethylene -propylene co-polymer. hhPP = hydrogenated poly(2,3 di -methyl) butadiene, model head to head polypropylene. PP = hydrogenated poly (2methyl 1,3 pentadiene), model head to tail polypropylene.
Krishnamoorty studied the micro-structure of BR/IR blends, using small angle neutron scattering (SANS) and found that blends containing poly-butadiene with less than 38% 1,2 units are phase separated at all temperatures above 25 °C. On the other hand, the blends containing more than 38% 1,2 content exhibit LCST. DSC measurements, however, showed that all blends other than the one containing 8% poly-butadiene have single Tg at room temperature. The influence of polymer microstructure on the miscibility of polymers and the limitation of experimental techniques have been discussed.

Chlorinated rubber (CR) is often the choice for power transmission belts because of its ozone resistance, oil resistance, toughness and dynamic flex life. However, its heat resistance is limited to 100 °C. Blending with saturated polymers such as EPDM can be used to improve its heat aging characteristics. Arjunan and Kusznir have shown that the blends are usually immiscible. Their blends can be compatibilized by using a dual mode compatibilizer, which while having composition similar to one phase, will interact or chemically react with other phase. They have successfully compatibilized CR/EPDM by using ethylene-maleic anhydride-acrylic acid ter-polymer and methyl methacrylate grafted EPDM. In the first case, the acrylic acid reacts with CR by nucleophilic displacement of allylic “Cl” atom; and, in the second case by hydrogen bonding with CR. A good viscosity match between the two components was also found important for fine particle size of the dispersed phase and enhancement of key properties. Use of compatibilizer also helped carbon black distribution between the two phases, due to improvement in polarity by the inclusion of MMA-g-EPDM and interaction between carbon black and the acrylic acid part of the first compatibilizer.

Both NR and IR suffer from deficiencies such as poor ozone and heat aging resistance and poor corrosion resistance. Blending of these polymers with saturated rubbers such as butyl rubber IIR and EPDM have not been successful to overcome this problem, because of the difficulty in co-vulcanization. Rankin has shown that this difficulty can be overcome by using chlorinated EPDM, because the chlorine atoms in third monomer will not only activate the double bonds but create more double bonds by dehydro-chlorination. He found that an EPDM with 1.5 to 2 % chlorine in ethylene norbornene provides a high rate of vulcanization of EPDM and overcomes the incompatibility problem. The combined system provides high cohesive strength, improved dynamic and mechanical properties, resistance to heat aging and ozone and good adhesion to metallic tire cords.

Lee, Koseki and Macosko have studied the morphology of ternary blend of EP rubber with NBR, acrylic and CM (chlorinated polyethylene) at a fixed composition 70/20/10 weight percent. They found that, in this blend, EPR forms the matrix and the dispersed phase shows encapsulated structures. In blends containing high nitrile content NBR, CM forms the encapsulating layer and with low nitrile NBR, the latter forms the encapsulating layer. This behavior has been explained on the basis of a spreading coefficient concept combined with solubility parameter of each component.

Earlier Callan et al. had shown that blending of EPDM with butyl improves the heat resistance of black and mineral filled stocks. Addition of unsaturated elastomers to EP rubber have been used to change their vulcanization characteristics. Where as addition of liquid polybutadiene retarded the scorch rate, that of polychloroprene promoted the same for peroxide cure. Addition of SBR, NBR and polysulfide rubber to peroxide cured EP and EPDM decreased their crosslink density, modulus, tensile strength and hardness. These properties were improved when 1,2 BR and CR were blended. Property changes were proportional to blend composition. The rate of sulfur cure of EPDM was enhanced by adding 1,4 diene rubbers such as SBR, NBR but was retarded by the addition of liquid 1,2 polybutadiene, although the latter improved hot air resistance of the compound. Improvement of butyl treadwear by incorporating EPDM has been discussed by Willis and Denecour, Loheac and Odam as well as Speranzini and Drost.
have investigated the use of chlorobutyl and EPDM for improving side wall compounds for radial ply tires.\textsuperscript{179,180}

