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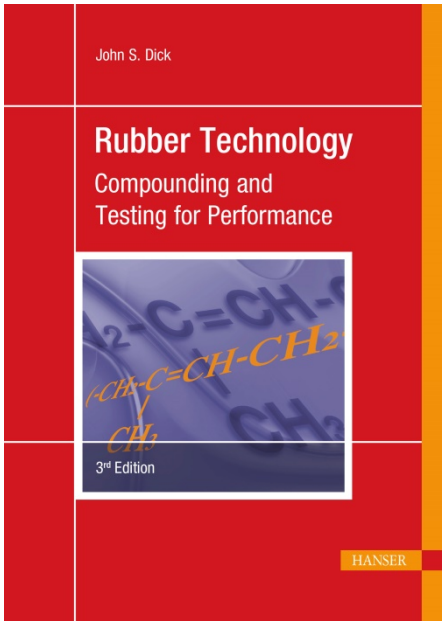

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Rubber Technology

John S. Dick

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Preface

This book is intended to be a practical guide for cost-effective formulating and testing of rubber compounds in order to help achieve optimal processing and product performance. Attention is also given to tradeoffs in properties. The book demonstrates some of these tradeoffs in various chapters.

In this book we covered rubber compounding as a series of interdependent "systems", such as the elastomer system, the filler-oil system, the cure system, the antidegradant system, etc. We endeavored to use more of a "holistic" approach to show how changes in these inter-related systems can affect specific compound properties.

Rubber compounding is a very diverse subject which draws its body of knowledge from many different areas of science and technology. To address this diversity in the most effective way, we have over 40 authors who are experts in many specific areas of rubber compounding, all contributing to the usefulness of this book. Emphasis was placed on the practical; however, theoretical explanations were used mainly when it was necessary to explain an important principle or concept.

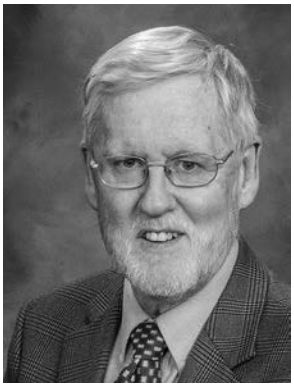
This book consists of 23 chapters and over 750 pages of text. In order to make this book an effective reference, a very extensive index of key words and rubber technology terms is provided.

It is my sincere hope that this book will benefit both new and experienced rubber compounders and technologists in their efforts to improve the art and science of rubber technology.

John S. Dick

www.rubberchemist.com

About the Editor



John S. Dick has over 45 years of experience in the rubber industry. He was with BF Goodrich and later Uniroyal Goodrich Tire Co. as a Section Manager and Development Scientist in R & D until 1991, when he joined Monsanto's Rubber Instruments Group (now Alpha Technologies) as a Senior Scientist – Applications until 2016. He is now the Technical Editor of Rubber & Plastics News and a consultant for Alpha Technologies. Additionally, he currently teaches 15 rubber technology courses each year at the University of Akron, University of Wisconsin–Milwaukee, and ASTM International.

Mr. Dick has authored over 80 journal and magazine publications, including five books on rubber technology. He consulted and has given technical papers and seminars in over 40 countries. Some of Mr. Dick's publications have been translated into nine languages.

He received the Monsanto Master Technical Service Award, the ACS Rubber Division "Best Paper Award", and the University of Akron and University of Wisconsin Appreciation Awards for teaching rubber compounding and testing courses in their continuing education programs. He is a Fellow in the American Society for Testing and Materials (ASTM), receiving the Award of Merit in 1990 and the Distinguished Service Award in 2005. Also, he has represented the United States as a delegate to the International Standards Organization (ISO) for the last 35 years. He was appointed in 1992 to be Leader of the USA Delegation to ISO TC-45 on Rubber. He is a member of the American Chemical Society, Society of Rheology, and ASQ with a CQE and CQA. He also is a co-recipient of the Rubber Division, American Chemical Society 2014 Fernley H. Banbury Award for Rheology.

Mr. Dick received his B.S. degree from Virginia Polytechnic Institute and an M.A. from the University of Akron. He is married with a son and a daughter, and his hobbies include photography and amateur radio.

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tear resistance, rebound, ultimate tensile strength, hysteresis, etc. do not occur at exactly the same time during vulcanization.

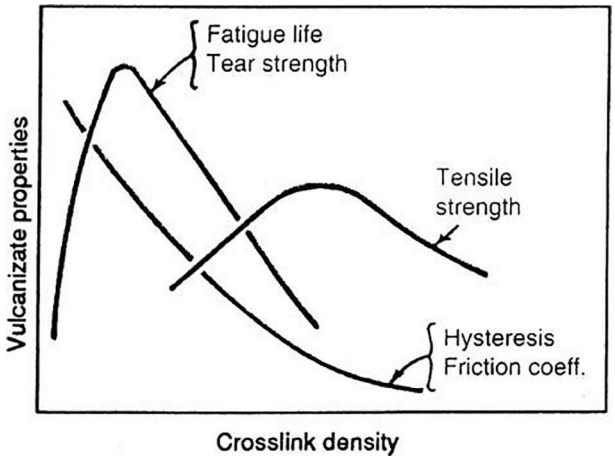


Figure 3.1 Optimum cure profiles for different vulcanizate properties (courtesy John Sommer, Elastech).

■ 3.2 Density

Density is simply weight (or mass) divided by volume at a specified temperature. This property determines the mass (weight) of a given rubber compound required to fill a specific mold cavity. Compounds with higher densities require greater weights of the compounded stock to fill a given size mold cavity. Because raw materials are usually purchased by unit weight and molded rubber products are produced from a mold cavity with a fixed volume, knowing the compound density is very important in product cost calculations. Usually, increasing compound filler loading, such as carbon black, silica, or clay, results in a higher compound density. However, many times increased filler concentration still reduces the product's cost. Also, measuring compound density is an effective quality procedure to detect variations in the rubber compound composition resulting from changes in ingredient weighing and mixing, among other reasons.

