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Morphology Development and Mechanical Response of Supramolecular Structures in Rubber Blends

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Introduction

The aims of elastomer property design with respect to end-user demands is to arrive at optimum combinations of physical properties common to the originating polymers. For instance, high elasticity, energy dissipation in a given frequency or temperature range and good abrasion resistance are property combinations which have to be achieved in quality tire treads. It has been suggested that energy dissipation in the low frequency region (or at high temperatures) is responsible for rolling resistance of tire treads, whereas energy dissipation in the high frequency region (or at low temperatures) for improving grip properties of treads. Because no polymer alone can fulfil this demand, different rubbers have to be blended. This route offers an economical realization of high performance target properties. The desired property combination does not, however, require miscible blends but some degree of physical autonomy of the phases (heterogeneous phase morphology) [1,2].

In addition the reinforcing effect of particulate colloidal fillers such as carbon black or silica and the success of co-crosslinking the polymer phases determine the technological performance of the final products. Reinforcement by nano-scaled fillers controls especially dynamic and ultimate properties of filled rubber products [3].The blends' physical properties thus do not depend on the size, shape and distribution of the polymer phases alone, but also on filler dispersion, filler transfer and selective distribution in the distinct polymer phases [4]. In heterogeneous blends, the intermolecular interactions demonstrate their efficiency mainly at polymer-polymer and polymer-filler interfaces. Due to these interactions supramolecular structures – like interpenetrating phase networks – are formed in unfilled polymer blends. The aggregation of filler particles, moreover, leads to filler networks that interpenetrate the rubber networks. The self-similar structure of the filler network leads to physical properties which can be described by scaling laws with fractal exponents [5].

The complex behavior arouses considerable scientific and technological interest as it is directly connected to the dynamic and ultimate properties of elastomers. In spite of advances made in relating morphology development during dispersive mixing to rheological factors (i.e. shear rate, viscosity ratio of the matrix and dispersed phase etc.) [6,7], the rather subtle role of interfacial tension has rarely been considered quantitatively in experimental investigations on rubber blends.

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While he development of blend morphology is no doubt directly connected to the processing strategy employed, driving forces of a thermodynamic nature also have to be taken into account. The aim of this contributions to underline the role of the thermodynamic parameters governing the formation of supramolecular structures in rubber blends and in the filler network architecture in relation to their mechanical consequences.

Morphology of unfilled rubber blends

Miscibility of polymers

A fundamental question which should be addressed first with respect to any blend system under consideration is whether the components are miscible or not. While the definition and estimation of compatibility in blends systems is not devoid of ambiguities, the use of thermodynamic criteria is an unambiguous way to judge the case. The necessary conditions for the miscibility of a binary system of a particular composition are connected to the shape of the free energy of mixing as a function of the volume fraction,ϕ:

$$\Delta G_m < 0 \tag{1}$$

$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} < 0 \tag{2}$$

The opposite applies for phase-separated systems.

For blends containing non-polar polymers (i. e. polydienes), the free energy of mixing can be described by applying a formal extension of the Flory - Huggins lattice theory [8,9] proposed by Scott [10]:

$$\Delta G_m = RT\left[\phi_1 \ln \phi_1 + \phi_2 \ln \phi + \chi_{12}\, \phi_1^2\, \phi_2^2\right] \tag{3}$$

where χ_{12} is the polymer-polymer interaction parameter and x_i the degree of polymerization of each blend constituent.

This expression contains the combinatorial entropy of mixing, which expresses the increase in positional disorder during the mixing process and is a simple function of the volume fractions of each constituent The entropy of mixing always contributes to misciblility. Because no theoretical provision can be made for the enthalpy of mixing, the contribution of this thermodynamic function and the excess entropy of mixing is included in the polymer-polymer interaction parameter χ_{12}, which by definition has the physical meaning of a "residual free energy of mixing." Any knowledge about χ_{12} must be deduced from the experiment. The cohesive energy density concept proposed by Hildebrand offers one possibility for estimating χ_{12} for non-polar systems. It predicts [11]:

$$\chi_{12} = V_r\,(\delta_1 - \delta_2)^2/RT \tag{4}$$

where δ_i is the cohesive energy density of the polymer.

The necessary condition for obtaining miscibility is a low-value tendency o the part of χ_{12} or $|\delta_1\text{-}\delta_2|$ ($\chi_{12} \rightarrow 0$).The conditions for phase separation obtained equating the binodal and the spinodal conditions lead to the definition of a critical χ_{12}-parameter which is a function of the molar mass. Predictions for miscibility can be made if the critical χ-parameter is considered [12].

In accordance with a lattice concept the interfacial tension γ_{12} is proportionate to the square root of χ_{12} [13].

$$\gamma_{12} \sim \chi_{12}^{1/2} \sim |\delta_1 - \delta_2| \qquad (5)$$

This approach makes it possible to predict the interfacial tension and the degree of incompatibility of the blend constituents as well. In a first approximation the thickness of the interface is inversely proportionate to the interfacial tension

$$a_I = \sim \frac{1}{\chi_{12}} \sim \frac{1}{|\delta_1 - \delta_2|} \qquad (6)$$

A useful tool for obtaining χ_{12} and δ for non-polar polymers is the inverse gas chromatography (IGC) [14,15]. The necessary condition for any sucses is the proper selection of the molecular probes and precisely defined experimental conditions [15]. There are certain advantages to thermodynamically selecting well characterized hydrocarbons (i.e. n-alkanes, iso-alkanes, cycloalkanes and aromates) as molecular probes for gas-liquid-chromatography (GLC) on melted polymer films. On the one hand, only dispersive and weak dipole forces contribute to the specific retention values and χ_{12}. On the other hand, the heat of evaporation of these molecular probes has to be precisely known [16]. Therefore δ_2-parameters reflect the enthalpy contributions of this range of interaction forces and entropy effects [15,17].