Blending of EPR and EPDM has been used extensively to improve aging properties of unsaturated elastomers.\textsuperscript{181} Spenadel and Sutpin have blended CR with EPDM to provide ozone shield.\textsuperscript{182} Leibu reported that EPDM with hexadiene comonomer improves the ozone resistance of NR and SBR.\textsuperscript{183} Sutton found that ozone resistance, chemical resistance and compression set are greatly improved by adding EPDM.\textsuperscript{184}

Satake and coworkers have studied heat aging, groove cracking, abrasion resistance and cornering behavior of SBR/EPDM and SBR/BR/EPDM blend both in the laboratory and field and have concluded that such blends can be used for tire treads without the use of antioxidant.\textsuperscript{185}

Butyl rubber is often added to NR and other elastomers to improve damping\textsuperscript{186} and to improve impermeability to air.\textsuperscript{187} Use of chlorobutyl in place of butyl alleviates the difficulty of getting good vulcanization.\textsuperscript{188} Vitolin has studied the effect of mineral fillers, oils and resins on the physicals of chlorobutyl and diene rubber blends.\textsuperscript{189} Morphological heterogeneity and crosslinking in similar blends have been investigated by Rehner and Wei.\textsuperscript{190} Patridge and Evans found that use of furnace black and addition of compounding ingredient directly to the rubbers instead of master-batching are beneficial in chlorobutyl / NBR blends.\textsuperscript{191} Blends of EPDM/NBR are used to provide acceptable levels of oil and ozone resistance with acceptable levels of mechanical properties. Devi and Manlenora have tried to improve the low temperature and abrasion properties of NBR by blending with cis BR.\textsuperscript{192} Wingrove has used blending of emulsion BR to achieve similar property enhancement of Neoprene. BR/Neoprene blends have lower tendency to soften and stick to the rolls (problems in calendaring) and provide faster extrusion rate and better moldability.\textsuperscript{193} Koldunovich has discussed the processing and properties of cis BR/neoprene blends\textsuperscript{194} and Orekhov has discussed the influence of vulcanization on physical properties of the blend.\textsuperscript{195} Blends of epichlorohydrin rubber with cis BR when cured with an organic accelerator, sulfur and metal oxide improves low temperature flexibility and reduces air permeability. Blending of silicone rubber with fluoro-silicone rubber not only reduces cost but also improves compression set and processability.\textsuperscript{196}

As mentioned earlier, extensive blending of unsaturated elastomers has been carried out in past to improve properties of individual elastomers and meet the property requirement of rubber products. Co-vulcanization and interphase chain entanglement as well as use of reactive fillers provide compatibilization, resulting in synergistic property enhancement.

Blending of BR with NR allows higher curing temperature and better physicals for the latter.\textsuperscript{197} Heat stability of NR and SBR blend are also improved by blending cis BR and that of emulsion BR.\textsuperscript{198} Difficulties of processing stereo-regular BR can be overcome by blending it with NR, SBR and by using specific blacks. Processing and physical properties of cis BR are improved by blending with liquid polybutadienes.\textsuperscript{199} Substantial amount of work has been carried out to reduce cost and improve tire performance. Blends of solution SBR with NR, emulsion SBR or BR reduces mixing times and modifies extrusion characteristics.\textsuperscript{200} Sarabach et al. showed that miles of service per unit compound cost, increases with addition of various black masterbatches when blended 50/50 with NR/SBR master batches. Addition of 10 to 30% of SBR, NR, IR and emulsion BR to cis BR along with an alkali or alkaline earth salt of a long chain fatty acid improves the cutting resistance of the vulcanizate.\textsuperscript{201} Epstein has shown that addition of liquid polybutadiene containing 10% carboxylic acid improves the properties of cis poly-butadiene elastomers.\textsuperscript{202}