The density of a vulcanized rubber compound specimen can be measured and calculated by Archimedes' Principle in which the specimen is weighed in water and weighed in air. ISO 2781 [1] gives detailed procedures for calculating the density of a cured specimen. Additionally, special cases are also addressed. For example, if cured tubing or cable insulation is tested with trapped air, this may lead to errone-

ous results. To overcome this problem, Method B of ISO 2781 calls for the specimen to be cut up into small pieces and tested in a density bottle, using an analytical balance.

■ 3.3 Hardness

Hardness is a simple, inexpensive, and fast test used throughout the rubber industry. Hardness is measured from the cured rubber's resistance to deformation when a force is applied to a rigid indentor. This results in a measure of "a modulus" of a rubber compound under very limited deformation (strain). When the force is applied to the indentor with a dead-load, this method is called the International Hardness in IRHD units (International Rubber Hardness Degrees), which is described in ASTM D1415 or ISO 48. This test normally uses a hemispherical indentor.

If the force is applied to the indentor by a spring, it is called the Durometer Hardness Method (usually a small pocket-size apparatus), described in ASTM D2240 and ISO 7619.

This method uses the Shore A scale, which is similar, but not identical, to the IRHD scale, and the Shore D scale, which is used for testing rubber vulcanizates with high hardness. Also, these methods refer to other hardness scales, as well. There is no completely accepted conversion between a Shore A and a Shore D scale, just a crude approximation. Also, the Shore type indentor has a different geometry from the IRHD indentor: truncated cone vs. hemispherical. Shore hardness is the more popular method because the handheld durometer is more portable and can be used in the laboratory or in the factory.

These hardness tests are somewhat crude and measure only under very limited deformations that may not relate to end product applications. Also, data from these tests can show much scatter. This variability and poor repeatability can be the result of variations in sample thickness, operator dwell time, how the instrument is set up and applied, sample edge effects (readings taken too close to the sample edge), or differences in sample geometry, to name a few. Therefore, these hardness tests should *not* be considered a reliable measure of a design or engineering property, but a quick and simple method of detecting gross differences in cured compound properties.

■ 3.4 Tensile Stress–Strain

Tensile stress-strain is one of the most commonly performed tests in the rubber industry. These tests are performed on tensile testing instruments where a cured, dumbbell-shaped rubber specimen is pulled apart at a predetermined rate (usually 500 mm/min) while measuring the resulting stress. Figure 3.2 shows a commonly used dumbbell shaped specimen. ASTM D412 and ISO 37 detail the standard procedures used to measure tensile stress-strain properties of a cured rubber compound.

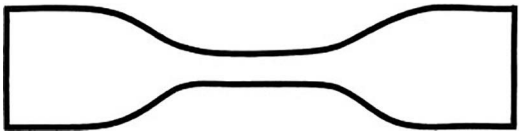


Figure 3.2 Rubber dumbbell test specimen.

Generally, (1) ultimate tensile strength, (2) ultimate elongation, and (3) tensile stress at different elongations are reported. Ultimate tensile strength is the maximum stress when the dumbbell specimen breaks during elongation. Ultimate elongation is the applied strain when the break occurs. The tensile stress is usually measured and reported at different predetermined strains (such as 100 and 300%) before the break occurs.

Figure 3.3 shows a stress-strain curve for a "typical" rubber compound. Unlike metals, this stress-strain curve shows no (or a very limited) linear portion. Therefore, it is usually not practical to calculate Young's modulus, which would be the slope of a straight line drawn tangent to the curve and passing through the origin. Instead, stress at selected elongations is usually reported. These stress values for different elongations are erroneously reported by some rubber technologists as 100% modulus, 300% modulus, etc. However, these measures are not actually modulus values.

Stress–strain properties, such as ultimate tensile strength, can be easily affected by poor mixing and dispersion, the presence of contamination, under-curing, over-curing, and porosity, among other factors. Undispersed particles of different compounding ingredients, such as carbon black agglomerates, cause stress concentrations during the stretching of a rubber dumbbell, causing premature breaks at lower stresses. Impurities, such as dirt or paper fragments, can also cause the dumbbell to break at a lower stress. Likewise, volatile compounding ingredients can cause porosity to form during cure. These voids can also cause lower tensile strength [2]. Lastly, laboratory-mixed batches usually have higher tensile strength than factory-mixed batches because laboratory mixes often are better dispersed.

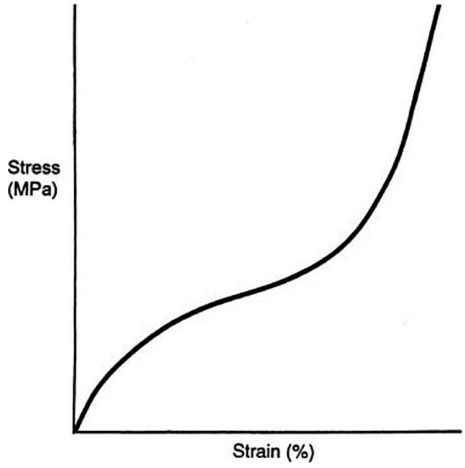


Figure 3.3 Typical stress–strain curve for rubber.

The tensile stress-strain testing discussed here involves non-prestretched specimens. However, if the dumbbell specimen is prestretched, for example, to more than 400% of its original length, and then tested in a normal manner, stress-strain would probably be significantly affected. This is particularly true of compounds containing high reinforcing filler loadings such as carbon black [3]. Prestretching causes "stress softening," which results from breakdown of the carbon black agglomerates. Many times, if prestretched dumbbells are allowed to rest, their modulus (or tensile stress) increases. Because many rubber products are exposed to repetitive stress-strain cycling, this phenomenon can affect end-use performance.

Many rubber products are not extensionally deformed more than 30%. So tensile stress-strain is usually not of great importance for product design, unless the product is a rubber band. On the other hand, tensile stress-strain testing of a given compound can be a valuable quality assurance tool to detect compounding mistakes in the factory and is very useful in compound development [4].

