2 Improving the Physical Properties of Cured Rubber Compounds

2.1 Increasing Tensile Strength

In the rubber industry, ultimate tensile strength is considered a fundamental material property. This test parameter measures the ultimate strength of the cured vulcanizate. Even though a typical rubber product probably never will be stretched anywhere close to its ultimate tensile strength, many rubber product users still consider it an important indicator of the overall quality of the compound. Therefore, tensile strength is a very common specification property that a compounder typically will need to find a way to meet even though its relevance to the specific product end use is usually poorly defined.

A compounder might consider trying the following ideas on an experimental basis if an additional improvement in tensile strength is needed. Also all relevant literature sources, including the ones cited below, should be researched and read. **Caution:** these general experimental ideas may not work in all specific situations. Changes to increase tensile strength will certainly affect other properties as well, for better or for worse, and this book does not purport to show how these other properties are affected. Also this book does not purport to address safety and health issues.

To achieve the highest tensile strength, generally one should start with strain crystallizing base elastomers such as natural rubber (NR), polychloroprene (CR), isoprene rubber IR, hydrogenated nitrile rubber (HNBR), or polyurethane (PU). RP: J.R. Halladay.

Compounds based on NR generally impart better tensile strength than similar compounds based on CR. RT: Chapter 6, “Elastomer Selection,” R. School, p. 133.

Of the various grades of NR, ribbed smoked sheet no. 1 gives the highest tensile value. RT: Chapter 7, “General Purpose Elastomers and Blends,”
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G. Day, p. 156.

Ribbed smoked sheet no. 3 reportedly may actually impart higher ultimate tensile strength than ribbed smoked sheets no. 1, at least in blackloaded compounds. RP: J.M. Long.

For NR-based compounds, avoid using a chemical plasticizer (peptizer) such as dibenzamido-diphenyl disulfide or pentachlorothiophenol (PCTP) because it may reduce the ultimate tensile strength of the compound. RT: Chapter 14, “Ester Plasticizers and Processing Additives,” C. Stone, p. 366.

Polychloroprene

Polychloroprene (CR) is a strain crystallizing polymer that imparts high tensile strength even without dependency on high loadings of reinforcing fillers. In fact sometimes the ultimate tensile strength can actually be increased by reducing the filler loading. Selecting a CR with a higher molecular weight may also increase the ultimate tensile strength. RP: L.L. Outzs.

SBR

Use emulsion SBR polymerized at +5 °C (41 °F) (or lower) instead of +50 °C (122 °F) for a significant improvement in tensile strength. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p.149. RP: J.M. Long.

Emulsion SBR usually provides higher tensile strength than solution SBR. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p.156.

Substituting an oil-extended high molecular weight SBR for an unextended SBR while making compound adjustments to keep the same oil level may improve the ultimate tensile strength. RP: J.M. Long.

NBR

Use nitrile rubber (NBR) grades with higher bound acrylonitrile (ACN) content for higher compound tensile strength. RT: Chapter 8, “Specialty Elastomers,” M. Gozdiff, p. 194.

Consider NBR grades with more narrow molecular weight distribution for higher compound tensile strength. RT: Chapter 8, “Specialty Elastomers,” M. Gozdiff, p. 197.
2.1 Increasing Tensile Strength

**Molecular Weight Effect**


**Carboxylated Elastomers**

Consider using carboxylated elastomers in place of noncarboxylated versions, that is, carboxylated NBR (XNBR) in place of NBR or XHNBR in place of HNBR. RP: J.R. Halladay.

Use XNBR with the appropriate zinc oxide in place of conventional NBR to achieve a higher compound tensile strength. RT: Chapter 8, “Specialty Elastomers,” M. Gozdif, p. 199.

**EPDM**

Use semicrystalline EPDM grades (with higher ethylene content) to impart higher ultimate tensile strength. RT: Chapter 8, “Specialty Elastomers,” R. Vara, J. Laird, p. 191.