Fujimoto et al. have studied the cut growth rate of gum and black filled SBR rubber and have found that resistance to cut growth can be improved by adding a small amount of low molecular weight material\textsuperscript{203} with higher Tg. It has been suggested that the reinforcing and retarding effect of the higher Tg material retards the translational and rotational motion of the polymer chains
and thereby reduces the rate of cut growth. Kienle has discussed the tread wear and skid resistance of SBR and its blends. Springer has discussed the flex cracking, vulcanization, and processing aspects of SBR/Butyl rubber blends. Levitin and coworkers found that 50/50 blends of cis polyisoprene rubber with methyl styrene butadiene co-polymers provide optimum processing and physical properties required for tire carcass. Similarly, a ternary blend IR/NR/BR provide good physics for giant tire treads used for trucks and agricultural equipment. Ghicroiau et al. found that addition of NR to oil extended polyisoprene rubber provided improved breaking strength, than IR500. Blends of IR with NBR, SBR and BR have been studied by Ghicroisoiu, Mahalia and Karkotov et al.

Flanigan has noted that substantial amount of EPDM with high percentage of cure site monomer will be used as blends with other elastomers in future because of its low cost and good aging properties.

Recently, Roger and Waddell have reviewed the past work on the use of blends of butyl (IIR), chlorobutyl (CIIR), bromobutyl (BIIR) and brominated methyl styrene-isobutylene co-polymer (BIMS) with natural rubber and SBR in many tire and non-tire applications. Presence of α methyl groups in BIMS chain, reduces its mobility, thereby reducing permeability. The impermeability is further enhanced by halogenation. The highly saturated structure of butyl also makes them resistant to oxidation and provides tack and adhesion capability. Hence, the blends find a variety of applications in tire products, particularly inner liners, black and white sidewalls, cover strips, bead and tread compounds. Replacement of 20% NR with CIIR doubles permeability resistance and reduces adhesion to the carcass. Replacement of chlorobutyl by bromobutyl further reduces the rate of gas transmission and enhances flex crack resistance. This helps in designing lighter tires with low rolling resistance and higher surface area to air volume, thereby making them suitable to high speed rating.

For black sidewalls, blending of halobutyl rubbers with NR/BR compound, increases both dynamic and static ozone resistance as well as resistance to flexural strain. Furthermore, addition of chlorobutyl rubber to NR/BR blend increases their tearing strength and reduces cut growth rate (Figure 25). Addition of carbon black to NR/BR/CIIR blends also provides a large reduction in crack propagation rate under fatigue stress. In non-staining tire black sidewalls based on a blend of NR/BR/EPDM, addition of BIMS provides superior adhesion to carcass and improved flex resistance, ozone resistance and rolling resistance.

Addition of butyl and halo-butyl rubber to tire tread compound based on NR/SBR or NR/BR blends can lower resilience and improve skid resistance. Addition of bromobutyl rubber to oil extended SBR/carbon black compounds improves wet traction but decreases tread wear in tire tests. In general, butyl rubber provides poor abrasion resistance, possibly because of its lower stiffness and high frictional coefficient. However, the butyls improve skid resistance, which is very important for tire application. In fact, addition of 30 phr CIIR, increases skid resistance by 5% at a sacrifice of 4% tread wear rating. When BIMS is added to carbon black filled NR/BR blends, the loss tangent increases at low temperatures at -30 to 10 °C but decreases above 30 °C (Figure 26). This is helpful because 30 °C and higher temperatures are close to most use temperatures. In addition, blending BIMS improves resistance to tread wear (Figure 27).

Butyl and halobutyl rubbers are also used in many automotive applications such as air conditioning fluid hoses, fuel line, and brake line hoses and engine mounts. The low fluid transmission rate and higher damping capability makes them especially suitable for the above application. Blends of natural rubber and BIIR are used for engine mount compound because of improved vibration and fatigue resistance. Addition of unvulcanized IIR improves these properties further. Improved resistance to heat ageing is obtained by blending BIMS with natural rubber. This also stabilizes the dynamic properties of the engine mount compounds.

