Immiscible Rubber Blends

C. M. Roland

Abstract Most polymer blends are thermodynamically immiscible, leading to a phase-segregated morphology. Control of this morphology, including the domain sizes and interfacial regions, along with partitioning of compounding ingredients such as filler and curatives between the phases, provides opportunities for achieving properties that are otherwise unattainable. This chapter reviews fundamental aspects of phase-separated rubber blends, with a survey of the important literature on the topic.

Due to the vanishingly small entropy gain accompanying the mixing of high polymers, most polymer blends are phase-separated; there is no mixing at the segmental level, and the morphology is heterogeneous. The few thermodynamically miscible rubber blends include those having components exhibiting specific interactions (e.g., chlorinated polymers with epoxidized rubber [1, 2]); trivial blends of copolymers (siloxanes [3], polyolefins [4–6], nitrile rubbers (NBR) [7], ethylene-propylene rubbers [8, 9], butyl and polyisobutylene [10, 11], 1,4-polybutadiene (PBD) and styrene-butadiene rubber (SBR) [12, 13]); and miscellaneous cases such as 1,2-polybutadiene/1,4-polyisoprene (NR) [14], polyisobutylene/head-to-head polypropylene [15], polyepichlorohydrin/poly(vinylmethylether) [16, 17], and acrylate rubber/fluorocarbon copolymers [18]. The focus of this chapter is immiscible blends, in which the components are segregated into spatially distinct domains. These domains can range in size from a few hundred nm to microns, and usually have a very broad size distribution (Fig. 1) [19]. Except at the interface of these phases, the dynamics of the components are essentially the same as for the pure materials. However, immiscible blends can still yield novel and useful properties, provided the components are “compatible”, a term loosely defined as a blend that does not undergo macroscopic phase separation and has some advantageous properties. Unlike miscible blends, the properties of which are roughly the average of

---

C. M. Roland (✉)
Chemistry Division, Naval Research Lab, Code 6120, Washington DC 20375-5342, USA
e-mail: mike.roland@nrl.navy.mil

P. M. Visakh et al. (eds.), *Advances in Elastomers I*,
Advanced Structured Materials 11, DOI: 10.1007/978-3-642-20925-3_6,

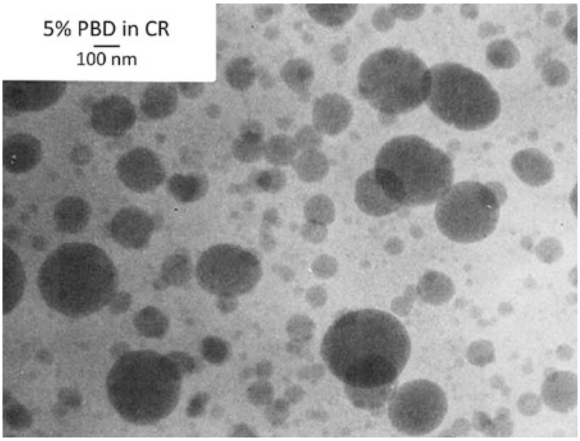


Fig. 1 Transmission electron micrograph of a blend of 5 % 1,4-polybutadiene in polychloroprene. The mean diameter of the dispersed particles is 80 nm, with a very broad size distribution. A 100 nm scale bar is shown in the *upper left corner*. From Ref. [19]

those of the pure component, phase-separated blends can exhibit behavior not otherwise attainable. Some aspects are sensitive to the size of the domains, as well as the composition and interconnectedness of the interfacial regions. An important variable in heterogeneous blends is the spatial distribution of crosslinks, filler, stabilizers, etc. The ability to alter the phase morphology and the distribution of compounding ingredients offers the potential for performance benefits, and many commercial elastomers are phase-separated mixtures.

1 Morphology and Properties

The phases of an immiscible blend can be co-continuous, or one component can be dispersed within a continuous matrix of the other. The former is favored by equal concentrations and equal viscosities; that is, $\eta_1 \approx \eta_2$ and $\phi_1 \approx 0.5$ [20, 21]. This is illustrated in Fig. 2 for a blend of PBD and ethylene-propylene-diene terpolymer (EPDM) [20]. Most blends consist of discrete particles in a continuous phase, with the latter usually the lower viscosity component, provided it is present at a sufficient concentration. During mechanical mixing, domains of the lower viscosity material deform and encapsulate the higher viscosity phase, to produce a "globular" morphology. However, for an immiscible blend the morphology is never at equilibrium (which would correspond to macroscopic phase separation). The size distribution of the dispersed phase represents a steady-state balance between the breakup of the particles and their coalescence (Fig. 3) [19, 22–24], processes that continue throughout mixing and processing. Since to a first approximation the breakup of particles by the flow field is independent of particle concentration, whereas the coalescence probability increases with concentration, the expectation is that the dispersed phase size increases with ϕ, in general accord with experimental results. The final particle size distribution depends both on the rheological

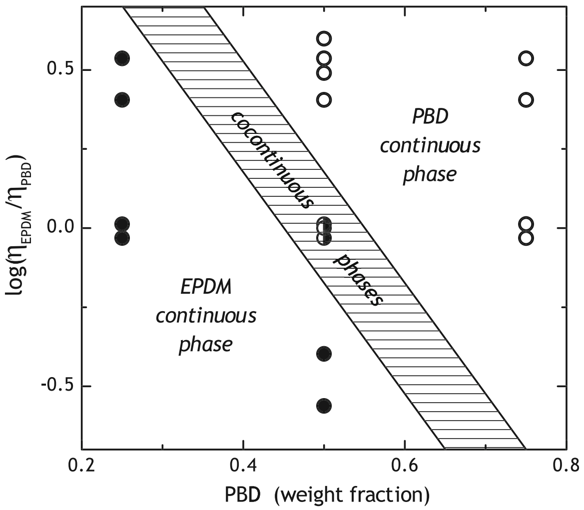


Fig. 2 Dependence of the phase morphology on the viscosity ratio and composition for blends of PBD and EPDM. Dispersed PBD and EPDM particles are indicated respectively by *open* and *filled symbols*; *half-filled symbols* indicate a co-continuous morphology. Data from Ref. [20]