■ 3.5 Stress–Strain Properties under Compression

Compression stress-strain testing often relates to actual product service conditions better than extension testing. Usually, test methods involve measuring the stress resulting from a compressive deformation applied to a standard, cured cylindrically-shaped rubber specimen between two plates. Compression test results depend on such factors as the shape of the rubber specimen, preconditioning, rate of defor-

mation, and the degree of bonding or slippage of the specimen to the two metal surfaces. The more slippage experienced with the test piece means less "barrelling." The degree or lack of "barrelling" greatly affects the test results [5,6]. ASTM D575 and ISO 7743 are both standard methods for measuring stress-strain properties under compression, although they are quite different. The ASTM method uses sandpaper to prevent slippage, while one part of the ISO method allows a lubricant to be used, and another part requires the samples to be bonded to the parallel metal plates. Of course, these different conditions result in different results.

■ 3.6 Stress–Strain Properties under Shear

Measuring the stress-strain properties under shear can also be very relevant to some rubber product applications. Generally, most rubber product applications do not exceed a strain of 75% [7]. The resulting stress-strain curve may be linear up to about 100% for "soft" compounds and up to 50% for "hard" rubber compounds [8]. ISO 1827 is a commonly used test method for measuring the stress-strain properties of a rubber compound under shear. Figure 3.4 shows the quadruple shear test piece which is separated, as noted by the arrow.

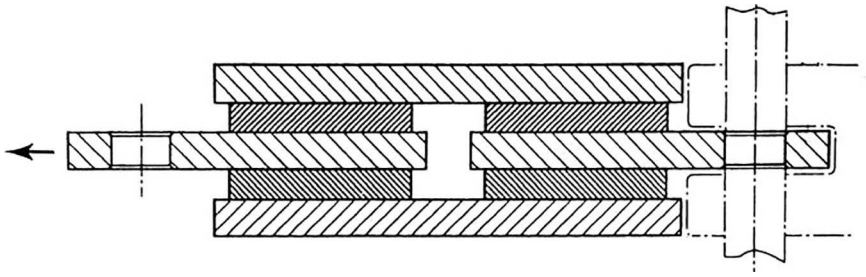


Figure 3.4 Quadruple lap shear test piece (ISO 1827).

■ 3.7 Dynamic Properties

Rubber products are used in many dynamic applications such as tires, belts, isolators, dampers, etc. The best way to measure and quantify the cured dynamic properties of a rubber compound is to mechanically apply a sinusoidal strain to a cured rubber specimen and measure the complex stress response and the resulting phase angle (δ), as was illustrated in Fig. 2.8. As discussed earlier in Section

■ 4.4 Cost Calculations

Having examined methods of determining densities, it is important to see how this impacts the costs of compounds used in applications.

4.4.1 Base Compound

Take, as an example, a rubber compound such as Model Compound I (Table 4.1), which includes the costs and densities as listed in Appendix 4.1 (Table 4.16). Examine the impact of varying the fillers and other ingredients on the actual costs of the compound both in terms of equivalent volumes and costs where only the cost per pound is involved.

Table 4.1 Model Compound I

Ingredient	PHR	Price/lb	Sp. Gr.	Volume	Price
SBR 1500	100.000	0.7200	0.94	106.38	72.00
N660	50.000	0.3275	1.80	27.78	16.38
Aromatic oil	15.000	0.0838	1.00	15.00	1.26
Zinc oxide	3.000	0.6000	5.57	0.54	1.80
Stearic acid	2.000	0.5100	0.85	2.35	1.02
TBBS	1.500	3.2900	1.28	1.17	4.94
Oil treated sulfur	2.000	0.1590	2.00	1.00	0.32
Total	173.500			154.22	97.71
Specific gravity	1.125				
Cost/lb	$0.563				
Cost/lb-vol.	$0.634				

4.4.2 Same Ingredient Volume and Equal Cost

If you are manufacturing a part in a fixed volume mold that requires 1 lb of Model Compound I, the materials cost is $0.563. Substituting silica and treated clay for the carbon black, to yield equal volumes of these filler ingredients and the same cost/lb, leads to Model Compound II (Table 4.2). This is for purposes of illustrating costs only.

Table 4.2 Model Compound II

Ingredient	PHR	Price/lb	Sp. Gr.	Volume	Price
SBR 1500	100.000	0.7200	0.94	106.38	72.00
Silica	32.000	0.5950	2.00	16.00	19.04
Treated clay	31.000	0.1470	2.62	11.83	4.56
Aromatic oil	15.000	0.0838	1.00	15.00	1.26
Zinc oxide	3.000	0.6000	5.57	0.54	1.80
Stearic acid	2.000	0.5100	0.85	2.35	1.02
TBBS	1.500	3.2900	1.28	1.17	4.94
Oil treated sulfur	2.000	0.1590	2.00	1.00	0.32
Total	186.500			154.28	104.93
Specific gravity	1.209				
Cost/lb	$0.563				
Cost/lb-vol.	$0.680				

In this illustration, a cost penalty of $0.041/part is incurred, even though the cost/lb is the same as with Model Compound I.

$$\begin{aligned}\text{part cost} &= \left(\text{compound volume} = 1/1.125 = 0.889\right) \\ &\quad \times \left[\text{lb vol cost}\ \left(\text{Model Compound I} - \text{Model Compound II}\right)\right. \\ &\quad \left. = \left(0.634 - 0.680\right)\right] \\ &= -0.041\end{aligned} \tag{4.6}$$

If one were pricing a product strictly in terms of weight, high loadings of an inexpensive, high specific gravity filler would be advantageous, such as seen in Model Compound III (Table 4.3).

Table 4.3 Model Compound III

Ingredient	PHR	Price/lb	Sp. Gr.	Volume	Price
SBR 1500	100.000	0.7200	0.94	106.38	72.00
Hard clay	200.000	0.0590	2.62	76.34	11.80
Aromatic oil	15.000	0.0838	1.00	15.00	1.26
Zinc oxide	3.000	0.6000	5.57	0.54	1.80
Stearic acid	2.000	0.5100	0.85	2.35	1.02
TBBS	1.500	3.2900	1.28	1.17	4.94
Oil treated sulfur	2.000	0.1590	2.00	1.00	0.32
Total	323.500			202.78	93.13
Specific gravity	1.595				
Cost/lb	$0.288				
Cost/lb-vol.	$0.459				

4.4.3 Low Cost/lb

As can be seen from Table 4.3, the cost/lb is about one-half that of Model Compound I (Table 4.1), but the lb-vol. cost is closer to three quarters that of Model Compound I. The physical properties of Compound III are significantly inferior to those of Model Compound I; however, if the inferior properties are not important and the compound is priced strictly based on cost/lb, then the lb-vol. cost is not a factor. As noted, the cost/lb-vol. is lower for Model Compound III. However, in the Model Compound II example, where the cost/lb-vol. is higher than Model Compound I, there was some attempt at maintaining reasonable physical properties.