Practical application of blending to obtain performance advantages has been well discussed
in a recent article by Kishine and Noguchi of Daikin, America. Fluoro-elastomers (FKM) are usually known for their chemical and thermal resistance but have poor low temperature properties. Hence, they are often used in engine peripheral parts such as seals and gaskets. However, the use of amine type additives in high performance engine oils is likely to increase hardness, decrease elongation at break and develop hair line cracks. Acrylic elastomers (ACM), on the other hand, have good low temperature

![Graph](image)

**Fig. 25.** Crack growth results for natural rubber/butadiene rubber (no. 1 and no. 2) and chlorobutyl rubber/EPDM rubber/natural rubber/butadiene rubber black sidewall compounds at 50 °C.
properties. But they lack resistance to aging at high temperature. The cost of FKM is much higher than ACM. Hence, development of cost effective elastomers with properties intermediate between FKM and ACM can be achieved by blending the two polymers. The important considerations are compatibility and selection of heat resistant co-crosslinking system. Poor compatibility leads to deterioration in mechanical properties. Higher compatibility, on the other hand, leads to an increase of T<sub>g</sub>, thereby decreasing the low temperature performance of ACM. Hence, compositions having intermediate compatibility were selected. ACM is cured by metallic soap, sulfur and amine curing systems. FKM is cured by bisphenol A and peroxides. Since FKM provides the best heat aging properties, it was selected to cure the blend using bisphenol A. Further, this curing is carried out under mild conditions to provide co-crosslinking of the two elastomers in the blend. The resistance to engine oil (SGW-30) is illustrated by changes in their elongation at break at 175 °C in Figure 28 and tensile strength in Figure 29.
FIG. 28.—Effect of hot air aging on elongation air aging.

FIG. 29.—Effect of hot tensile strength.

Where as the tensile strength of the blend (AG) show superior performance than FKM, the elongation at break shows intermediate resistance to hot oil aging. Similar behavior is also seen in compression set. The properties of the blend also depend on fluorine content. Thus the blend has considerable amount of design flexibility, which can be adjusted to deal with amine resistance, low temperature performance and cost effectiveness. The performance characteristics of the blend are compared with other high temperature polymers such as AEM and HNBR in Figure 30.

FIG. 30.—Property change with blend composition (design flexibility).

Adhesion of elastomers to wire components in wire reinforced rubber articles, such as steel belted radial tires, hoses and belting, is very important. Failure at rubber to wire interface can cause catastrophic consequences. Although adhesion is partly promoted by coating the wire with an interactive primer, the choice of the rubber compound plays a vital role in rubber to wire adhesion. Croft has discussed the use of elastomer blends to improve rubber to wire adhesion in wire reinforced hoses. Adhesion between rubber and wire is important in hoses because the latter is often used in harsh environments, such as engine compartments, machinery housing, etc., at high temperature, in contact with oil and corrosive organic vapors. It is important that the two wire plies in the hose move radially and in unison to avoid independent lateral motion. Otherwise, weak spots develop resulting in early failure. Further, any wire movement may cause
dimensional change, leading to loose couplings and wire flare. Although adhesion promoters often help to improve adhesion of rubber compounds, they cause problems such as the sticking of the hose tube to mandrel during extrusion and the cover material sticking to mandrel wrap during lamination process. Croft found that blending of nitrile rubber and NBR/PVC blends with a small amount chlorinated rubber (CR) and SBR, provides substantial improvement in both post-curing adhesion as well as heat aged adhesion. The formulation of the control (NBR and NBR/PVC blend) and their blends with CR and SBR are given in Table XV and their adhesion to wire as measured by ASTM D2229 are given in Table XVI. However, there was some positive volume change in oil aging. The increase in adhesion was ascribed to increase in unsaturation, which helps in improving interaction between the brass-coated steel wire and the rubber. Croft emphasizes that to get real improvement in adhesion, the blend components should be compatible, adequately resistant to oil and are equally compatible with filler and curatives.