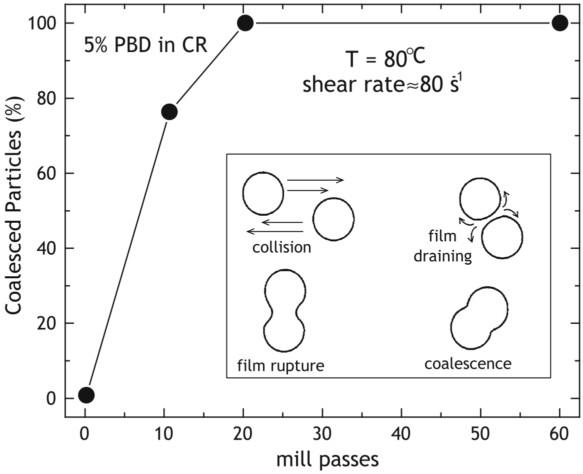


Fig. 3 Amount of PBD (M_w = 89 kg/mol) dispersed in polychloroprene (M_w = 255 kg/mol) that has coalesced with other particles, as a function of the number of passes through a two-roll mill at the indicated conditions. The mean particle radius was 40 nm. The coalescence was monitored from the small-angle neutron scattering intensity; initially half the dispersed PBD was deuterated, so that coalescence reduced the scattering. Despite the highly viscoelastic nature of the materials and the brief contact time of the particles during flow, coalescence readily occurs and thus exerts a major effect on the blend morphology. In the *inset* is an idealized depiction of shear-induced coalescence of dispersed particles. From Ref. [19]

properties of the components and the type of mixing. Stretching flows are more effective at dispersion than shear fields (the latter a combination of stretching and rotational flow), and generally high stresses and strain rates produce a more finely dispersed phase. Nevertheless, the particle size distribution usually has only a modest effect on bulk properties, as seen in mixing rules for blend properties, which consider only the pure component properties and the relative amounts of the components [25, 26]. These include (written for the viscosity) series

$$\eta_{12} = \varphi_1\eta_1 + (1 - \varphi_1)\eta_2 \tag{1}$$

and parallel representations

$$\eta_{12}^{-1} = \varphi_1\eta_1^{-1} + (1 - \varphi_1)\eta_2^{-1} \tag{2}$$

and a log-additivity rule

$$\eta_{12} = \eta_1^{\varphi_1}\eta_2^{1-\varphi_1}. \tag{3}$$

These expressions are strictly empirical and can be generalized with a power-law expression [27]

$$\eta^n = \phi\eta_1^n + (1 - \phi)\eta_2^n. \tag{4}$$

Equations (1)–(4) ignore the effect of phase size and connectedness. The lack of predictive capability limits their utility [28], fitting to actual data often requiring additional adjustable parameters. Even for the simple case of Newtonian fluid mixtures, the viscosity can depend on the particle size, which in turn depends on the mixing or flow conditions [29–31]. Figure 4 [32] shows the variation of the

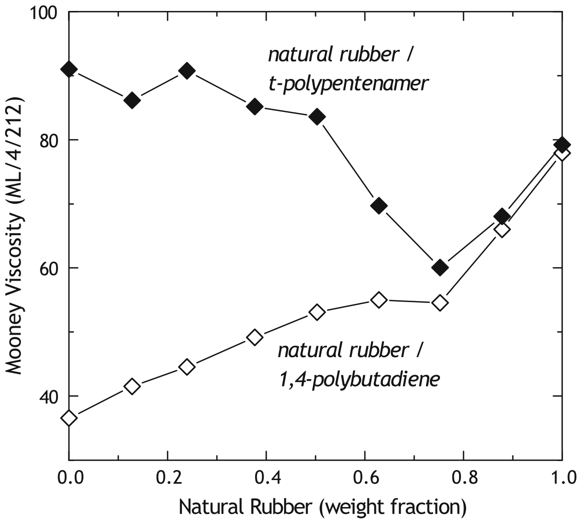
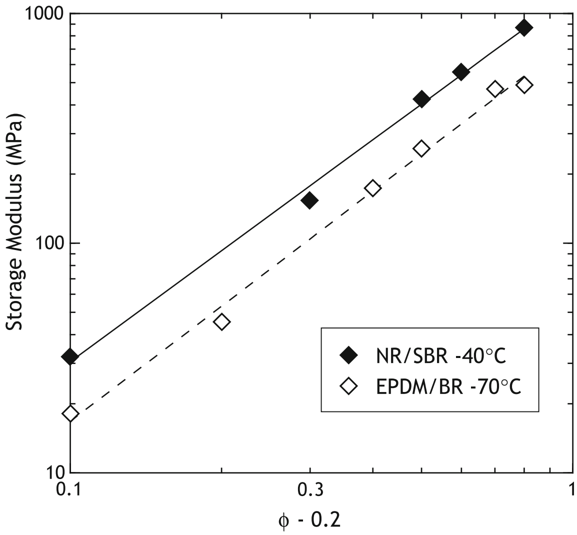


Fig. 4 Mooney viscosity of blends of natural rubber with 1,4-polybutadiene (*filled squares*) and with *trans*-polypentenamer (*open circles*). Data from Ref. [32]

Fig. 5 Dynamic storage modulus of blends of natural rubber and styrene-butadiene copolymer (*filled symbols*) and EPDM and 1,4-polybutadiene (*open symbols*) at the indicated temperatures plotted versus the concentration of the glassy component minus 0.2 (the latter representing the weight fraction at the percolation threshold). Vitrification of the higher T_g component governs the magnitude of G'. Data from Ref. [35]



viscosity with composition for a blend of PBD and polypentenamer; the dependence is very complex and not obviously described by any mixing rule.