Influence of molecular weight

It can easily be seen that for various rubber blend combinations the critical molar masses above which phase separation occurs, M_{cr} (calculated for the symmetrical case $M_{cr,2} = M_{cr,3}$), are far below the molecular weights of technical rubber grades. Consequently, irrespective of the mixing technique employed, the result will be heterogeneous phase morphology (Fig. 1). The value of δ_2-parameters as an indication of the degree of non-miscibility was proved for various polydienes and polyolefines [2,18]. The hyperbolic phase evolution diagram (Fig. 1) shows that miscible blends are obtained from technical rubber grades only if the δ-parameter difference is less than 0.2 $J^{1/2} cm^{3/2}$

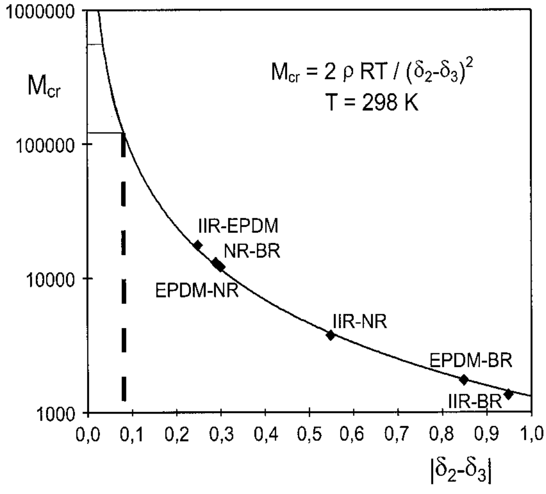


Figure 1: Phase diagram indicating the critical molar mass of the polymer as a function of the δ-parameter difference of rubber blends.

Contributions of microstructure and specific interacting groups

Based on the precise GLC determination of δ-parameters, the thermodynamic contribution to the morphological development of the butadiene microstructure units and phenyl groups was established by covering a large compositional range of BR (cis-BR, vinyl-BR) and SBR (E-SBR; S-SBR) types (Fig. 2).

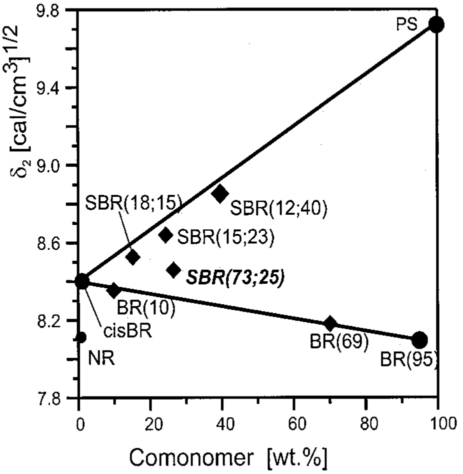


Figure 2: δ-Parameter of BR-copolymers as a function of the comonomer content.

Although both the vinyl unit and the styrene unit contribute to chain dynamics in a similar way by increasing proportionately the T_g and thus have an influence on damping behavior and grip properties, their thermodynamic behavior is completely opposite. Increasing the vinyl content in the cis-BR decreases polarizability and interaction potential. This leads to a linear decrease in the δ-parameter as vinyl content increases. As a consequence, the degree of compatibility of BR with all polymers with a lower δ_2-parameter (i.e. NR, EPDM, IIR, PP, PE) increases. At a vinyl content of 70-80%, the δ-parameter of BR equals that of natural rubber or synthetic polyisoprene [18]. As a result the mixing enthalpy becomes practically zero and the blend demonstrates miscibility as shown by indirect methods [19,20]. This notable example of miscibility of two non-polar homopolymers demonstrates the typical behavior of an athermal mixture ($\Delta H_m \cong 0$; $\Delta S_m > 0$). In contrast to the common conclusion drawn for the majority of polar systems in which miscibility is achieved only with high negative mixing heats , this result shows miscibility to be responsible for combinatorial entropy [19]. Because the expansion coefficients are nearly the same for both polymers, the equation of state contribution and excess mixing entropy is negligible. However, the broadness of the glass transition region at equal polymer volume fractions indicates micro-heterogeneity which cannot be predicted by the thermodynamic estimation [2].

A pronounced linear increase in the δ-parameter with increasing styrene content indicates that more exothermic interactions govern the thermodynamic behavior of SBR types. As a result the compatibility with less polar rubbers like BR, NR, EPDM decreases as the styrene content increases. On the basis of these observations it can be stated that randomly distributed chain segments of different chemical constitution deliver specific incremental contributions to the overall thermodynamic behavior of the polymer. As a result, the δ-parameter of any SBR under consideration can be expressed by the parameter equation [3]:

$$\delta_{(SBR)} = 17.17 + 0.0272(S) - 0.0069(V) \tag{7}$$

where S and V denote the weight percentage of styrene and vinyl units in the product and δ is expressed in $J^{1/2}\ cm^{3/2}$.

Equation (7) describes quantitatively the opposite effects of vinyl and styrene units on the thermodynamic behavior of the polymer. However, the effect of blockiness and tacticity are still unknown.

Temperature dependence

As the temperature is varied during the mixing process, the nature of the free energy as a function of composition may change and can result in transitions through the coexistence curve from the solubility gap into the homogeneous region in the phase diagram. For scientific and technical reasons it is interesting to know whether the phase separated system is below a UCST or above an LCST. Because rubbers are blended exclusively by mechanical mixing, the effect of increasing mixing temperature can decisively influence the final phase morphology.

A shortcoming when describing real systems is that there is no theoretical provision made for temperature dependence of χ_{12}. A real advantage of GLC is the estimation of the temperature dependence of δ- or χ_{12}-parameters. It was experimentally proven that for blends from non-polar rubbers the δ-parameter difference $|\delta_1 - \delta_2|$, which is directly proportionate to the interfacial tension γ_{12}, is decreasing when the temperature is increased [21] (Fig. 3). Consequently, by increasing the mixing temperature the interfacial thickness in all non-polar blend systems is increased (Fig. 3).

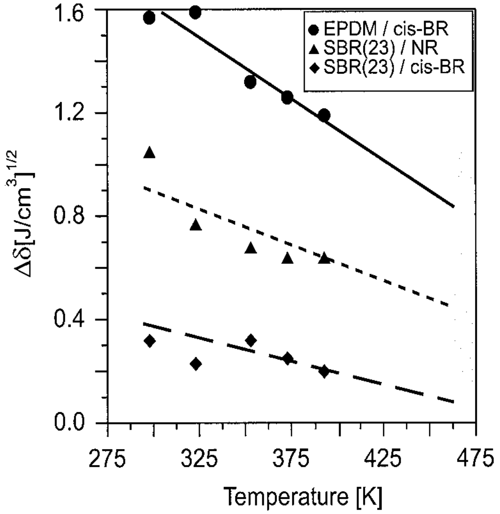


Figure 3: Temperature dependence of the interfacial tension for non-polar rubber blends.