### Table XV

**Formulations of NBR and Blends with PVC, CR and SBR**

<table>
<thead>
<tr>
<th>Formulations</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>100</td>
<td>85</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBR/PVC</td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>85</td>
<td>70</td>
</tr>
<tr>
<td>CR</td>
<td></td>
<td>15</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>N762 Black</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>DOA</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>BBTS</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

### Table XVI

**Adhesion and Wire Coverage of Compounds based on NBR and its Blends**

<table>
<thead>
<tr>
<th>Formulations</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original adhesion, lb/in. (Cured 30 min at 330 °F)</td>
<td>37.8</td>
<td>48.6</td>
<td>55.1</td>
<td>31.5</td>
<td>46.7</td>
<td>51.2</td>
</tr>
<tr>
<td>Wire coverage, %</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>50</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Heat aged adhesion, lb/in. (Aged for 70 hrs at 212 °F)</td>
<td>36.1</td>
<td>44.6</td>
<td>52.8</td>
<td>25.9</td>
<td>39.8</td>
<td>43.8</td>
</tr>
<tr>
<td>Wire coverage, %</td>
<td>60</td>
<td>70</td>
<td>70</td>
<td>50</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

Hamed, Kim and Gent measured cut growth rate in vulcanizates of NR, cis BR, and a 50/50 blend of NR and cis BR. A compound, having typical passenger sidewall composition, was studied. Tensile strips with edge cuts were stretched to failure either by increasing strain up to failure or by stretching them progressively to higher strains until failure occurs. In both cases, tensile strength decreased continuously with cut depth. However, in case of NR and NR/BR blend, the tensile strength decreased abruptly at a critical cut depth \( d_c \). This was attributed to the crystallization of NR throughout the specimen at high strain when the cut depth ‘d’ is smaller than \( d_c \), and crystallization is continued to crack tip till \( d > d_c \). Further, where as, secondary cracks did not develop in neat cis BR specimen, the NR and the NR/BR blends showed the growth of
two parallel secondary cracks and the growth of a third crack from the smooth torn surface of the secondary crack, leading to failure. This may be attributed to NR being susceptible to crystallization and illustrates the fact that the components in the blend maintain their individual characteristics even after blending and co-vulcanization.

B. COMMERCIAL APPLICATIONS

As mentioned earlier, rubber blends are being used in most rubber products for a long time. This is evident in the competition for patents on rubber blends by large tire manufacturers. In 1984-85 time period, at least five patents were issued to four tire manufacturers. Gen Corp (now Continental Tire) patented a blend of star shaped solution polymerized butadiene or isoprene with regular diene polymers for lowering rolling resistance of tires. Bridgestone of Japan took a patent on a blend of random SBR with BR of specified cis content and chain length to improve wet skid and rolling resistance. Toyo Rubber patented a carcass composition, consisting of a blend of a solution polymerized star shaped SBR and NR. Sumitomo Rubber Industries, patented a high and low molecular weight diene rubber blends for improving wet grip and rolling resistance. The company also took another patent on a blend of high and low molecular weight SBR to improve rolling resistance and wet grip, easy processability, durability and better abrasion resistance. Another patent on a blend of isoprene and butadiene co-polymer with close to 90% cis content for BD, was taken to obtain better skid resistance. In view of this, it may be desirable to look at the current practice briefly, in order to appreciate the important role the blends play in the rubber industry.

Rubber products can be generally divided in two categories, tire and non-tire. Approximately 70% of rubber is used for making tire and tire related products. The non-tire products contain a variety of extruded and molded products, including automotive hoses and belts, footwear, seals, and ‘O’ rings and roofing membrane.

Pneumatic tire is a highly engineered product made of several components including chafer, apex, black side wall, white side wall, belts, radial ply, bead and liner (Figure 31). The elastomer blends used for making them are given in Table XVII. The tread compound is designed for high abrasion resistance, traction, low rolling resistance, durability and protection of the coating. Where as SBR and BR provide high abrasion resistance and low rolling resistance, natural rubber provides resilience and low-heat build up. The tack provided by NR helps to bond different components in the tire.