Expressions similar to Eqs. (1)–(4) are used to describe the modulus of blends. If the temperature is intermediate between the component T_g's, the phase morphology can affect the blend stiffness in interesting ways, as any applied strain is manifested very differently for each phase. If the discrete particles are glassy, their influence on the modulus is similar to that of a conventional filler. Rubbery particles dispersed in a continuous glassy phase represents the morphology of rubber-toughened plastics [33, 34]. A continuous phase of higher T_g gives rise to a dramatic increase in the modulus, as seen in blends of NR and PBD in Fig. 5 [35].

The failure properties of rubber blends are more sensitive to the details of the domain structure than other mechanical properties. Clarke et al. [36] obtained greater tensile and tear strengths in blends of NR and PBD when mixing was sufficient to reduce the domain size below 1 μm; no further improvement in properties was observed with further mixing (Fig. 6). Blends of a fluoropolymer with hydrogenated nitrile rubber exhibited the highest strength for intermediate compositions, associated with co-continuity of the phases (Fig. 7) [37].

The strain-crystallizability of NR can govern the cut growth behavior and other failure properties of its blends (Fig. 8) [38–40], in particular when the NR is present as a continuous phase [41]. Interestingly, one study found that NR/PBD blends exhibited a maximum in elongation to break for roughly equal concentrations of the components [42], which presumably yields a co-continuous phase morphology. Blends of polychloroprene (CR), which is also strain-crystallizable, with synthetic 1,4-polyisoprene (which has lower cis content and reduced crystallizability than natural rubber) exhibited greater tear strength with increasing CR content [43]. When dispersed as small particles, crystallization of a polymer proceeds more slowly than in the bulk, although the ultimate degree of crystallinity

Fig. 6 Effect of mixing time on tensile and tear strength of 50/50 blend of natural rubber and 1,4-polybutadiene [36]

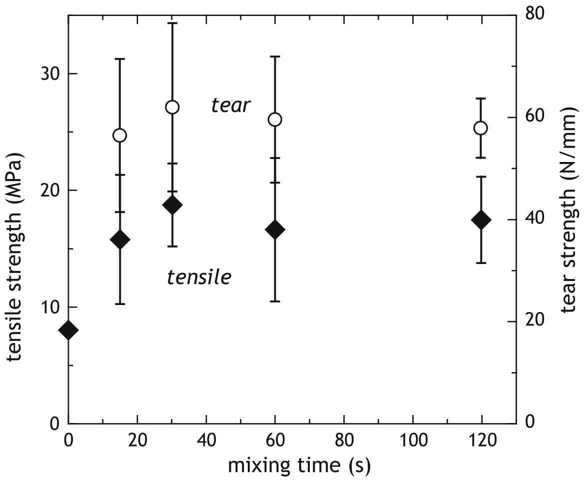
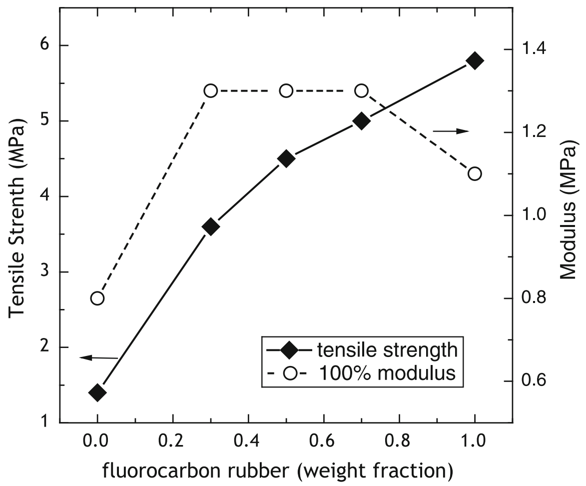


Fig. 7 Stress at break (*diamonds*) and at 100 % extension (*circles*) for a blend of a perfluoromethyl vinyl ether polymer with hydrogenated nitrile rubber. Data from Ref. [37]



is the same [44, 45]. This effect is ascribed to a reduced nucleation rate, similar to the slower crystallization of NR latex when the rubber particles are smaller than 1 μm [46].