Despite the fact that producing miscible rubber blends is not a technological target, in most cases the phase transition into the homogeneous region cannot be achieved due to a residual value of unlike segmental interactions. Partial solubility can, nevertheless, be attained. On the basis of the temperature dependence of $|\delta_1 - \delta_2|$, the existence of a UCST in the temperature region 130-140 ^{0}C is predicted for the blend SBR(23)/SBR(40). By way of confirmation, the uncured blend system SBR(23)/SBR(40) exhibits two damping maxima in blending operations at 80 ^{0}C. This indicates a phase-separated system. The same blend system demonstrates single phase behavior if the mixing temperature passes the critical value of 130-140 °C[23]. However, reducing the temperature during storage triggers an equilibration into a two-phase morphology in uncross-linked blends.

Morphology development in heterogeneous rubber blends

Rubber blends with co-continuous phase morphology provide good ultimate properties due to the three-dimensional interpenetrating phase network formed. Despite the technological advantages of such systems, blends with one phase dispersed in a continuous matrix aroused the greatest scientific interest . In the case of such blends, the resulting domain size, d, can be theoretically described as a function of both thermodynamic and the rheological contributions [24]

$$\bar{d} = (c\gamma/\eta_m)\,[dV_x/dy]^{-1} \cdot f\,(\eta_m/\eta_d) \qquad (8)$$

where dV_x/dy - shear rate

η_m - viscosity of the matrix phase

η_d - viscosity of the dispersed phase.

Certainly, the development of blend morphology is directly connected to the processing conditions employed and the viscosity of the blend constituents [7,25], but driving forces of a thermodynamic nature also have to be taken into consideration.

Dispersion kinetics

In the early stage of polymer dispersion the phase break-up is related to the stress level exerted on the droplets of the minor component by the flowing matrix [26]. The effectiveness at which stress can sustain particle deformation depends on the degree of interdiffusion of the polymer chains at the phase boundary. Due to the fact that chain length and frictional coefficients of non-polar rubber are not very dissimilar, the interdiffusion, which is governed by the degree of thermodynamic similarity, creates interphases whose thickness could be assumed to be at the same order of magnitude. The phase break-down of the minor component starts with a typical exponential decrease of the domain size and levels at prolonged mixing into a stationary state (Fig. 4).

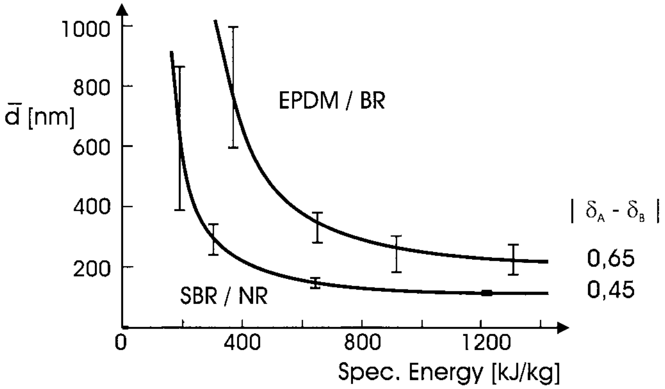


Figure 4: Domain size reduction during mixing of rubber blends.

If the process is treated as a reaction of the first order, the corresponding reaction rate constants demonstrate a dependency on the thermodynamic dissimilarities of the blend constituents. From a comparison of the dispersion rate of BR in EPDM with that of SBR in NR it is obvious that systems with a higher degree of compatibility tend to form more rapid a stationary phase morphology than those with a poor compatibility.

$$k_{EPDM/BR} = 11.5 \cdot 10^{-3}\ [s^{-1}]$$
$$k_{NR/SBR} = 18.3 \cdot 10^{-3}\ [s^{-1}]$$

These thermodynamically driven dispersion kinetics was confirmed for blends of cis-1,4-BR with SBR containing an increasing amount of styrene units. It was shown that keeping the viscosity ratio η_m/η_d at constant the dispersion rate is a linear function of the δ-parameter difference [21]. More detailed investigations of the domain size reduction by TEM revealed a multimodal size distribution. The value of the ratio of consecutive size maxima is asymptotically lowered from higher values in the early stages of mixing to 1.26 in the stationary mixing stage. This evolution indicates that longitudinal domains (fibrillas) are formed first. These are disrupted into a sequential reducing number of smaller drops, which again form fibrillas in the shear field. The final ratio of 1.26 demonstrates that in this mixing stage the domains are divided into two similar sized parts.

Influence of shear during mixing

As long as the chemical nature and molecular weight of the constituents are kept constant, the shear rate employed during mixing dominates the domain size reduction (Table 1). When the ratio of shear rate to interfacial forces is taken into account, it became obvious from this quantitative data that interfacial interactions are graded similarly to rheological influences.

Table 1: Influence of rotor speed on domain sizes in selected blends.

System	Rotor speed (rpm)	Domain size (nm)	$\lvert\delta_1 - \delta_2\rvert$ $(J/cm^3)^{1/2}$
NR/SBR (23)	65	260	0.92
	95	120	
EPDM/BR	65	650	1.33
	95	240	

This basic result for unfilled rubber blends cannot be transferred to filled systems without reservation. When mixing rubbers without fillers, the effects of polymer incompatibility and shear rate are of the same order of magnitude, whereas in the presence of fillers – especially above the percolation threshold – the influence of shear rate is predominant. Domain sizes are also affected by the presence of particulate fillers [27]

Stationary Domain Size

For the most clear-cut picture in which the dispersed phase is surrounded by a continuous one, the relationship between the stationary average domain size and the interfacial tension was investigated for a large number of non-polar rubber blends under properly controlled mixing conditions (constant rotor speed and temperature)[21,27]. For uncured NR/E-SBR blends (7/3) it was observed that the stationary average domain size increases with both the styrene content and the δ-parameter difference (Fig. 5) [28]. Outside of this group the linear dependency of the stationary average domain size on δ-parameter difference was proved for various NR-blends with BR, vinyl-BR, E-SBR, S-SBR and EPDM and for more incompatible blends based on EPDM or CIIR with the polydienes mentioned, in accordance with the equation [18]

$$d = 1260\,(\Delta\delta - 0.204) \qquad (9)$$

where d denotes the average domain size in nm and δ is given in $J^{1/2}\,cm^{3/2}$.