![Figure 31: Cross-section of a radial passenger tire](image)
Table XVII
RUBBER BLENDS USED IN TYPICAL TIRE COMPONENT FORMULATIONS

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber Blends (Parts By Weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passenger tire tread</td>
<td>SBR (Pleoflex 1502) 50 / NR (TSR20) 50</td>
</tr>
<tr>
<td>Sidewall (black)</td>
<td>NR (SMR5) 50 / BD (BR 1220) 50</td>
</tr>
<tr>
<td>Sidewall (white)</td>
<td>NR (SMR5) 25 / CIIR (1056) 55 / IIR (Vistalon 6505)</td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Body ply (carcass)</td>
<td>NR (SMR 10) 70 / BD (BR 10) 30</td>
</tr>
<tr>
<td>Inner liner</td>
<td>BIIR (X-2) 70 / NR (SMR 50) 30</td>
</tr>
<tr>
<td>Truck tire</td>
<td></td>
</tr>
<tr>
<td>Tread</td>
<td>BR (Budene 1207) 50 / SBR (Pleoflex 1712) 68.75</td>
</tr>
<tr>
<td>Carcass (bias)</td>
<td>NR (SMR - 50) 80 / BD (BR 1220) 20</td>
</tr>
</tbody>
</table>

A large number of rubber blends have been patented for tire application. The earlier patents have been discussed by Baranwal, Mc Donel and Andries, Walsh and Higgins, as well as by Hess and Vequari et al.

Rubber blends also find frequent application in flat belting. The latter is largely used to transport heavy tonnage over long distance. It usually consists of a load bearing component, carcass and a protective component called cover. The carcass consists of layers of fabric reinforcement impregnated with rubber. It not only supports heavy load but also provides conformability to the contours of troughing idlers and to hold to the mechanical fasteners. SBR and NR or IR blends with BR provide the bulk of the rubber compounds used for belt applications. NBR and CR are blended to the base rubbers to resist oils present in grain or treated coal transport. EPDM and chlorosulfonated polyethylene (CSM) rubbers are used for high temperature belts. Table XVIII gives the elastomers used in flat belt compounds.

Table XVIII
RUBBER BLENDS USED IN BELT COMPOUNDS

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction &amp; skim coat</td>
<td>1st grade SBR (Plioflex 1500) 80/NR (Grade 5) 20</td>
</tr>
<tr>
<td></td>
<td>Heat resistant SBR 90/NR 10</td>
</tr>
<tr>
<td>Belt cover</td>
<td>1st grade NR (Grade 5) 80/BD (Budene 1207) 20</td>
</tr>
<tr>
<td></td>
<td>2nd grade NR 10/Budene 20/ SBR (Plioflex 1500) 20</td>
</tr>
<tr>
<td></td>
<td>High temp EPDM (Nordel 1040) 80/ CSM (Hypalon 40) 20</td>
</tr>
</tbody>
</table>

Covers of rubber hoses, whose main function is to protect the carcass from deterioration by environmental conditions, use blends of nitrile rubber with PVC resin or Hypalon with polybutadiene.

Rubber blends are used frequently in footwear. The latter consists of a sole cemented to an upper part having the configuration of the foot. They are either injection molded or calendared followed by cutting in size and bonding. The important requirements are therefore conformability to the foot, adhesion to the upper part and wear resistance for durability. Easy mixing, reusability of the scrap, low shrinkage on molding, consistent colorability and durability are other important considerations. In case of athletic shoes, high tensile strength, high tear and abrasion resistance and reasonable coefficient of friction are important. Comfort shoes may need capability of containing gases or fluids over a long period of time. Table XIX provides rubber
blends used in foot wear components.\textsuperscript{214d}

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outsole (injection molded)</td>
<td>NR (smoked sheet #2) 50/SBR (PlioFlex 1502) 50</td>
</tr>
<tr>
<td>Boot upper (inj. molded)</td>
<td>NR (smoked sheet #2) 80/SBR (1000) 20</td>
</tr>
<tr>
<td>Outsole/foxing (calendared)</td>
<td>NR (SMR-10 80 / SBR (1000) 20</td>
</tr>
<tr>
<td>Outsole (compression molding)</td>
<td>NR (SMR-10 70 / SBR (PlioFlex 1778) 30</td>
</tr>
<tr>
<td>Boot lining gum</td>
<td>NR(AMR-10) 40 / SBR (1009) 20 / IR (Natsyn 2200) 40</td>
</tr>
<tr>
<td>Heel (high quality)</td>
<td>SBR (PlioFlex 1502) 30 / BD Budene 1208 60 / IR</td>
</tr>
<tr>
<td></td>
<td>(Natsyn 2200) 10 / SBR (1505) 5</td>
</tr>
<tr>
<td>Heel (standard quality)</td>
<td>SBR (PlioFlex 1502) 70 / Budene 1208 20 / SBR (1805)</td>
</tr>
<tr>
<td></td>
<td>15 / Budene 10 / NBR (Chemigum 90) / SBR 10</td>
</tr>
</tbody>
</table>