2 Compatibilization

Improving the compatibility of the blend components yields smaller and/or more interconnected phases, both of which can potentially improve the properties. This can be achieved through the use of compatibilizing agents or chemical modification of the components. Compatibilizers are surfactants that modify the

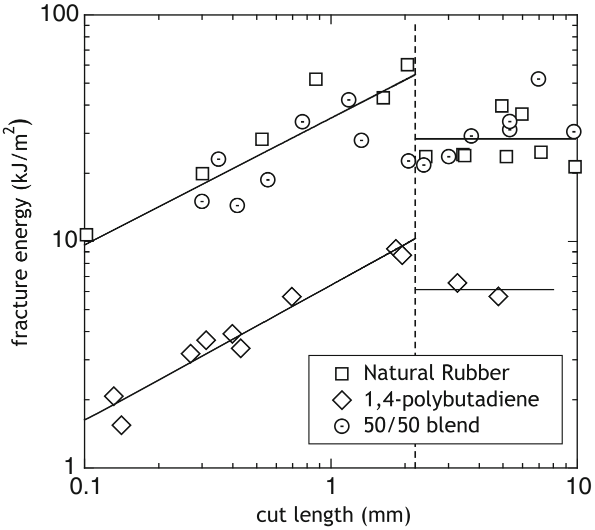


Fig. 8 Fracture strength of NR, PBD, and a 50/50 blend as a function of size of edge cracks introduced into the test specimens. For cracks beyond about 2.2 mm, the material fails before reaching stresses sufficient to induce bulk crystqallization of the NR. Data from Ref. [39]

interfacial tension to decrease the dispersed particle size. Generally higher concentrations of modifiers yield smaller domains sizes up to the saturation point [47]. The compatibilizer may have other functions. For example, immiscible blends of NR and SBR intended for pressure-sensitive adhesives show a single glass transition in dynamic mechanical spectra when plasticized by large quantities of tackifying resin, the latter evidently functioning as a compatibilizer, in addition to improving adhesive performance [48]. Block copolymers can be used to compatibilize phase-segregated blends, by reducing the surface tension [49] and simultaneously enhancing the strength of the interfacial regions [50–52].

Examples of chemical modification to achieve better homogeneity include: EPDM modified with maleic anhydride [53]; acrylamide-grafted polydimethylsiloxane (PDMS) with sulfonated EPDM [54]; and mercapto-modified ethylvinyl acetate rubber in blends with NR [55]. Similar efforts have been made to compatibilize EPDM with PDMS [56, 57], NR [58] and PBD [59]. A variation on this approach is to obtain interphase crosslinking by oxidatively crosslinking the blend components. Molding at very high temperatures (200 °C) for extended times have been shown to compatibilize certain rubber blends [60].

Compatibilizers can have an indirect effect on blend morphology and properties when they function as plasticizers. Plasticizers and processing aids are used to reduce the resistance to flow of polymers by lowering the internal friction (viscosity), as well as the friction with the walls of mixers, extruders, roll mills, etc. By inducing slippage at the interface with the mixing vessel, shear flow is suppressed without affecting the extensional flow that most effectively disperses the components and any filler particles. (Note that dispersive mixing refers to breakup of these constituents into smaller sizes, and is different from distributive mixing, which gives a more spatially uniform concentration of the ingredients). However, lubricants can be depleted and

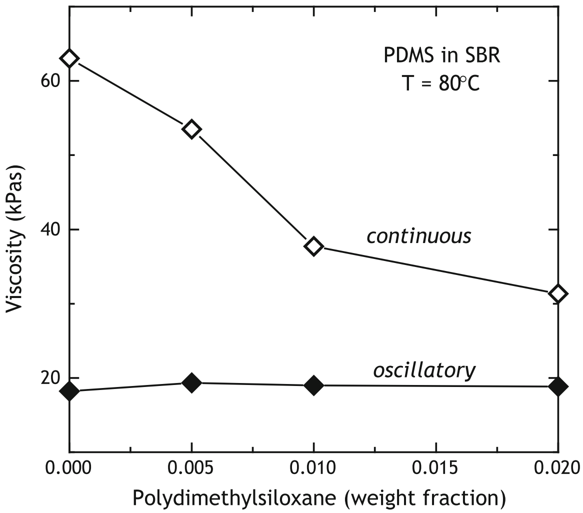


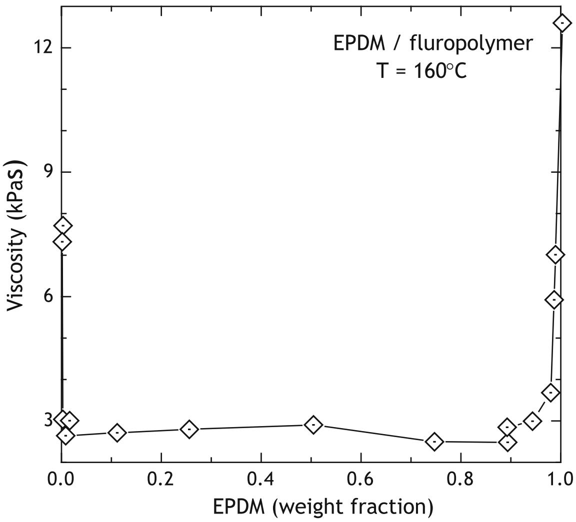
Fig. 9 Viscosity of an SBR with 50 phr N326 carbon black as a function of added PDMS measured by oscillatory (*open symbols*) and continuous (*filled symbols*) shearing at a rate equal to 4.5 s^{-1}. Data from Ref. [64]

at high concentrations may affect the properties of the cured rubber. An alternative is to add small quantities of a polymeric component of lower viscosity. During processing, the lower viscosity component of a phase-separated blend tends to accumulate at the surface, where the shear rates are largest [61, 62]. The phenomenon of the morphology arranging to accommodate the applied stresses is referred to as the principle of minimum viscous dissipation [63].