**EPDM Catalysts**

Single site constrained geometry (CGC) metallocene catalyst technology for commercial polymerization has made it possible to produce efficiently commercial grades of EPDM with very high ethylene content and higher crystallinity. These special grades with higher ethylene content impart higher ultimate tensile strength to the vulcanizate. In addition, by substituting a higher concentration of ENB for propylene at constant ethylene content, still higher ultimate tensile strength values can be achieved using this unique technology. GEN: D. Parikh, M. Hughes, M. Laughner, L. Meiske, R. Vara, “Next Generation of Ethylene Elastomers,” Presented at ACS Rubber Div. Meeting, Fall, 2000.

Consider using Buckminsterfullerene C_{60} in an EPDM with exposure to ultraviolet light to develop tensile strength significantly higher than that generated by free-radical crosslinking from dicumyl peroxide. This forms a “nanocomposite” from the EPDM/C_{60} combination. GEN: G. Hamed, “Reinforcement of Rubber,” *Rubber Chemistry and Technology*, July–August, 2000, Vol. 73, p. 524.


Raw synthetic rubber such as SBR usually contains stabilizers. However, mixing SBR compounds at high temperatures such as 325°F (163°C) or above can cause the formation of both redispersible gel (or “loose” gel that can be milled out) and so-called “tight” gel (which cannot be milled out and remains insoluble in the appropriate solvents). Both of these types of gel can reduce the ultimate tensile strength of the rubber compound. Therefore it might be prudent to restrict how high the dump temperature should be. GEN: R. Mazzeo, “Preventing Polymer Degradation During Mixing,” Rubber World, February 1995, p. 22.


2.1 Increasing Tensile Strength

Step-down Cure

For autoclave-cured products, avoid porosity and low tensile strength by slowly reducing pressure toward the end of the cure cycle. This is called a “step-down cure.” RP: L.L. Outzs.

Cure Time and Temperature


Processing


Polyurethane

For very high ultimate tensile strength properties, base the compound on either polyester or polyether urethane polymers. RT: Chapter 6, “Elastomer Selection,” R. School, p. 126.

The ultimate tensile strength for a two-part cast polyurethane system usually can be increased by adjusting the curative ratio. The curative ratio refers to the relative amounts of prepolymer and curative. The amount of curative [such as methylene-bis-orthochloroaniline (MBCA)] needed to match exactly the isocyanate groups on the prepolymer is referred to as a “100% theory” or “100% stoichiometry.” For example, if the curative is reduced by 5%, it is referred to as “95% theory” or “95% stoichiometry.” On the other hand, if the curative is increased by 5% from theory, it is referred to as “105% theory” or “105% stoichiometry.” Generally going to a lower stoichiometry, such as 95%, may improve ultimate tensile strength. RT: Chapter 9, “Polyurethane Elastomers,” R.W. Fuest, p. 251.

Usually, but not always, selecting an ester type polyurethane provides an advantage for tensile strength in demanding applications. RT: Chapter 9, “Polyurethane Elastomers,” R.W. Fuest, p. 257.
To ensure good tensile strength, avoid basing a compound on either silicone or fluorosilicone rubber. RT: Chapter 6, "Elastomer Selection," R. School, p. 136.

To significantly increase the ultimate tensile strength for terpolymers of ethylene-acrylic elastomer (AEM) (under the trade name of Vamac, from DuPont), which uses a traditional diamine cure system based on hexamethylenediamine carbamate (HMDC) and DPG, consider the addition of dicumyl peroxide and a 1,2-polybutadiene (Ricon, 152) to reportedly increase the ultimate tensile strength. GEN: H. Barager, K. Kammerer, E. McBride, "Increased Cure Rates of Vamac Dipolymers and Terpolymers Using Peroxides," Presented at ACS Rubber Div. Meeting, Fall, 2000, Paper No. 115.


Using zinc oxide to crosslink a gum carboxylic butadiene rubber that possesses one carboxyl group for approximately every 100 carbons on the backbone can produce a cured rubber that has higher tensile strength than those produced using normal sulfur cures. This becomes an “ionomeric elastomer” in which ionic crosslink sites form nanometer-sized domains. GEN: G. Hamed, "Reinforcement of Rubber," Rubber Chemistry and Technology, July–August, 2000, Vol. 73, p. 524.