4.4.4 High Specific Gravity

In some cases where it is mandatory that a high specific gravity compound be used, such as in aircraft wheel chocks, the high weight is essential for product performance. The key is to use the most cost-effective filler system to obtain high specific gravity compounds consistent with other physical property restraints. Model Compounds IV (Table 4.4) and V (Table 4.5) illustrate two methods of obtaining the same specific gravity compound, but Model Compound IV is more cost-effective.

Table 4.4 Model Compound IV

Ingredient	PHR	Price/lb	Sp. Gr.	Volume	Price
SBR 1500	100.000	0.7200	0.94	106.38	72.00
Barytes	200.000	0.1270	4.45	44.94	25.40
Aromatic oil	15.000	0.0838	1.00	15.00	1.26
Zinc oxide	3.000	0.6000	5.57	0.54	1.80
Stearic acid	2.000	0.5100	0.85	2.35	1.02
TBBS	1.500	3.2900	1.28	1.17	4.94
Oil treated sulfur	2.000	0.1590	2.00	1.00	0.32
Total	323.500			171.39	106.73
Specific gravity	1.888				
Cost/lb	$0.330				
Cost/lb-vol.	$0.623				

Table 4.5 Model Compound V

Ingredient	PHR	Price/lb	Sp. Gr.	Volume	Price
SBR 1500	100.000	0.7200	0.94	106.38	72.00
Zinc oxide	177.320	0.6000	5.57	31.83	106.39
Aromatic oil	15.000	0.0838	1.00	15.00	1.26
Stearic acid	2.000	0.5100	0.85	2.35	1.02
TBBS	1.500	3.2900	1.28	1.17	4.94
Oil treated sulfur	2.000	0.1590	2.00	1.00	0.32
Total	297.820			157.74	185.92
Specific gravity	1.888				
Cost/lb	$0.624				
Cost/lb-vol.	$1.179				

These models are illustrations of cost effectiveness, not of real world compounds. One obvious material that increases the compound's specific gravity is Litharge (PbO), which has a specific gravity of 9.35. Examples of this material are not included because of the strict regulatory restrictions placed on the use of lead in manufacturing and environmental considerations.

■ 4.5 Compound Design and Cost

There is a natural tendency to over-design a product just to be "on the safe side." While it is necessary and very important to design a product with sufficient safety margins, one must be realistic. Setting unrealistic safety margins limits the choices of filler and polymer that can be used with the potential of much higher compound costs. It makes no sense to design a component product to last 100,000 hours, when the main product is designed to last for only 1,000 hours. There is also a tendency to specify particular physical characteristics as engineering requirements that are not important to product performance, but may be considered in the industry as measures of "quality." Tensile strength can be one of those properties, for example.

In the opposite context, for those products where failure results in severe economic consequences or potential loss of life or injury, efforts must be focused on zero failures. For example, if the failure of a part of a larger system results in the equipment shutdown, loss of productivity, and additional labor costs to effect the repair, increasing safety margins in the part simply makes sense. When worker safety is involved, costs must take a back seat to assuring product performance. When safety is assured, there may be opportunities to reduce product costs, but they can be implemented only after thorough testing.

5.2.5 Prepare Report

The end product of any technical project is a full report. The report begins with a statement of the problem addressed or project undertaken, followed by a summary of the conclusions and/or technical decisions made as a result of the program. This can be followed by a detailed account of all the planning, work, and analysis conducted. If a complete solution is found for any project, no future action is needed. If, however, new questions arise, unanticipated technical problems are discovered, or only partial answers and/or decisions are attained, a recommendation should be made for either a Stage 2 iteration of all five steps or for a future work program. Any Stage 2 operation needs to be carefully organized so as to build on and take full advantage of the work conducted in Stage 1.

■ 5.3 Part 2: Using Experimental Designs

Although technical objectives may vary, all experiments have the same operational objective – to provide maximum information of the highest quality possible for minimum cost. Experimental design is the process of efficiently planning and executing a series of experiments with this objective in mind. Many problems, especially for complex systems, should be approached in a sequential manner. The Stage 1 process should provide basic understanding along with an approximate solution. Subsequent stages build on what is learned in Stage 1, where unanticipated new information frequently leads to new ideas on how to proceed. This approach provides for more efficient and less costly problem resolution. Refer to Appendix 5.1 for all of the designs as discussed in Section 5.3.

5.3.1 Screening Designs – Simple Treatment Comparisons

The most elementary technical project is the comparison of the mean (or average) for two sets of measurements that represent potentially different populations. The sets are characterized by two different treatments. The word treatment implies some distinguishing feature, such as a specified material composition, a physical or chemical modification, or a processing operation to produce certain production parts. Typical examples are the use of two different antioxidants for the heat aging behavior of rubber or two surface treatments of rubber to reduce friction. Part 1 of Appendix 5.1 contains screening designs, the simplest of which are for simple experiments (C1 and C2) where two or more treatments are compared. Experimental design, C1, may be used in two ways:

1. All replicates for both treatments can be conducted under uniform test conditions
2. Testing conditions or some other operational factors are uniform for treatments 1 and 2 for each replicate set, but may be different among the replicate sets as a group.