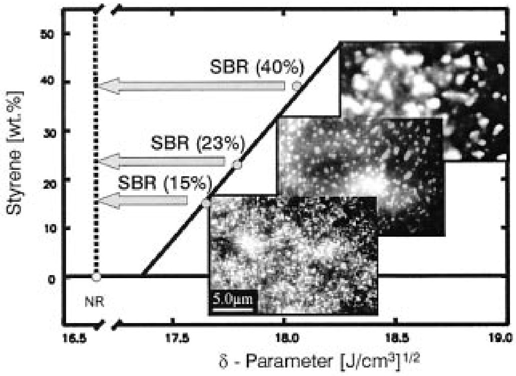


Figure 5: Domain size vs. δ-parameter difference for various rubber blends.

With increasing shear rate (rotor speed) the slope of d ~ Δδ will decrease. Consequently, the rheological influences will affect blends with a low degree of compatibility to a proportionately higher extent. The temperature in the mix increases because of high shear flow. If the δ-parameter of blend constituents shows a convergent temperature dependency, this effect can offset the decrease of shear stress by bringing about a reduction in melt viscosity. In such a case the decreased interfacial tension will result in a finer dispersion. If the temperature dependencies of δ-parameters are not convergent like they are for NR/E-SBR(23) or NR/SBR(40), the increase in rotor speed, and therefore in mixing temperature, leads to an increase in the average domain size, especially as a result of broader domain size distribution. The effect observed is attributed to a reduction of the matrix viscosity due to both the molecular weight breakdown in the NR phase and the increased temperature [27].

From TEM investigations on NR/SBR blends it became obvious that the aspect ratio (AR) of the domains is increased if the degree of compatibility of the blend constituents is decreased [18]

$$AR = d_{min}/d_{max} = 0.671 + 0.178\,\Delta\delta \qquad (10)$$

Equ. 10 indicates that in more compatible blends the interfacial interaction is able to sustain domain shapes with a less favorable volume surface fraction than that of a sphere (i.e. ellipsoidal or fibrilla like domains).

Phase inversion

Regarding the contribution of interfacial interactions to the concentration region where phase inversion or the co-continuous phase morphology occurs, significant publications have demonstrated that the viscosity ratio influences the location of the phase inversion region [25]. From TEM investigations on NR/SBR blends, preformed in the author's laboratory, it became obvious that the concentration region in which co-continuous phase morphology does appear is enlarged when the degree of compatibility of the blend constituents increases [29] (Fig. 6). However, since the co-continuous structures result in enhancement of mechanical blend properties, more detailed knowledge about phase inversion and its extent can be rewarding.

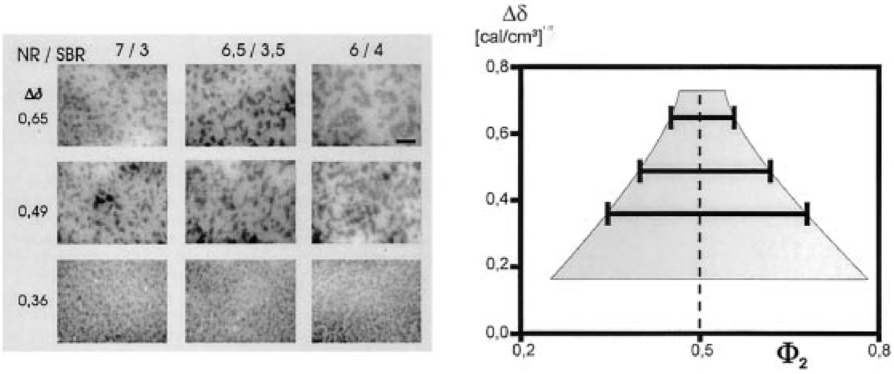


Figure 6: Concentration range of the phase inversion region as a function of the interfacial tension of the blend constituents (System NR/SBR).

Structure of interpenetrating phase networks

Information about the architecture of co-continuous phase morphologies can be gained from dynamic-mechanical properties of the blend systems in the glass transition region [30]. The dynamic-mechanical response of multi-component rubber blends follows from the general principles of energy conservation, which state that the total energy stored or dissipated in a dynamically excited blend system results additively from the energy contributions of the different phases. Since the energy stored and dissipated per unit volume can be expressed by the storage and loss modulus, G' and G", multiplied by the square of the mean strain, the complex modulus G* = G' + i G" fulfills the relation:

$$G^*_{\text{blend}} = \sum_i G^*_{P,i}\,\phi_i \left(\frac{\gamma_{0,i}}{\gamma_0}\right)^2 \qquad (11)$$

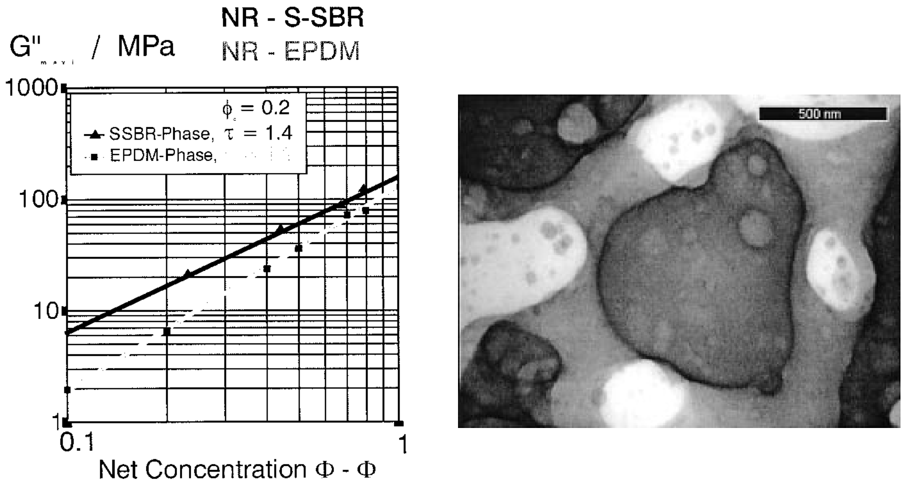
Here, G^*_{blend} is the modulus of the blend and γ_o is the external strain, i.e. the mean strain averaged over the whole blend system. Both quantities are macroscopically observable parameters. Since any measurement on a rubber blend averages over the whole sample, evidently. $G^*_{P,i}$ is the complex modulus, ϕ_i the volume fraction and $\gamma_{o,i}$ the average strain of the i-th blend component.