Increase the percent dispersion of reinforcing fillers such as carbon black through better mixing techniques. RT: Chapter 3, "Vulcanizate Physical Properties, Performance Characteristics, and Testing." J.S. Dick, p. 49.
2.1 Increasing Tensile Strength


### Phase Mixing

For an SBR/BR blend, a lower tensile strength was reported when there was a higher concentration of carbon black in the SBR phase through phase mixing techniques. GEN: W. Hess, C. Herd, P. Vegvari, “Characterization of Immiscible Elastomer Blends,” Rubber Chemistry and Technology, July–August, 1993, Vol. 66, p. 329.

It has been reported that through phase mixing techniques of a NR/BR blend, one can achieve an increase in the amount of carbon black dispersed in the BR phase which may increase the ultimate tensile strength. Other reports have found different effects. Also Hess reported a large drop in tensile strength if all the carbon black is concentrated in the NR phase. GEN: E. McDonel, K. Baranwal, J. Andries, Polymer Blends, Vol. 2, Chapter 19, “Elastomer Blends in Tires,” Academic Press, 1978, p. 282; W. Hess, C. Herd, P. Vegvari, “Characterization of Immiscible Elastomer Blends,” Rubber Chemistry and Technology, 1993, Vol. 66, p. 329.

### Blending

Compounds based on polyoctene and NR give high tensile strength values, although generally not as high as those based on polyurethane. RT: Chapter 6, “Elastomer Selection,” R. School, p. 126.

### NR/IR

Although high molecular weight is reported to have a positive effect on tensile strength and elongation, strain-induced crystallization as found with high cis-IR and NR shows a greater positive effect. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p. 156.

Adding a given quantity of millable polyurethane incrementally to an NBR/PVC-based compound reportedly will improve the compound’s tensile strength. GEN: T. Jablonowski, "Blends of PU with Conventional Rubbers," Rubber World, October, 2000, p. 41.

The use of SBR 4503 (an SBR that is a divinylbenzene crosslinked, hot-polymerized emulsion polymer at 30% bound styrene) with an NBR/PVC blend was reported to improve the ultimate tensile strength. GEN: J. Zhao, G. Ghebremeskel, J. Peasley, “SBR/PVC Blends with NBR as a Compatibilizer," Rubber World, December, 1998, p. 37.

The performance of thermoplastic vulcanizate (TPV) for tensile strength is derived directly from the high degree of crosslinking in the elastomer phase. Select a TPV with a higher crosslink density in the rubbery domain from dynamic vulcanization to improve tensile strength. RT: Chapter 10, “Thermoplastic Elastomers,” C.P. Rader, p. 274. RP: C.P. Rader.

In addition, it is important to achieve an extremely fine particle size (< 1 µm in diameter) for these crosslinked elastomer particles to impart good tensile strength to the TPV. These crosslinked particles must be evenly dispersed throughout the matrix of the TPV. Select a TPV with a very fine particle size for the rubber phase to improve tensile strength. RT: Chapter 10, "Thermoplastic Elastomers," C. P. Rader, p. 274. RP: C. P. Rader.

Thermoplastic elastomers often exhibit anisotropy, especially in the case of higher shear rate processes such as injection molding, which can affect the ultimate tensile strength depending on the direction in which the rubber sample is taken in relation to the flow direction. RT: Chapter 10, “Thermoplastic Elastomers,” C. P. Rader, p. 274.
2.1 Increasing Tensile Strength

**Ground Rubber**

If ground rubber is used to extend a rubber compound, select one with a higher mesh size (finer particle size) to avoid a drop-off in tensile strength. The finer that the average particle size of the ground rubber is, the lower will be the decrease in the ultimate tensile strength. RT: Chapter 11, “Recycled Rubber,” K. Baranwall, W. Klingensmith, p. 291.