5.3.1.1 Design C1 for Uniform Replication Conditions

For this situation a decision on the statistical significance for the means of two potentially different populations is determined by *t*-test. A typical testing project might consist of five replicates for each of the two treatments. The variance among the five replicates is used to evaluate test variation with the assumption that, although the means may be different, there is no difference in variance for the two treatments. The decision on the significance of the difference, $(\acute{y}_1 - \acute{y}_2)$, for the means of the five replicates for each treatment is based on the calculated *t* value, t_{calc}, obtained from

$$t_{calc} = (\acute{y}_1 - \acute{y}_2)/S_{dy} \tag{5.13}$$

where

$\acute{y}_1$ = mean of 5 replicates for Treatment 1
$\acute{y}_2$ = mean of 5 replicates for Treatment 2
S_{dy} = standard deviation of difference of means (5 values each)
$S_{dy} = \left[\left(S_1^2/n\right) + \left(S_2^2/n\right)\right]^{1/2}$
S_1^2 = variance among 5 replicates for Treatment 1
S_2^2 = variance among 5 replicates for Treatment 2
n = number of replicates = 5

The expression for S_{dy}, a pooled value of both sets of replicates, is obtained from theorems on the propagation of error, i.e., the variance of a sum or difference of two values taken from potentially different populations is the sum of the variances of the two populations. If t_{calc}, with degrees of freedom df = $2(n - 1) = 8$, is larger than the critical *t* value, t_{crit}, at some selected confidence level, $(1 - \alpha)100$, or $P = \alpha$, then the null hypothesis, H_0: $\mu_1 = \mu_2$, is rejected and the alternative, H_0: $\mu_1 \neq \mu_2$, is accepted. If α is 0.05, the confidence level is 95%. From standard *t* tables for df = 8, the double-sided value of $t_{crit} = 2.31$ for $\alpha = 0.05$.

5.3.1.2 Design C1 for Non-Uniform Replication Conditions

When it is not possible to have uniform conditions for all replicates, a paired comparison test can be used. The response parameter in this case is the difference in measured or observed behavior between the individual paired values.

A typical example is as follows. The performance of a rubber compound is determined by the loss of plasticizer. Two different plasticizers, designated A and B,

may be used. It is desired to determine if one plasticizer is more fugitive than the other. The testing is a long term outdoor exposure evaluation in different weather conditions. A test specimen of each formulation (plasticizer A or B) is exposed for a fixed period at eight different locations. The data obtained are:

	Plasticizer content (%)		
Exposure condition	After exposure:		Difference, d (A − B)
	A	B	
3 months – Ohio	10.1	10.0	0.1
3 months – Maine	8.9	8.9	0.0
6 months – Georgia	8.9	8.8	0.1
3 months – Arizona	8.4	8.2	0.2
6 months – Texas	9.2	9.0	0.2
6 months – Florida	8.7	8.4	0.3
3 months – California	9.0	8.8	0.2
3 months – Oregon	8.8	8.7	0.1
Average	9.00	8.85	0.15
Std Dev (individual)	0.501	0.535	0.093
Std Dev (average 8)	0.177	0.189	0.0329

The difference across the range of locations, d = 0.15%, is small but consistent. These eight differences are a sampling of the distribution of differences, d, and the standard deviation of these eight values is 0.093. The standard error (or deviation) of means of eight values is $0.093/(8)^{1/2}$ = 0.0329, and t_{calc}, the ratio of the mean difference, 0.15, to the standard error of means, 0.0329, equals 4.56. The df for this is 8 − 1 = 7 and the value of t_{crit} at the 99% confidence level or P = 0.01 is 3.499. Thus, the mean difference of 0.15 is highly significant.

5.3.1.3 Design C2 for Multi-Treatment Comparisons

When more than two treatments are compared, a design such as C2 may be used with a selected number of replicates for each treatment. When the testing process is in control, all treatments, 1 to j, may be evaluated under uniform conditions. Typically, an analysis of variance (ANOVA) is conducted to determine if the variation among treatments is significant compared to the pooled variance among all replicates. However, an ANOVA does not pinpoint which of the treatments among the j total treatments is different from other treatments. To sort the treatments into a hierarchy of values with indicated significant differences among the j (j − 1)/2 treatment pairs, a multi-comparison analysis is required. A number of analysis techniques have been proposed for this; see Duncan [1], Tukey [2], and Dunnet [3]. Computer statistical analysis programs usually include these multi-comparison analysis routines.

The Dunnet procedure uses a control and permits a decision on the statistical significance of differences between the control and the experimental treatments. The procedure ensures that the decision on the entire set of treatments is controlled at the selected $P = \alpha$ level rather than individual comparisons. The references mentioned above plus Winer [4]; Box, Hunter, and Hunter [5]; and Diamond [6] provide additional background on multi-comparison analysis. The last text is oriented toward manufacturing processes and the use of α and β errors. If it is not possible to have uniform testing conditions for all j treatments, the program may be conducted in two or more uniform condition blocks, with a control in each block. Using the Dunnet procedure for each block permits decisions on differences between the control and the treatments in that block.

5.3.2 Screening Designs – Multifactor Experiments

Much of the experimental effort in rubber compounding is devoted to evaluating the effect of variations in compound formulation and processing conditions. Experimental layouts with two or more factors, called factorial designs, are especially useful for this purpose, especially two-level factorial designs. Part 1 of Appendix 5.1 contains 11 designs for multi-factor screening experiments. Seven is a reasonable maximum number of factors to be evaluated in any program or project. Any system with more potential factors needs to be reviewed for ways to consolidate or otherwise reduce the number of operational factors on the basis of engineering or scientific analysis.

5.3.2.1 Two-Level Factorial Designs

These designs are characterized by special selected combinations of lower and upper levels across all the selected factors. When the factor levels are set at the values called for in a particular combination and a response measurement is made for this combination, this is called a (test) run. Each design has some number of specified runs and the total list of these runs is called the design matrix. A complete factorial design matrix is one where for each factor, all factor levels of the other factors appear equally at their lower and upper levels. Thus, for two factors investigated at two levels each, a complete factorial design requires four (2^2) response measurements or runs, each of which has a different combination of the two levels of the two factors. Design S1 in Appendix 5.1 is an example.

When the number of factors is large, a complete or full factorial requires too many test runs and designs called fractional factorials are used. In fractional factorials, a certain fraction of the full factorial number of runs is selected on the basis that the design is balanced with respect to the number of selected levels of each factor. The fractional factorials are designated as 1/2 fraction, 1/4 fraction, etc. of the full de-

sign. With the exceptions noted below, all of these designs allow for the evaluation of two-factor interactions that often are important in many technical investigations. Any design that allows for direct calculation of two-factor interactions is usually sufficient to give a good evaluation of any system. Usually three-factor interactions have no real significance.