Figure 9 [64] shows the viscosity measured dynamically and during continuous shear flow of an SBR containing low levels of a PDMS. The silicone has a viscosity ten times lower than the SBR (due to the lower molecular weight and higher entanglement molecular weight of the silicone polymer). Since the strain in the oscillatory experiment is spatially homogeneous, the PDMS is uniformly distributed and has negligible effect on the dynamic viscosity, given its low concentration. However, the apparent viscosity for flow through a capillary die is much lower for the blend, because the material at the surface becomes enriched with the PDMS [64]. The consequence is a non-uniform velocity profile and lower resistance to flow. Note that since the extensional flow is unaffected (being determined by the geometry of the die), the dispersion of carbon black in this compound was unaffected by the PDMS [64]. And since the total amount of the PDMS is low, bulk properties were also unchanged by its presence.

This segregation of two incompatible polymers can continue over time under quiescent conditions, governed by the diffusive mobility of the polymers. For example, Bhowmick et al. [65] observed that PDMS diffuses to the surface during aging of blends. (The opposite phenomenon—miscible components spontaneously interdiffusing—has also been reported [1].) Surface accumulation of one component can also result from interaction (chemisorption) with the walls of the processing equipment. This can lead to contamination of the walls by the adhering polymer. If there is strong incompatibility with the main component, the result can

Fig. 10 Viscosity of a blend of EPDM and a Viton® fluoroelastomer measured in a capillary rheometer at a nominal shear rate equal to 14 s^{-1}. Data from Ref. [66]



be slippage at the interface. This is seen in the enormous reduction in apparent viscosity in blends of EPDM and a fluorelastomer (Fig. 10) [66]. The blend exhibits a resistance to flow almost an order of magnitude smaller than for either of the neat components.

3 Distribution of Crosslinks

The distribution between the phases of curatives, plasticizers, antioxidants, fillers, etc. can have an effect on the cured properties of blends. Thus, non-uniformity of plasticizers can affect the phase morphology, through their influence on the component viscosities. Unequal partitioning of the antioxidants in a blend can result in inferior resistance to degradation and a shortened service life. A major issue in heterogeneous blends is the distribution of crosslinks. Uniform crosslinking generally gives the best properties, with severe imbalances resulting in over- or undercured material. Since crosslinking increases the glass transition temperature, a disparity in crosslinking of the components can alter their respective T_g's in the blend (Fig. 11) [67]. Achieving uniform states of cure can be difficult, since the components may have different affinities for the curatives, common for blend components differing in polarity or degree of unsaturation. Even components of similar polarity and unsaturation can have cure imbalances if their crosslink reactivities are different, as has been observed in vulcanization and peroxide curing of NR/PBD blends [68, 69]. Curative depletion in the faster-reacting phase can induce diffusion from the other component [70]. The levels of sulfur and accelerators are usually below their solubility limits, which engenders curative migration [71–75].

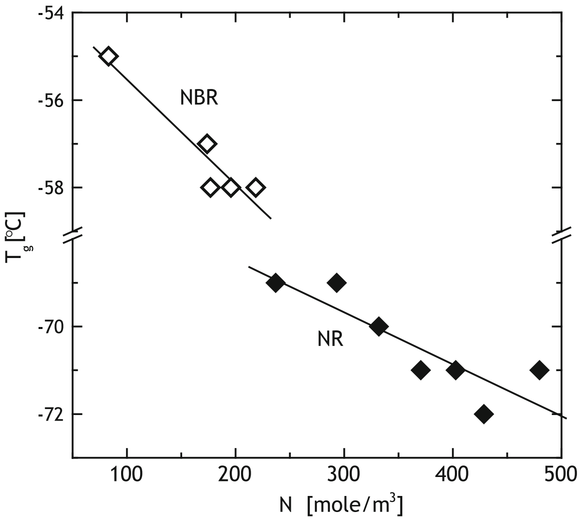


Fig. 11 Glass transition temperature of each component in blends of natural and nitrile rubbers as a function of the number of repeat units between crosslink junctions. The cure system, tetramethylthiuram monosulfide with either *bis*-alkylphenol disulfide or free sulfur, preferentially resides in the more polar NBR phase, causing the latter to be two to five times more crosslinked. Data from Ref. [67]

An obvious solution to crosslink imbalances is to use curing chemicals with more nearly equal solubility and reactivity for the components, for example through judicious selection of vulcanization temperature [76] and accelerators [77, 78]. For example, changes in the accelerator altered the tensile strength of NR blends with acrylic rubber by more than a factor of two [77]. The curatives can also be premixed into the components at optimal concentrations prior to blending of the rubbers [79]; however, this increases the potential for prevulcanization (scorch) and does not address curative migration. One study found that when uniformly distributed initially, curatives are prone during mixing to take up residence within the continuous phase [79]. Precuring the more saturated component prior to blending can alleviate crosslink misapportionment [80, 81], although this may be impractical and will affect the phase morphology. Covalent bonding of the curatives to the polymers, of course, precludes migration [58, 82, 83].

For strength properties there is an additional requirement of achieving interfacial crosslinking in order to mutually adhere the domains. This is difficult when the blends have different reactivities, a common example being EPDM with NR or PBD. One approach to circumvent the problem is grafting accelerators to the components [82].