In view of the fact that majority of rubber products are made out of rubber blends and rubbers in general are immiscible, it is important to consider several factors before designing a compound based on a rubber blend. The end properties of the elastomer blend does not only depend on the composition, viscosity and shear history of individual component but also on interfacial tension, rubber-rubber and rubber-additive compatibility. The processing parameters, particularly the methodology followed in mixing, plays a dominant role. This has been nicely illustrated in a recent study of SBR/EPDM blend by Zhao, Ghebremeskel and Peasly.\textsuperscript{218} The objective of the study was to replace 30 parts of EPDM with SBR to reduce the cost and improve select properties. The general formulation is given in Table XX. The three curing systems used include sulfur, peroxide, and a coagent system included in both sulfur and peroxide cure systems. Each system was used both at high and low levels. The cure characteristics are given in Table XXI. It may be seen that where as the torque maximum does not vary much with high curative level, it is substantially different at low curative level. Cure rate index is the highest with sulfur system. The mechanical properties of the blends are illustrated in Figure 32. The tensile strength of both sulfur and peroxide cure system are substantially lower than that of the coagent curative system. This indicates that when a small amount of sulfur is added to peroxide, some sulfur crosslinks are formed between EPDM and SBR and the potential for co-vulcanization is improved. The use of co-agent appears to provide the best tensile strength, and modulus, indicating the higher level of crosslink density. This is confirmed by the lower compression set of coagent system, particularly after heat aging.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>EPDM (phr)</th>
<th>EPDM/SBR (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>SBR1502</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>CB (N330)</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Sunpar 2280</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Variable</td>
<td>Variable</td>
</tr>
<tr>
<td>Accelerators</td>
<td>Variable</td>
<td>Variable</td>
</tr>
</tbody>
</table>
### Table XXI

**Cure Characterization of the SBR/EPDM Blends with Varying Cure Systems**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>HP</th>
<th>HC</th>
<th>HS</th>
<th>LP</th>
<th>LC</th>
<th>LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. torque, dNm</td>
<td>36.7</td>
<td>36.02</td>
<td>36.7</td>
<td>26.7</td>
<td>33.9</td>
<td>25.9</td>
</tr>
<tr>
<td>Min. torque, dNm</td>
<td>7.1</td>
<td>6.01</td>
<td>7.5</td>
<td>5.9</td>
<td>6.7</td>
<td>6.2</td>
</tr>
<tr>
<td>Delta torque, dNm</td>
<td>29.58</td>
<td>30.01</td>
<td>29.13</td>
<td>20.80</td>
<td>27.24</td>
<td>19.68</td>
</tr>
<tr>
<td>Scorch time, minutes</td>
<td>1.76</td>
<td>1.72</td>
<td>1.57</td>
<td>2.46</td>
<td>2.05</td>
<td>1.90</td>
</tr>
<tr>
<td>TS0, minutes</td>
<td>6.36</td>
<td>3.79</td>
<td>2.72</td>
<td>7.12</td>
<td>5.03</td>
<td>3.10</td>
</tr>
<tr>
<td>T90, minutes</td>
<td>17.90</td>
<td>12.26</td>
<td>7.23</td>
<td>18.17</td>
<td>15.42</td>
<td>7.62</td>
</tr>
<tr>
<td>Cure rate index, 1/min</td>
<td>6.20</td>
<td>9.49</td>
<td>17.67</td>
<td>6.37</td>
<td>7.48</td>
<td>17.48</td>
</tr>
</tbody>
</table>

HP: high peroxide system  
HC: high coagent system  
HS: high sulfur system  
LP: low peroxide system  
LC: low coagent system  
LS: low sulfur system

---

![Graph](image_url)