A purely geometrical expression for $\gamma_{o,i}$ can be derived if a critical behavior, e.g. a percolation structure, is assumed for the phase network and the i-th phase is glassy, while all other phases are rubbery. The complex modulus is then governed by the glassy i-th phase and the contributions of the other phases can be neglected, i.e. the sum in Equ. (11) reduces to a single summand. By introducing the glass transition temperature $T_{g,i}$ of the i-th phase, the complex modulus at this particular temperature fulfills a critical scaling law for $\phi_i > \phi_c$:

$$G^*_{\text{blend}}(\phi_i;T_{g,i}) = G^*_{P,i}(T_{g,i}) \left(\frac{\phi_i - \phi_c}{1-\phi_c}\right)^{\tau} \qquad (12)$$

Here, ϕ_c is the critical volume fraction above which a phase network is formed. It equals the percolation threshold if a percolation model is assumed. The elasticity exponent τ depends on the particular structure of the interpenetrating phase network. It is affected mainly by the distribution of flexible connections in the phase network that are not arranged in close loop structures and dead ends.

For G' and G" analogue relations are valid.



Scaling law G" vs (ϕ_i - ϕ) for NR - S-SBR and NR - EPDM and TEM-micrograph of an IPN (NR - EPDM)

Figure 7: Double logarithmic plot of G" vs. (ϕ_i - ϕ_c).

The double logarithmic plot of G" vs $(\phi_i - \phi_c)/(1 - \phi_c)$ delivers a straight line with the slope τ. The experimental results leads to fractal exponents. Depending on the system the τ-values are in the range of 1.5 to 1.9. The result indicates that the interpenetrating phase network corresponds to a supramolecular organized fractal object which contain a given fraction of stiff loops of dimensions similar to the diameter of a polymer coil. With decreasing degree of compatibility, the exponent also decreases because the diameter of the loops in the blend system becomes smaller (Fig. 7).

Dimension of interphase

The thickness of the interphase and their development during the mixing process and when stored was examined by thermoanalytical methods. By using blends of semi-crystalline cis-BR and a sequence of amorphous polydienes, it was shown that the normalized loss of crystallization increases when the blend constituent demonstrates a higher degree of compatibility [21]. The thickness of the blend interphase a_I was derived from the volume fraction of non-crystallizing cis-BR. The experimental results confirm the theoretically expected relation (6): $\gamma \sim a_I^{-1} \sim |\delta_A - \delta_B|$ (Fig. 8).

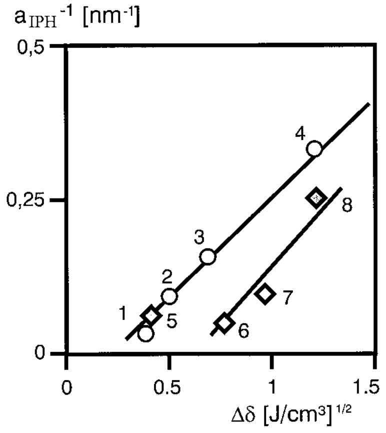


Figure 8: Reciprocal thickness of the interphase vs. interfacial tension uncrosslinked Systems: 1 - cis-1,4-BR/E-SBR (17;23), 2 - cis-1,4-BR/E-SBR (17;29), 3 - cis-1,4-BR/E-SBR (17;40), 4 - cis-1,4-BR/EPDM crosslinked Systems: 5 - NR/cis-1,4-BR, 6 - NR/S-SBR (50;25), 7 - NR/E-SBR (17;25), 8 - NR/EPDM.

With the help of a new method the interphase signal can be obtained from the temperature dependency of the loss modulus maximum [30]. It was shown that the interface of crosslinked blends is larger than of non-crosslinked ones, but that it is also inversely proportional to the interfacial tension. The estimated thickness of the interphase ranges from 1.5 nm for highly incompatible blends (i.e. EPDM/BR) up to 15-20 nm for highly compatible blends (cis-BR/SBR).

Physical properties of unfilled blends

The main motivation for blending rubbers is to improve and enlarge the property spectrum the elastomers exhibit in ultimate use. A deeper knowledge as to the influence of blend morphology on physical properties – especially ultimate ones – is therefore of critical interest. One can observe that both tensile strength and energy at break increases when the average domain size of the dispersed phase decreases during the mixing process (Fig. 9).

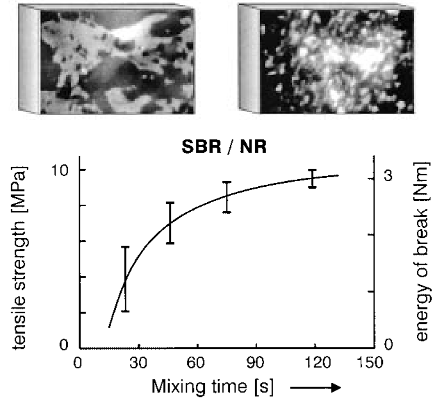


Figure 9: Evolution of tensile strength and energy at break as a function of mixing time.

Increasing the volume fraction of the interphase by reducing the nominal domain size effects a considerable improvement in the physical properties. As the volume fraction of the interphase increases, the concentration of flaws is reduced because of an increased region in which disparate polymer chains are co-crosslinked. The mechanical integrity of the intercrosslinked morphology also leads to greater tear strength than in either of the pure components. This proves that phase morphology of a heterogeneous rubber blend contributes in a determinant way to the physical property level of the final elastomer.

Filled rubbers

The quality of rubber products containing particulate reinforcing fillers is highly dependent on a high degree of dispersion and an optimum distribution of filler particles in the mix [3]. It is, therefore, very important to ensure good dispersion of carbon black or silica in order to obtain products with tailor-made mechanical properties (low hysteresis, high tensile strength, abrasion resistance, cut growth resistance etc.) [31]. Since filler loading is typically high in most of the rubber products (≥ 50 phr) and the mixing time is as short as possible, filler dispersion is often less than optimum. The detrimental consequences of poor dispersion are [31]:

- reduced product life,
- poor performance during service,

- poor product appearance,
- poor processing and manufacturing uniformity,
- waste of raw materials,
- excessive energy usage.

The avoidance of premature product failure was the driving force for the development of better mixing procedures, the investigation of the dispersion influencing factors, a better knowledge of the dispersion mechanism and, last but not least, reliable testing methods for filler dispersion.

The process of dispersion depends: on:

(i) the chain length of the polymer
(ii) the share of specifically interacting groups along the chain,
(iii) the surface activity (interacting potential),
(iv) distribution of energetically effective adsorption sites
(v) fractal dimensions of the filler.

Dispersion of fillers is by definition the process of mechanical breakdown of hard filler pellets (commercially available size 1-3 mm) into smaller entities like agglomerates (of 1-50 µm) and, after extended mixing, into aggregates (of 100-300 nm). Distribution means the process in which agglomerates or aggregates are pulled apart and spread out by random patterns of flow in the rubber melt.