4 Distribution of Filler

Non-uniform filler distribution is an important issue with blends, since reinforcement of both phases is necessary to optimize physical properties. The affinity of carbon black, for example, varies among polymers (usually being higher in the more polar or unsaturated component [84]), so that non-uniform distributions in

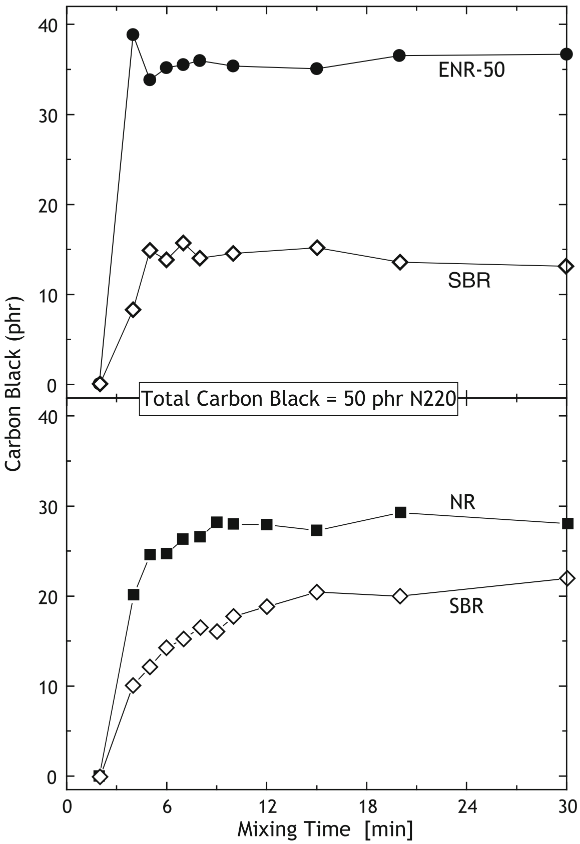


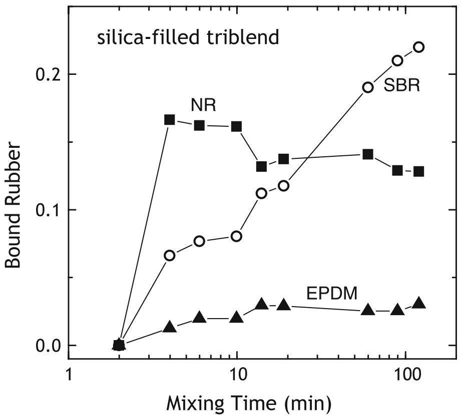
Fig. 12 Carbon black content of each component in immiscible blends of SBR with (*top*) 50 % epoxidized natural rubber and (*bottom*) natural rubber. The filler preferentially incorporates into the more polar phase. Data from Ref. [85]

blends are common. This is illustrated in Fig. 12 [85], showing the different uptake of carbon black in blends of SBR with NR, a relatively non-polar polymer, and with a polar, epoxidized natural rubber. The carbon black distribution is more inhomogeneous for the latter.

At least for carbon black, the filler distribution obtained during mixing is irreversible, because the polymer chains adhere strongly to the particle surface. This can be taken advantage of by sequential addition of the filler or by adding the filler to the components prior to their blending; thus, the distribution between blend components is controlled by the mixing procedure [86]. Silica bonds weakly to polymers, so that the particles can transfer between phases during mixing. This is illustrated in Fig. 13 [87], in which the bound rubber was measured for each component as a function of mixing time. The higher rate of wetting of silica by NR leads to high silica content initially; however, over the course of the mixing some silica transfers to the SBR component.

Since the concentration of filler affects the melt viscosity, its inhomogeneous distribution can influence indirectly the phase morphology (see Fig. 1). Properties such as the elasticity and hysteresis depend non-linearly on filler concentration, so

Fig. 13 Bound rubber measured for each of the components of a blend of NR, SBR, and EPDM during mixing. *Note* transfer of the silica from the NR to the SBR. Data from Ref. [87]



that a non-uniform distribution can be exploited to achieve properties that depart from the mean of those of the components. This approach has been demonstrated to afford control of the die swell and elastic rebound of rubber blends [88–90]. Carbon black particles located at the interface between the components can give rise to electrical conductivity higher than achievable with neat elastomers [91–93], which can be useful for antistatic or shielding applications.

5 Summary

Among commercial elastomers, the volume of blends is probably as large as the volume of pure rubbers, and certainly the vast majority of the former are phase separated; i.e., thermodynamically immiscible but not incompatible. The problems with rubber blends outlined in this brief review are well-known, and various solutions have been developed. Given the difficulty and expense of producing new polymers, blends will continue to be an attractive source of new properties. One promising approach that is largely unexplored is nanoconfinement. It is well-established that unusually large surface to volume ratios and the intrusion of an external dimension on the length scale of polymers, including their coil size, changes the behavior from that in the bulk state [94–97]. It has been reported that in a blend, one component can experience nanoconfinement by the other, leading to large changes in the dynamic behavior [98, 99]. The effect of confinement on polymers is complex and there are many anomalies; however, with this complexity is the expectation of unique properties.

Acknowledgment This work was supported by the Office of Naval Research.