**Fig. 32.** — Plot of tensile, elongation and modulus versus blend composition.

The tear strength of the co-agent cured compounds are somewhat lower than that of sulfur cured system, indicating that the latter provides a tougher material. The mechanical physical properties of the compounds mixed by conventional method (Brabender plasticorder) and dynamic method are given in Table XXII. It appears that dynamic mixing provides better physicals for the blends than conventional blending. In conclusion, it may be said that by proper selection of curatives and processing techniques, thirty percent of EPDM can be replaced by SBR without significant loss of properties (Figure 33).
### Table XXII
MECHANICAL AND PHYSICAL PROPERTIES OF THE EPDM AND EPDM/SBR BLENDS

<table>
<thead>
<tr>
<th>Sample mixing</th>
<th>EPDM</th>
<th>EPDM/SBR</th>
<th>EPDM/SBR</th>
<th>EPDM/SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Dynamic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress—Strain</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength, (Mpa)</td>
<td>13.9</td>
<td>8.99</td>
<td>9.34</td>
<td>11.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>255</td>
<td>265</td>
<td>304</td>
<td>217</td>
</tr>
<tr>
<td>100% modulus, (Mpa)</td>
<td>5.64</td>
<td>3.32</td>
<td>3.18</td>
<td>4.52</td>
</tr>
<tr>
<td>200% modulus, (Mpa)</td>
<td>11.3</td>
<td>6.97</td>
<td>6.57</td>
<td>10.2</td>
</tr>
<tr>
<td>300% modulus, (Mpa)</td>
<td></td>
<td></td>
<td>9.29</td>
<td></td>
</tr>
<tr>
<td>Compound Mooney</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mooney (1+4min) 100 °C</td>
<td>68</td>
<td>43.8</td>
<td>57.1</td>
<td>59.2</td>
</tr>
<tr>
<td>Hardness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Shore A”</td>
<td>70</td>
<td>66</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>Die C-Tear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tear strength, (kN/m)</td>
<td>31.1</td>
<td>24.2</td>
<td>28.4</td>
<td>23.4</td>
</tr>
<tr>
<td>Compression Set Method B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 °C for 70 hours, %</td>
<td>23.4</td>
<td>29.7</td>
<td>30.8</td>
<td>30.3</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig. 33.** — Stress—strain curves of EPDM and EPDM/SBR blends cured with peroxide and sulfur coagent.

### IX. SUMMARY AND CONCLUSIONS

Rubber blends have been used in industry over a long period of time to meet the contradictory property requirements of rubber products. However, most blends are immiscible and the
compounding ingredients distribute into different blend components differently depending on their compatibility and the rates of diffusion and reactivity in different components. As a result, most rubber blend compounds like thermoplastic blends have a heterogeneous morphology. However, the heterogeneity is not always reflected in their end properties due to co-vulcanization at the interface. Theoretical models developed for thermoplastics and thermoplastic elastomers have not been adequately applied to the understanding and evaluating the heterogeneity of rubber blends. Important theoretical approaches based on polymer—polymer interaction, solubility parameter, and free volume concepts have not been used often to quantify the miscibility of rubber blends. In recent years, there has been substantial amount of interest in determining thermodynamic and morphological features of rubber compounds and their blends. Instrumental techniques such as Inverse gas liquid chromatography, small angle neutron scattering, thermoanalytical techniques, atomic force microscopy, and computer-assisted electron microscopy are helping these new developments. Hopefully, the black art of rubber compounding will soon find a more scientific framework.

Compatibilization is as important to rubber blends as to thermoplastic blends. This is reflected in lower mechanical properties of incompatible blends of elastomers. There is a distinct need to understand and use compatibilization not only to make better rubber compounds but to obtain better thermoplastic elastomers and toughened plastics. Compatibilization between recycled rubber grit (or ground rubber) and gum rubber is very important to successful recycling of used tires.

However, study of rubber blends is more challenging than study of thermoplastics blends because rubber compounds, in addition to having polymeric materials, contain large amounts of both reactive and non-reactive ingredients. However, the challenge needs to be met as better methods of processing and characterization are developed.

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