Avoid extending tire compounds with ground rubber tire (GRT) extenders because these additives will decrease the compound’s tensile strength. However, the larger particle size GRT degrade tensile strength even more. GEN: A. Naskar, S. De, A. Bhowmick, P. Pramanik, R. Mukhopadhyay, “Characterization of Ground Rubber Tire and Its Effect on Natural Rubber Compounds,” *Rubber Chemistry and Technology*, November–December, Vol. 73, p. 902.

**Fillers**


**Carbon Black**

Increasing carbon black loading to an optimum will usually increase ultimate tensile strength, as long as it can be dispersed. This optimum loading occurs at a lower level for finer particle sized carbon black. RT: Chapter 12, “Compounding with Carbon Black and Oil,” S. Laube, S. Monthey, M-J. Wang, p. 308. RP: J.M. Long, M-J. Wang.

Increasing the surface area of the carbon black used in a compound will usually increase ultimate tensile strength. RT: Chapter 12, “Compounding with Carbon Black and Oil,” S. Laube, S. Monthey, M-J. Wang, pp. 308, 317.

Improving the dispersion of carbon black through longer mix cycles will usually improve ultimate tensile strength of the compound. RT: Chapter 12, “Compounding with Carbon Black and Oil,” S. Laube, S. Monthey, M-J. Wang, p. 308.
Consider using precipitated silica with higher surface area to increase significantly the ultimate tensile strength of a rubber compound. To improve tensile properties even more, consider using precipitated silica treated with a silane coupling agent. RT: Chapter 13, “Precipitated Silica and Non-black Fillers,” W. Waddell, L. Evans, p. 333.

**Nonreinforcing Filler Effects**

To achieve the highest ultimate tensile strength, one should avoid using nonreinforcing or “extending fillers” such as clay, calcium carbonate, whiting, talc, ground sand, and so forth. RP: J.R. Halladay.

**Clay**

To improve the ultimate tensile strength of a clay-loaded rubber compound, consider using a clay that is treated with a silane coupling agent. RT: Chapter 13, “Precipitated Silica and Non-black Fillers,” W. Waddell, L. Evans, p. 333.

**Oil Effects**

Minimize the use of plasticizers to achieve high ultimate tensile strength. RP: J.R. Halladay.

**Sulfur**

When curing compounds based on NBR polymers, sometimes it is difficult to achieve good dispersion of conventional “rubber maker’s sulfur.” Therefore magnesium carbonate treated sulfur is used as the curative for nitrile-based compounds because it disperses more effectively in this polar elastomer. If good dispersion of curatives is not achieved, then tensile strength properties will be hurt. RT: Chapter 16, “Cures for Specialty Elastomers,” B.H. To, p. 398.
2.1 Increasing Tensile Strength

Make sure that accelerators [such as MBTS with a high melting point about 167 to 179 °C (332.6 to 354.2 °F), which is usually above the dump temperature with most internal mixers] are fine enough in particle size (below 100 µm) so as not to adversely affect tensile strength. If the particle size of these rubber chemicals with high melt points is not fine enough, the ultimate tensile values will be lower (as much as 50%), which could affect the service life of the rubber product. The reason for this is that large particles cause nonhomogeneous distribution of crosslinks in the rubber matrix. It is reportedly also possible for accelerators to have too fine a particle size, which can cause a decrease in ultimate tensile as well (as much as 10% or more). GEN: W. Helt, “Accelerator Dispersion,” ASTM D1 Meeting, July 28, 1990.


Use a cure system that will give a higher preponderance of polysulfide crosslinks (a conventional cure) to achieve higher tensile strength (compared to an EV cure with a preponderance of mono- and disulfide crosslinks). RP: J.R. Halladay.

Consider using a traditional ethylene thiourea (ETU) cure with all the appropriate safety and health precautions for a significant improvement in ultimate tensile strength when curing a polychloroprene-based compound. RT: Chapter 16, “Cures for Specialty Elastomers,” B.H. To, pp. 400–401, 406.