All of the two-level screening designs (as well as the exploratory designs) are orthogonal in the independent variables, i. e., there is no correlation among these variables. Orthogonality permits the use of the matrix for easy analysis via a spreadsheet program. The designs are balanced; for any factor level for factor *i*, the levels of all other factors appear at their upper and lower values the same number of times. The designs and the model equations are set up using special coded units for the independent variables.

As discussed in Section 5.2, for any response variable y and two independent variables x_1 and x_2, a model equation that allows for the evaluation of any interaction between x_1 and x_2 is

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 \tag{5.14}$$

where

b_0 = a constant; in system of units chosen, it is the value of y when $x_1 = x_2 = 0$

b_1 = change in y per unit change in x_1

b_2 = change in y per unit change in x_2

b_{12} = an interaction term for specific effects of combinations of x_1 and x_2; see discussion for Eqs. (5.3) and (5.4)

The coded units are obtained for each factor by selecting a value that constitutes a center of interest or a reference value and then selecting certain values that are below and above that center of interest by an equivalent amount. This is a straightforward process for quantitative, continuous variables or factors, but may not be possible for some qualitative or categorical factors which can exist at only two levels. In this case, the center of interest is considered theoretical or conceptual. If a system contains a number of categorical factors, the final expression for the analysis may be given in terms of main effects and their interactions. The coded units for any x_i are defined by:

$$x_i = \left(\mathrm{v_E} - \mathrm{cv_E}\right) / \mathrm{su} \tag{5.15}$$

with

$\mathrm{v_E}$ = selected factor value for x_i, in physical (experimental) units

$\mathrm{cv_E}$ = center of interest value for x_i, in physical units

su = scaling unit, i. e., change in physical units equal to 1 coded unit

When $\mathrm{v_E}$ is higher than $\mathrm{cv_E}$ by an amount equal to su then $x_i = 1$; when $\mathrm{v_E}$ is less than $\mathrm{cv_E}$ by an equal amount, $x_i = -1$; and when $\mathrm{v_E} = \mathrm{cv_E}$, $x_i = 0$. The center of inter-

est values for all factors constitutes the central point in the multi-dimensional factor space for the experiment. The constant b_0 is the value for y at this center in the factor space; it is the (grand) average of all responses.

The design matrix for a full factorial 2^2 design is given in Design S1. An additional matrix called the interaction matrix is also listed, which for this simple design is only one column headed by X_1X_2. Design S2, for three x-variables, has a more extensive three-column interaction matrix. For each row of the design, the entry for any column, X_iX_j, of the interaction matrix is obtained by multiplying the design matrix entries for column X_i by column X_j.

5.3.2.2 Analysis of the Designs

The use of coded units and spreadsheet calculations simplifies the analysis. Each design can also be analyzed by multiple regression analysis with computer software programs. The effects of the independent variables may be calculated in one of two ways:

1. As main effects, defined as the change in the response for a change in the x-variable from the lower to the upper level
2. As effect coefficients, defined as the change in the response for one positive scaling or coded unit change in the x-variable

On the basis of coded units there are two units of change in moving from the lower (−1) to the upper (1) level; thus, effect coefficients are one-half the numerical value of main effects and main effect interactions. All analysis algorithms in Appendix 5.1 are given in terms of effect coefficients. To express the results of any analysis in terms of main effects and their interactions, multiply each calculated linear or interaction effect coefficient by 2.

5.3.2.3 Calculating the Effect Coefficients

The design and interaction matrixes are used to calculate the effect coefficients of the independent variables. The generalized equations for a design with any number of factors are as follows:

The coefficient b_0 is evaluated from the first or Y column of the design

$$b_0 = \left(\sum y_1 \text{ to } y_i\right) \Big/ 2n \tag{5.16}$$

with y_1 to y_i = the measured responses; there are a total of i rows (four for S1); n = the number of runs with $X = 1$ (as well as $X = 1$), for each X variable; and $2n$ = total number of runs for the design.

Each b_i, or linear effect coefficient, is evaluated by using the column Y and column X_i in the design matrix:

$$b_i = \frac{1}{2}\left\{\left[\sum y_i^*(+X_i)/n\right] - \left[\sum y_i^*(-X_i)/n\right]\right\} \tag{5.17}$$

where $y_i^*(+X_i)$ = the product of y_i and X_i for each of n rows where $X_i = 1$; the sum is taken over all $2n$ runs in the design and divided by n; and $y_i^*(-X_i)$ = product of y_i and X_i for each of n rows where $X_i = -1$; the sum is taken over all $2n$ runs in the design and divided by n.

Each b_{ij}, a two-factor interaction coefficient, is evaluated by using column Y and column X_iX_j in the interaction matrix:

$$b_{ij} = \frac{1}{2}\left\{\left[\sum y_i^*(+X_iX_j)/n\right] - \left[\sum y_i^*(-X_iX_j)/n\right]\right\} \tag{5.18}$$

where $y_i^*(+X_iX_j)$ = the product of y_i and X_iX_j for each of n rows where $X_iX_j = 1$; the sum is taken over all $2n$ runs in the design and divided by n; $y_i^*(-X_iX_j)$ = the product of y_i and X_iX_j for each of n rows where $X_iX_j = -1$; the sum is taken over all $2n$ runs in the design and divided by n.

Each b_{ijk}, a three-factor interaction coefficient, is evaluated by using column Y and column $X_iX_jX_k$ in the interaction matrix

$$b_{ijk} = \frac{1}{2}\left\{\left[\sum y_i^*(+X_iX_jX_k)/n\right] - \left[\sum y_i^*(-X_iX_jX_k)/n\right]\right\} \tag{5.19}$$

where $y_i^*(+X_iX_jX_k)$ = the product of y_i and $X_iX_jX_k$ for each of n rows where $X_iX_jX_k = 1$; the sum is taken over all $2n$ runs in the design and divided by n; $y_\mathrm{i}^*(-X_iX_jX_k)$ = the product of y_i and $X_iX_jX_k$ for each of n rows where $X_iX_jX_k = -1$; the sum is taken over all $2n$ runs in the design and divided by n.

These generalized effect coefficient equations are given in Appendix 5.1 as notes for Design S1. The specific coefficient equations for S1 and S2 are also given to illustrate the use of the generalized equations.