A necessary condition for the pellet breakdown is the transmission of shear forces from the mixing device to the filler pellets or agglomerates through the rubber matrix [32]. This can be done only if the rubber matrix exerts a "wetting" influence, or in other words, if there is good interaction (or affinity) between the polymer and the filler [31]. The energetic balance between filler-filler interactions in the agglomerates, on the one hand, and filler-polymer interaction, on the other, is thus controlled by the dispersion process.

The general effects of dispersion on rheological properties are shown in the decrease of Mooney viscosity (Fig. 10)and the evolution of the extrusion shrinkage as a function of mixing time. Viscosity, which is an important processing parameter, decreases markedly as mixing time and rotor speed increase. During the early stage of mixing the voids of the fractal filler aggregates are penetrated by a part of the polymer. After this incorporation and the subsequent dispersion stage the filler aggregates are more uniformly distributed and therefore the melt viscosity is reduced [33].

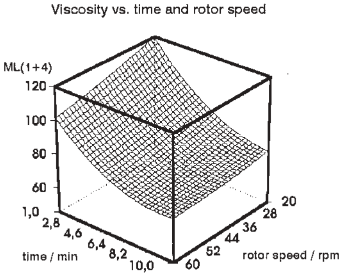


Figure 10: Decrease of the melt viscosity after mixing as a function of mixing time and rotor speed (ML (1-4) = Mooney viscosity; SBR and carbon black N 326 50 phr [34].

As far as filled crosslinked rubber networks are concerned, the large and poorly dispersed filler agglomerates act as flaws and contribute significantly to failure properties such as tensile strength, elongation, energy at break, fatique life and abrasion [35]. Properties dependent upon crack initiation and crack propagation are significantly determined by the dispersion and distribution of the filler. As mixing time and rotor speed and therefor the degree of dispersion increase, tensile strength and crack propagation resistance also increase [35](Fig. 11). The loss in tensile fatigue life as a function of decreasing dispersion (or by increasing the frequency of large agglomerates) is common for all elastomer systems.

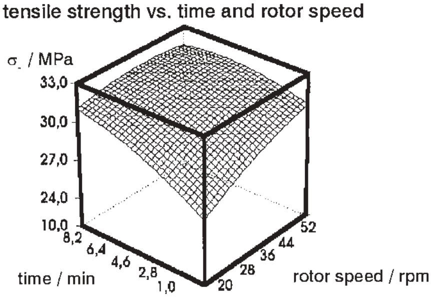


Figure 11: Evolution of tensile strength of a filled SBR vulcanizate as a function of the mixing conditions [35].

Filler networks

Supra-molecular fractal structures (filler network) are formed as filler concentration ϕ increases. It was demonstrated by using polymeric filler particles ranging in size from 30-400 nm that at low filler concentrations the individual particles first tend to cluster together. Above a critical filler concentration ϕ* (gel point) the clusters agglomerate and form a three-dimensional filler network by kinetic cluster-cluster aggregation (CCA) [36-38] The filler network obviously interpenetrates the polymer network. Once the filler network is formed the macroscopic stress is no longer transmitted through the rubber matrix alone, but merely through the self similar branches of the filler network [39].The mechanical properties are thus changed in a characteristic manner on all length scales. Because at length scales longer than the size of a cluster, ξ, the filler network can be considered as homogeneous, the modulus of the entire CCA-network equals the modulus of a single cluster. The clusters behave to some degree as elastic units capable to store energy during twisting, bending or stretching the sample. For very small deformation amplitudes above the gel point ϕ^* at which the filler network is built up, the storage modulus G'_o can be expressed [5] as:

$$G'_0 \cong G_F \left(\frac{a}{\xi}\right)^{3+d_{f,B}} \cong G_F\ \phi^{\frac{3+d_{f,B}}{3-d_f}} \cong \phi^{3,5} \qquad (13)$$

with d_f = 1.8 - fractal dimension of the filler cluster

$d_{f,B}$ = 1.3 fractal dimension of a filler cluster

ξ = size of the clusters

a = size of the particles

This scaling law is observed irrespective of the filler type, or the size of the filler particles and the chemical or physical structure of the surface. A typical example is shown in Fig. 12

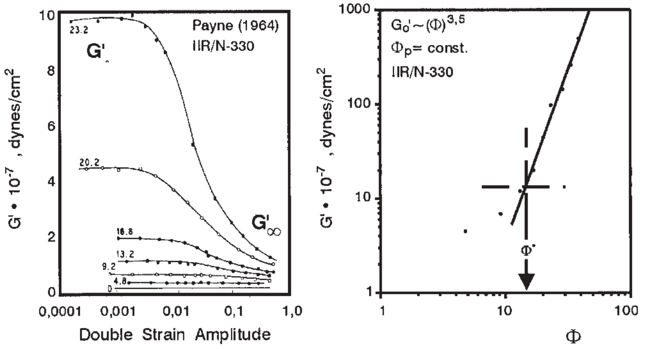


Figure 12: Influence of the filler concentration on the strain amplitude dependency of G' (low strain).

However, the process of self-organization of the nano-particles is controlled by the interaction of the filler clusters with the surrounding matrix [38]. It was shown that the location of the gel point ϕ^* depends on the intensity of the polymer filler interaction. The smaller this interaction, the greater the tendency to particle cluster formation, so that the gel point ϕ^* is reached at lower filler concentrations. The degree of interaction is basically related to the interfacial tension [40]. A high interfacial tension thus tends to support cluster formation at low filler concentrations. Owing to the scaling law, this again results in a higher storage modulus at constant filler concentration, as in the case of systems with strong polymer-filler-interactions. Cluster formation is avoided in better polymer-filler interaction up to a certain degree. This contributes to better dispersion and mixing quality, which is directly evident in the dynamic and ultimate properties.

However, the filler network is not too stable. Deformations of filled elastomer bodys lead to a decrease of the Van der Waals forces which hold the cluster aggregates together. By increasing the strain amplitude in a dynamic test the values of G' are decreasing in a characteristic manner. This non-linear viscoelastic behaviour is typical for filled elastomers and well known as "Payne effect" [41].