References

1. Nagode, J.B., Roland, C.M.: Polymer **32**, 505 (1991)
2. Roland, C.M., Santangelo, P.G., Baram, Z., Runt, J.: Macromolecules **27**, 5382 (1994)
3. Kuo, C.M., Clarson, S.J.: Polymer **41**, 5993 (2000)
4. Lohse, D.J., Garner, R.T., Graessley, W.W., Krishnamorti, R.: Rubber Chem. Technol. **72**, 569 (1999)
5. Reichart, G.C., Graessley, W.W., Register, R.A., Lohse, D.J.: Macromolecules **31**, 7886 (1998)
6. Crist, B., Hill, M.J.: J. Polym. Sci., Polym. Phys. Ed. **35**, 2329 (1997)
7. Bartenev, G.M., Kongarov, G.S.: Rubber Chem. Technol. **36**, 668 (1963)
8. Ellul, M.D., Gent, A.N.: J. Polym. Sci. Polym. Phys. Ed. **23**, 1823 (1985)
9. Dikland, H.G., Van Duin, V.: Rubber Chem. Technol. **76**, 495 (2003)
10. Ellul, M.D., Gent, A.N.: J. Polym. Sci. Polym. Phys. Ed. **23**, 1953 (1984)
11. Hamed, G.R., Ogbimi, F.: Rubber Chem. Technol. **59**, 347 (1986)
12. Maier, T.R., Jamieson, A.M., Simha, R.: J. Appl. Polym. Sci. **51**, 1053 (1994)
13. Sakurai, S., Izumitani, T., Hasegawa, H., Hashimoto, T., Han, C.C.: Macromolecules **24**, 4844 (1991)
14. Tomlin, D.W., Roland, C.M.: Macromolecules **25**, 2994 (1992)
15. Krishnamoorti, R., Graessley, W.W., Fetters, L.J., Garner, R.T., Lohse, D.J.: Macromolecules **28**, 1252 (1995)
16. Alegria, A., Elizetxea, C., Cendoya, I., Colmenero, J.: Macromolecules **28**, 8819 (1995)
17. McGrath, K.J., Roland, C.M.: Rubber Chem. Technol. **67**, 629 (1994)
18. Kader, M.A., Bhowmick, A.K.: Rubber Chem. Technol. **73**, 889 (2000)
19. Roland, C.M., Bohm, G.G.A.: J. Polym. Sci. Pt. B-Polym. Phys. **22**, 79 (1984)
20. Avgeropoulos, G.N., Weissert, F.C., Biddison, P.H., Bohm, G.G.A.: Rubber Chem. Technol. **49**, 93 (1976)
21. Paul, D.R., Barlow, J.W.: J. Macromol. Sci. Rev. Macromol. Chem. **C18**, 108 (1980)
22. Peng, X., Huang, Y., Xia, T., Kong, M., Li, G.: Eur. Polym. J. **47**, 1956 (2011)
23. Sirisinha, C., Saeoui, P., Guaysomboon, J.: J. Appl. Polym. Sci. **90**, 4038 (2003)
24. Chen, X., Xi, J., Guo, B.H.: J. Appl. Polym. Sci. **102**, 3201 (2006)
25. Nielsen, L.E.: Predicting the Properties of Mixtures. Marcel Dekker, New York (1978)
26. Utracki, L.A., Kamal, M.R.: Polym. Eng. Sci. **22**, 96 (1982)
27. Nielsen, L.E.: Mechanical Properties of Polymers and Composites. Marcel Dekker, New York (1974)
28. Han, C.D.: Multiphase Flow in Polymer Processing. Academic, London (1981)
29. Frankel, N.A., Acrivos, A.: J. Fluid Mech. **44**, 65 (1970)
30. Choi, S.J., Schowalter, W.R.: Phys. Fluids **18**, 420 (1975)
31. Grizzuti, N., Buonocore, G., Iorio, G.: J. Rheol. **44**, 149 (2000)
32. Folt, V.L., Smith, R.W.: Rubber Chem. Technol. **46**, 1193 (1973)
33. Riew, C.K. (ed.): Rubber Toughened Plastics, Adv. Chem. Ser, Amer. Chem. Soc. Washington **222** (1989)
34. Collyer, A.A. (ed.): Rubber Toughened Engineering Plastics. Chapman and Hall, London (1994)
35. Kluppel, M., Schuster, R.H., Schaper, J.: Rubber Chem. Technol. **72**, 91 (1999)
36. Clarke, J., Clarke, B., Freakley, P.K.: Rubber Chem. Technol. **74**, 1 (2001)
37. Hirano, K., Suzuki, K., Nakano, K., Tosaka, M.: J. Appl. Polym. Sci. **95**, 149 (2005)
38. Hamed, G.R., Kim, H.J., Gent, A.N.: Rubber Chem. Technol. **69**, 807 (1996)
39. Hamed, G.R., Kim, H.J.: Rubber Chem. Technol. **72**, 895 (1999)
40. Lee, M.-P., Moet, A.: Rubber Chem. Technol. **66**, 304 (1993)
41. Kim, H.J., Hamed, G.R.: Rubber Chem. Technol. **73**, 743 (2000)
42. Taghvaei-Ganjali, S., Motiee, F., Fotoohi, F.: Rubber Chem. Technol. **81**, 297 (2008)
43. Kardan, M.: Rubber Chem. Technol. **74**, 614 (2001)