When fractional factorial designs are used, confounding may exist in the interpretation of the effect coefficients. This confounding, or dual meaning of output information, is called aliasing. An alias exists in fractionated designs when the exact sequence of −1, 1 values is the same for two or more columns among all the columns of the total matrix (both design and interaction). An alias also exists for any two or more columns with sign reversal for all entries. Thus, no unique evaluation of the individual coefficients represented by the columns is possible.

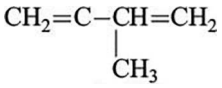
Aliases in the designs are indicated by an expression of the type given in Design S3. For Block I, the expression $b_3 = b_3 + b_{12}$ indicates that the calculation of the linear effect coefficient b_3 has the same set of 1 and −1 combinations (i.e., in column X_3) as the calculation for the interaction coefficient b_{12} (i.e., column X_1X_2). The calculation actually evaluates the sum $b_3 + b_{12}$. If b_{12} has no real effect (gives a mean of zero in long run) the calculation actually evaluates only b_3.

■ 7.2 Natural Rubber and Polyisoprene

Natural rubber and polyisoprene share the same monomer chemistry. Isoprene is the building block of these polymers and can polymerize in four different configurations. Polyisoprene can be polymerized with either a coordination catalyst (Ziegler) or alkyl lithium catalyst. Coordination catalysts are usually trialkyl aluminum and titanium tetrachloride. At a ratio around 1 : 1, the Al/Ti system can produce *cis* contents from 96 to 98%. The alkyl lithium catalyst system produces *cis* contents between 90 and 93%.

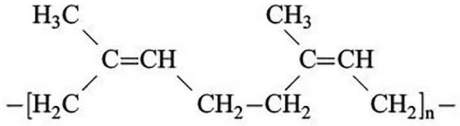
Natural rubber has a *cis* content of almost 100%. These microstructures give natural rubber a glass transition temperature (T_g) of approximately −75 °C and polyisoprene a slightly higher T_g (−70 to −72 °C) because of the presence of *trans*, 1,2 and 3,4 configurations.

Isoprene monomer:

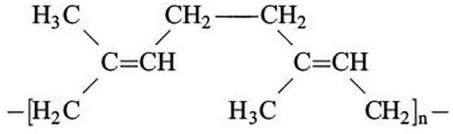


Isoprene can polymerize in four different configurations:

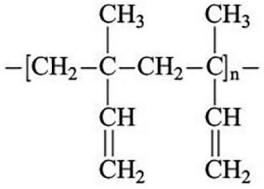
Cis-1,4



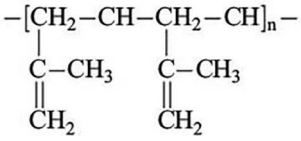
Trans-1,4



1,2



3,4



There are three general forms of polyisoprene commercially available: high *cis* content, high *trans* content and high 3,4 content. A significant advantage in high *cis* content polyisoprene lies in its ability to undergo strain-induced crystallization. This crystallization phenomenon gives *cis*-polyisoprene very high tear strength and excellent De Mattia cut-growth resistance. This exceptional tear strength translates into superb physical properties and performance in the end product.

Gutta-percha or balata is a high *trans* content polyisoprene and is very hard at room temperature. Upon heating to 80 °C, the crystallinity "melts" and the rubber becomes soft and workable. When cooled to room temperature, the crystallinity reforms and the rubber becomes hard and unworkable again.

A commercially available polyisoprene with 60% 3,4 content is available. It has a reported T_g of about –5 °C and is processable at normal operating temperatures. For most applications, neither the high *trans* nor the high 3,4 polymer can match the high *cis* polymer for performance.

There are a number of important differences between synthetic polyisoprene and natural rubber. Synthetic polyisoprene has the advantage of consisting of up to 99% rubber hydrocarbon (RHC), while natural rubber is usually around 93% RHC. Synthetic polyisoprene is usually lighter in color, and more consistent in chemical and physical properties. Its lower molecular weight leads to easier processing. On the other hand, natural rubber has higher green strength and modulus, especially at higher strain levels and temperatures.

The weight average molecular weight (M_w) of natural rubber ranges from 1 million to 2.5 million while a typical synthetic polyisoprene ranges between 755 thousand and 1.25 million. Molecular weight distribution (MWD) is defined as the ratio of weight average molecular weight (M_w) divided by number average molecular weight (M_n) or (M_w/M_n). Molecular weight distributions vary from less than 2.0 for lithium-catalyzed polyisoprene to almost 3.0 for Al/Ti-catalyzed polyisoprene to greater than 3.0 (and widely variable) for natural rubber.

The 13th edition of the *Synthetic Rubber Manual* [1] lists 11 different producers of polyisoprene. Only one manufacturer produces low *cis* (91%) polyisoprene, Shell Nederland Chemie B.V. There is one listing for high *trans* polyisoprene, TP-301 from Kuraray Company, Ltd., and one listing for high 3,4 content (60%) from Karbochem of South Africa. Kuraray also produces a liquid polyisoprene that is often used as a processing aid. Because it is a liquid, it does not increase the green compound viscosity, but upon vulcanization, it crosslinks into the compound and cannot be extracted. There are nine producers manufacturing *cis* content greater than 96%: Goodyear Tire and Rubber Co., Nippon Zeon Co. Ltd., Japan Synthetic Rubber Co. Ltd., Kuraray, Nizhnekamskneftechim, Kauchuk Co., SK Premyer Co., Togliattisyntezkauchuk, and Volzhski Kauchuk Co. Not listed in the IISRP manual is a high *trans* IR from NCHZ Sterlitamak Co. in Russia.

There are two generic classifications of natural rubber, the crepes and sheets, and the technically specified grades. The conventional crepes and sheets are classified by the International Standards of Quality and Packing for Natural Rubber Grades (otherwise known as *The Green Book* [2]). There are eight grades of crepes and sheets with 35 subdivisions. Grading is done on a visual basis. Table 7.1 lists these grades [3].