The breakdown of the filler network can be modelized by treating it like a percolation lattice [42]. By increasing the deformation strain a random fracture of single clusters and disconnection of clusters in the space -filling configuration of the CCA-network can be assumed. Therefore the mechanical stress can be transmitted only through the remaining clusters of the network. Modeling the strain dependency of the number of surviving clusters the strain dependent modulus can be approximated by a function of the Havriliak-Negami type[42]

$$G'_{\varepsilon\rightarrow 0} = (G'_0 - G'_\infty)[1+(\varepsilon/\varepsilon_{1/2})^{\beta}]^{-\tau} + G'_\infty \qquad (14)$$

where $\tau = 3.6$ is the elasticity exponent of percolation,β is an empirical exponent and $\varepsilon_{1/2}$ is the strain amplitude at which half of the clusters in the lattice are vanished at high deformations.

The drop of G' with increasing strain amplitude corresponds to a gel - sol transition of the filler network at moderate strain and a breakdown of remaining sub-clusters at larger strain. The first process can be described by a monotonic function which reaches the level of hydrodynamic effects of dead ends and broken sub-clusters. The second contribution passes through a maximum because the resulting sub-clusters exert furthermore hydrodynamic reinforcing effects. This contribution become larger and passes through a maximum when the sub-clusters are destroyed. The summation of both contributions leads to the shape of the strain amplitude dependency shown in Fig. 12.The breakdown of the filler network as the dynamic deformation amplitude increases is paralleled by energy dissipation [43]. The process leads to a maximum value of G" at the strain amplitude where G' shows a characteristic inflection point. The position of the G" maximum and the absolute value of G''_{max} depend on the balance of the filler-filler and the filler -matrix -interactions. If one of these influencing parameters are controlled by chemical or physical procedures energy dissipation can be triggered on with useful consequences in application.If the strain amplitude dependence of G' and G" are considered for different types of fillers the influence of the filler surface activity become obvious. Fillers with efficient interparticle and interaggregate interactions demonstrate a high tendency to agglomerate and show the most pronounced Payne effect. If the polymer segments are able to respond with similarly graded interactions, the balance of inter-aggregate and filler-matrix interactions can lead to a higher degree of dispersion, a lower value of the gel point ϕ*and of G'_0. Consequently, any change in surface activity leading to reduced filler-filler interaction result in less pronounced Payne effect. Therefore, the major factors to minimise the difference $G'_0(\omega)-G'_\infty(\omega)$ are:

(i) suitable surface activity
(ii) better polymer-filler interaction
(iii) high structure of the filler
(iv) effective mixing

Filler surface activity

Phase bonding between polymer and filler particles is frequently realized by adsorption of polymer segments on the filler surface and deliberately established via functional groups or bifunctional cross-linkers by chemical bonds. Recently it was demonstrated that on the surface of carbon black particles four types of adsorption sites with discrete energy levels occur. The amount of high energetic sites decreases with the increasing primary particle size[44] Because the high energetic sites on the filler surface are supporting stronger interaggregate interactions it become clear why carbon blacks with high surface specific area show poor degree of dispersion and large Payne effect [3].

The surface activity of carbon blacks can be changed by controlled surface treatment which reduces the concentration of the high energy sites. This weakens the interaggregate interactions and promotes filler-matrix interactions. As can be seen from the Cole-Cole plot in Fig. 13, this leads to a minimization of G' and especially of G". Therefore interaggregate interactions which give rise to a high portion of energy dissipation with amplitude dependent dynamic deformation are effectively reduced.

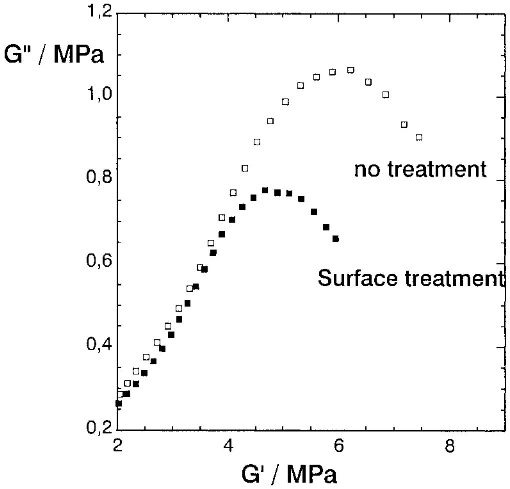


Figure 13: Cole-Cole plots of SBR vulcanizates filled with untreated and treated carbon black (each point corresponds to a given strain amplitude starting from the right with the lowest ε values).

Compared to carbon black, silica can form stronger and more developed agglomerates which would be reflected in higher storage modulus at low strain amplitude and larger Payne effect at low and high temperatures. In a hydrocarbon polymer the polymer-silica interaction which is determined by the dispersive component of filler surface energy is lower than the inter-particle interaction which is supported by the polar silanol groups. Consequently the poor compatibility with the polymer and the strong interaction filler – filler interaction due to the high surface activity lead to a more developed filler network. Changing the surface activity of silica by treatment with mono- or bifunctional silanes the Payne effect can be gradually reduced to a desired level (Fig.14)

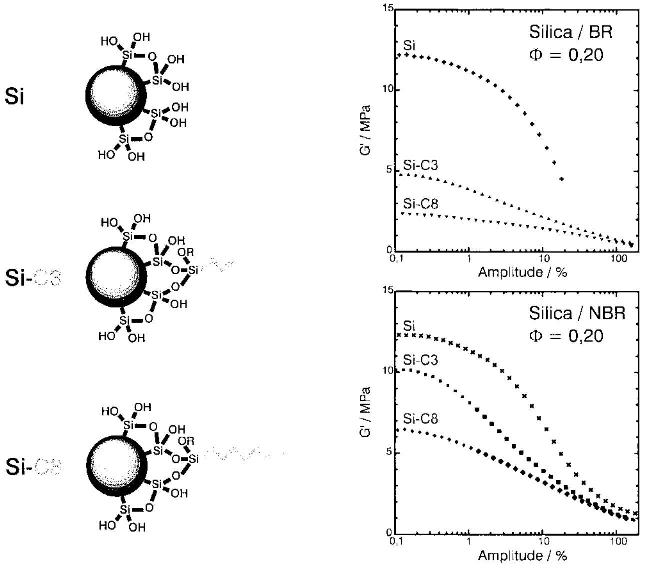


Figure 14: Payne effect for filled BR-compounds with surface treated silica.