44. Gent, A.N., Kawahara, S.: Rubber Chem. Technol. **71**, 837 (1998)
45. Kawazura, T., Gent, A.N., Kawahara, S.: Rubber Chem. Technol. **76**, 1164 (2003)
46. Wathen, G.D., Gent, A.N.: J. Nat. Rubber Res. **5**, 178 (1990)
47. Favis, B.D.: Polymer **35**, 1552 (1994)
48. Copley, B.C.: Rubber Chem. Technol. **55**, 416 (1982)
49. Virgilioa, N., Desjardinsb, P., L'Espérancec, G., Favis, B.D.: Polymer **51**, 1472 (2010)
50. Teyssie, P., Fayt, R., Jerome, R.: Makromol. Chem. **187**, 837 (1986)
51. Galloway, J.A., Jeon, H.K., Bell, J.R., Macosko, C.W.: Polymer **46**, 183 (2005)
52. Puskas, J.E., Kaszas, G.: Rubber Chem. Technol. **74**, 583 (2001)
53. Kole, S., Roy, S., Bhowmick, A.K.: Polymer **37**, 625 (1996)
54. Kole, S., Roy, S., Bhowmick, A.K.: Polymer **35**, 3423 (1994)
55. Jansen, P., Gomes, A.S., Soares, B.G.: J. Appl. Polym. Sci. **61**, 591 (1996)
56. Kole, S., Bhattacharya, A., Tripathy, D.K.: J. Appl. Polym. Sci. **48**, 529 (1993)
57. Kole, S., Santra, R., Bhowmick, A.K.: Rubber Chem. Technol. **67**, 119 (1994)
58. Coran, A.Y.: Rubber Chem. Technol. **61**, 281 (1988)
59. Go, J.-H., Ha, C.-S.: J. Appl. Polym. Sci. **62**, 509 (1996)
60. Mukhopadhyay S., De S.K.: J. Appl. Polym. Sci. **45**, 2283 (1991); **45**, 181 (1992)
61. White, J.L., Ufford, R.C., Dharod, K.R., Price, R.L.: J. Appl. Polym. Sci. **16**, 1313 (1972)
62. Everage, A.E.: Trans. Soc. Rheol. **17**, 629 (1973)
63. MacLean, D.L.: Trans. Soc. Rheol. **17**, 385 (1973)
64. Roland, C.M., Nguyen, M.: J. Appl. Polym. Sci. **35**, 2141 (1988)
65. Bhowmick, A.K., Konar, J., Kole, S., Narayanan, S.: J. Appl. Polym. Sci. **57**, 631 (1995)
66. Shih, C.K.: Polym. Eng. Sci. **16**, 742 (1976)
67. Tinker, A.J.: Rubber Chem. Technol. **63**, 503 (1990)
68. Ellul, M.D., Patel, J., Tinker, A.J.: Rubber Chem. Technol. **68**, 573 (1995)
69. Mangaraj, D.: Rubber Chem. Technol. **75**, 365 (2002)
70. Bhowmick, A.K., De, S.K.: Rubber Chem. Technol. **53**, 960 (1980)
71. Gardiner, J.R.: Rubber Chem. Technol. **41**, 1312 (1968)
72. Van Amerongen, G.J.: Rubber Chem. Technol. **37**, 1065 (1964)
73. Shershnev, V.A.: Rubber Chem. Technol. **55**, 537 (1982)
74. Huson, M.G., McGill, W.J., Wiggett, R.D.: Plast. Rub. Proc. Appl. **5**, 319 (1985)
75. Bauer, R.F., Crossland, A.H.: Rubber Chem. Technol. **61**, 585 (1988)
76. Groves, S.A.: Rubber Chem. Technol. **71**, 958 (1998)
77. Wootthikanokkhan, J., Clythong, N.: Rubber Chem. Technol. **76**, 1116 (2003)
78. Mastromatteo, R.P., Mitchell, J.M., Brett, T.J.: Rubber Chem. Technol. **44**, 1065 (1971)
79. Leblanc, J.L.: Plast. Rub.: Proc. Appl. **2**, 361 (1982)
80. Suma, N., Joseph, R., George, K.E.: J. Appl. Polym. Sci. **49**, 549 (1993)
81. Sahakaro, K., Naskar, N., Datta, R.N., Noordermeer, J.W.M.: Rubber Chem. Technol. **80**, 115 (2007)
82. Baranwal, K.C., Son, P.N.: Rubber Chem. Technol. **47**, 88 (1974)
83. Hashimoto, K., Miura, M., Takagi, S., Okamoto, H.: Int. Polym. Sci. Tech. **3**, 84 (1976)
84. Callan, J.E., Hess, W.M., Scott, C.E.: Rubber Chem. Technol. **44**, 814 (1971)
85. Le, H.H., Ilisch, S., Kasaliwal, G.R., Radusch, H.-J.: Rubber Chem. Technol. **81**, 767 (2008)
86. Varughese, S., Tripathy, D.K.: J. Appl. Polym. Sci. **49**, 1115 (1993)
87. Le, H.H., Ilisch, S., Heidenreich, D., Osswald, K., Radusch, H.-J.: Rubber Chem. Technol. **84**, 41 (2011)
88. Lee, B.L.: Polym. Eng. Sci. **21**, 294 (1981)
89. Hess, W.M.: Rubber Chem. Technol. **64**, 386 (1991)
90. Sircar, A.K., Lamond, T.G., Pinter, P.E.: Rubber Chem. Technol. **47**, 48 (1974)
91. Sircar, A.K.: Rubber Chem. Technol. **54**, 820 (1981)
92. Miyasaka, K., Watanabe, K., Jojima, E., Aida, H., Sumita, S., Ishikawa, K.: J. Mater. Sci. **17**, 1610 (1982)
93. Ibarra-Gomez, R., Marquez, A., Ramos de Valle, L.F., Rodriguez-Fernandez, O.S.: Rubber Chem. Technol. **76**, 969 (2003)

94. G.B. McKenna, J. Phys. IV **10**, Pr7-53 (2000)
95. Fakhraai, Z., Sharp, J.S., Forrest, J.A.: J. Polym. Sci. Polym. Phys. Ed. **42**, 4503 (2004)
96. Koh, Y.P., Simon, S.L.: J. Polym. Sci. Polym. Phys. Ed. **46**, 2741 (2008)
97. Roland, C.M.: Macromolecules **43**, 7875 (2010)
98. Schwartz, G.A., Colmenero, J., Aglegria, A.: Macromolecules **40**, 3246 (2007)
99. Tyagi, M., Arbe, A., Colmenero, J., Frick, B., Stewart, J.R.: Macromolecules **39**, 3007 (2006)