Such changes in surface energy distribution lead not only to a better filler dispersion and lower G' and G" but also to a more pronounced energy dissipation in the Tg region. In other words, the better the filler-matrix interaction the higher the amount of energy necessary to convey the same degree of mobility to polymer chains attached to the filler surface or entangled with such chains. Keeping in mind that energy dissipation in the T_g region is a high frequency phenomenon connected with grip properties the possibilities for monitoring complex physical processes by adjusting the surface interaction potential become clear

In conclusion, changing the surface energy distribution of the filler during the production process or by physical or chemical post treatment has a profitable effect on the filler network formation, the percolation threshold and the placement of the energy dissipation maximum. Therefore energy dissipation can be influenced in the low temperature region mainly by selecting the proper rubber matrix and in the high temperature region by adjusting the surface energy distribution of the filler surface.

The intensity of rubber-filler-interactions can be influenced also by icorporating specific monomers and selective interacting groups in polymer chains. As competing absorption experiments have demonstrated, segmental interaction towards carbon black increases in the following order [18]:

Propylene < Ethylene < 1,4-Isoprene ≅1,2-Butadiene < 1,4-Butadiene << Styrene

With increasing the content of better interacting monomer units in a polymer chain the percolation limit is shifted towards larger filler concentration, the degree of dispersion is increased and the difference G'_0 -G'_∞ as well as G'' is reduced. By introducing functional groups able to specifically interacting with the filler the energy dissipation in the low temperature region is significantly increased [45].

Filler distribution in rubber blends

One major consequence of the polymer - filler interaction is the particular distribution of the filler in rubber blends.With decreasing polymer viscosity, or molar mass, the influence of segmental interaction-capacity with the active centers of the filler on the preferential distribution of the filler increases. Based on a recently developed dynamical-mechanical method, the filler distribution is determined by recording the influence of the filler on the energy dissipation in the Tg-region [43]. Quantitative results show that the filler transfer occurs during mixing and the distribution of the filler in polymer blends is equivalent to an equilibrium. It was demonstrated that filler partition occurs between the two discrete phases and the interphase. Except for cases in which the filler-matrix interaction is preferentially oriented towards one polymer, a reinforcement of the interface and, at the same time, an increase in their volume fraction is observed (Fig. 15).

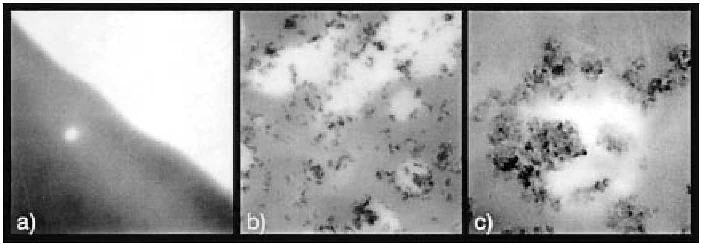


Figure 15: Distribution of surface modificated silica in EPDM/NBR blends. a) unfilled blend b) EPDM/NBR/silicanized silica c) enlarged view of an EPDM domain surrounded by surface modificated silica.

The phase morphology can be adjusted selectively either by functionalizing filler and polymer as well as by changing the mixing order. Especially interesting are those cases in which interpenetrating polymer networks are reinforced by the filler network that is distributed in the phase interface. By recording the dynamic mechanic response for filled NR/S-SBR in the Tg-region it was shown that the majorpart of the filler is located in the interphase (Fig. 16). As a consequence the volume fraction of the interphase and the interphase signal (between the two damping maxima) become significanlty larger. Especially such effects can be exploited for designing high frequency energy dissipation and grip properties of tire treads [43].

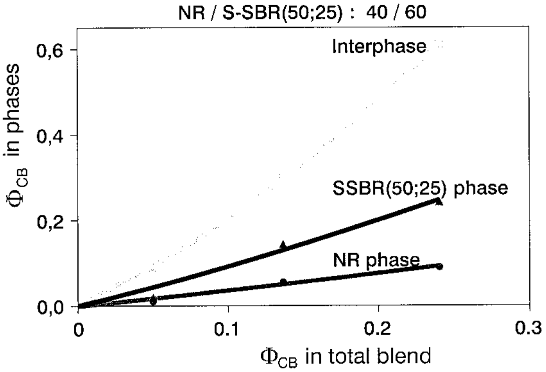


Figure 16: Concentration of CB in the blend phases and the interphase.

Mechanical consequences from filler distribution

Carbon black distribution exerts a significant effect on dynamic modulus at low strain amplitudes (non linear dependence) . The low-strain modulus increases with an uneven distribution of carbon black between the blend components. As for energy dissipation, it was shown that in the case of NR/SBR-lends, a higher loading of the NR-phase reduces heat build-up and increases rolling resistance It was concluded that hysteresis can be minimized by:

(i) large carbon black agglomerate size and broad size distribution,

(ii) higher carbon black loading in discrete domains,

(iii) selecting the polymer with lower hysteresis as the continuous phase.

In blends of NR with either SBR or BR, lower tensile strength has been reported with a lower carbon black loading in SBR or BR. The most pronounced loss of tensile strength was observed when all of the carbon black was added to the NR-phase [31]. For SBR/BR-blends, a lower-tensile pattern has been observed with higher carbon black in the SBR-phase. Usually the changes caused by phase distributions are found to be greater than the differences between carbon black grades.

The main influences on tear resistance came from

- small carbon black aggregate sizes
- low filler structure
- higher loading of the continuous phase,
- the polymer with higher strength than the continuous phase.

Conclusions

The configuration of supramolecular structures in phase-separated rubber blends is determined by the type and frequency of intermolecular interaction. The degree of compatibility and the interfacial tension can be reliably described with the help of the solubility parameter determined by means of inverse gas chromatography. Without neglecting the influence of rheological factors, it can be shown that the concentration range of the phase inversion region is determined by the interfacial tension. The weaker the compatibility of the components, the narrower the concentration range in which co-continuous phase morphologies occur. The co-continuous phase morphologies correspond to supramolecularly organized fractal interpenetrating phase networks, the structures of which influence the dynamic-mechanical properties in the glass-transition region. Phase bonding, which depends largely on the – likewise predictable – thickness of the interphase, decisively influences ultimate properties.

Analogous thermodynamically motivated mechanisms determine the rubber-filler interaction. Under identical mixing conditions, the dispersion of the fillers depends on the intensity of the adsorptive interaction between polymer segments and active sites of the filler. The degree of dispersion attained has a crucial influence on the magnitude of energy dissipation at low and high frequencies, on the one hand, and on the ultimate properties, on the other hand. Filler distribution is, moreover, a direct consequence of the respective interaction between the filler and the chain segment of the polymers. The dispersion obtained after long mixing corresponds to the states of quasi equilibrium obtained and has a crucial influence on the mechanical behavior of filled elastomers.

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