Table 7.1 Grades of Natural Rubber

Type	Source
1. Ribbed Smoked Sheet	Coagulated field latex
2. Pale Crepe	Coagulated field latex
3. Estate Brown Crepe	Estate cuplump, tree lace
4. Compo Crepe	Cuplump, tree lace, wet slab, RSS cuttings
5. Thin Brown Crepe	Cuplump, tree lace, wet slab, unsmoked sheet
6. Thick Blanket Crepe	Cuplump, tree lace, wet slab, unsmoked sheet
7. Flat Bark Crepe	Cuplump, tree lace, earth scrap
8. Pure Smoked Blanket Crepe	Remilled RSS and RSS cuttings

The technically specified grades of natural rubber (TSR) are different from crepes and sheets in several respects, most noticeably in that TSR rubber comes in 75 lb bales rather than 250 lb blocks. TSR is not graded visually, but by chemical tests. Some of the more important TSR grades are listed in Table 7.2 [3].

Table 7.2 Technical Grades of Natural Rubber

Property	SMR L, CV	SMR 5	SMR 10	SMR 20	SMR 50
Dirt content, %	0.03	0.05	0.10	0.20	0.50
Ash content, %	0.50	0.60	0.75	1.00	1.50
Nitrogen content, %	0.60	0.60	0.60	0.60	0.60
Volatile matter, %	0.80	0.80	0.80	0.80	0.80
Wallace plasticity	30.00*	30.00	30.00	30.00	30.00
PRI, %	60.00	60.00	50.00	40.00	30.00

* Does not apply to SMR CV.

SMR L: This is a very clean, light colored rubber.

SMR CV: This is referred to as constant viscosity rubber. It is produced by adding hydroxylamine neutral sulfate before coagulation. It comes in several viscosity grades. The CV rubbers have fewer Mooney viscosity variations between lots and change less with age.

SMR 5: SMR 5 and SMR 1 are produced from a factory-coagulated latex but do not go through the RSS process first. This is a very clean grade of rubber, but is darker than SMR L.

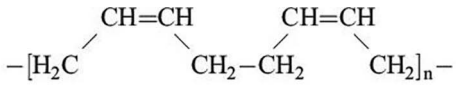
SMR 10, 20, and 50: These grades are produced from field coagulation but may contain some RSS.

There are several other forms and grades of natural rubber, such as Oil Extended Natural Rubber, which is made by adding either aromatic or naphthenic oil to the latex before coagulation, or by blending in an extruder with the dry rubber. One of the newer and more interesting variations of natural rubber is epoxidized natural rubber, called Epoxyprene[1]. Epoxyprene comes in two grades, ENR-20 and ENR-50. The double bonds in the backbone are epoxidized to 20 mole% and 50 mole%, respectively, to make these grades. Epoxidation changes several physical properties, including increasing the T_g of the polymer. These polymers have higher damping, lower permeability to gases, and increased polarity, which reduces swelling in non-polar oils and increases compatibility with polar polymers such as polyvinyl chloride. The increased damping can be put to use in footwear and acoustic devices; the increased T_g can be used to improve wet traction in tire treads [4].

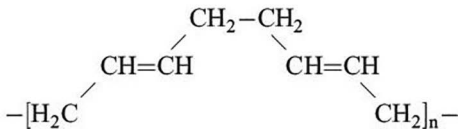
■ 7.3 Polybutadiene

Polybutadiene (BR) comes in a wide range of micro- and macrostructures. BR is produced from the butadiene monomer and can be polymerized in three configurations:

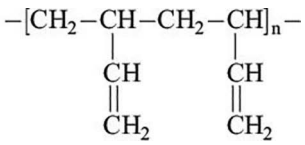
Cis-1,4



Trans-1,4



1,2-vinyl



There are currently four popular variations of BR: high *cis* content, low or medium *cis* content, vinyl BR, and emulsion BR. A fifth variation, high *trans* content BR, is now under evaluation.

[1] Epoxyprene is a registered trademark of Kumpulan Guthrie Berhad.

Within each classification, there can be many variations. High *cis* content polymers are produced with the use of Ziegler-Natta catalysts; the low/medium *cis* BR is produced with alkyl lithium catalysts; vinyl BR is produced with alkyl lithium in conjunction with a polar additive. All three types are produced in a hydrocarbon solution. Emulsion BR is produced in water using free radical initiators.

Emulsion polymerization is the oldest technology used to produce BR. The technology was first developed in the early 1940s, but it was not considered satisfactory for tires at that time. Not until "cold polymerization" was developed was acceptable emulsion BR produced. Even then, it was not until the development of the solution polymerization techniques that truly acceptable BR was produced. These solution polybutadienes found a market niche that emulsion BR could never find. Today, BR is the second largest commercial synthetic elastomer in production; SBR is the first.

There are several different Ziegler-Natta coordination catalysts in commercial use. The highest *cis* content is produced with neodymium. It is reported to give *cis* contents as high as 98% and a T_g of –102 °C [5]. The cobalt BRs produce materials next highest with *cis* contents (97%) and a –101 °C T_g. Nickel gives *cis* contents from 94 to 96% and titanium runs from 92 to 94% [6]. Alkyl lithium is used in anionic polymerization and gives *cis* contents of 35%, *trans* contents of 55%, and vinyl contents of 10% with a T_g of –94 °C. These polymers are referred to as medium or low *cis* solution BR. The addition of polar solvents such as diglyme, TMEDA, THF, or oxolanyl alkanes [7–9] can raise the vinyl content up to 90%. Commercial polymers with 70% vinyl content, which are often referred to as high vinyl BR, have a T_g as high as –25 °C. Because of the added cost of the modifier and the need to remove it from the hydrocarbon solvent before unmodified BR is made, the cost of these types of polymers is much higher than that of conventional BR. Emulsion BR has a microstructure in the same ratio as in emulsion SBR (ESBR). The *cis* content is 14%, *trans* content is 69%, and the vinyl content is 17% with a T_g of –75 °C.

The microstructure dictates the glass transition temperature of the polymer, which in turn controls some of the performance of the compounds. Table 7.3 [10] lists typical T_g and T_m values for various microstructures.

Table 7.3 Microstructure Effect on Polybutadiene T_g and T_m

	T_g (°C)	T_m (°C)
cis	−106	2
trans	−107	97/125
syndiotactic 1,2	−28	156
isotactic 1,2	−15	126
atactic 1,2	−4	none

■ 11.6 Physical and Rheological Properties of Rubber Compounds Mixed with Recycled Rubber Powder

This section will present compound test data of recycled rubber powder mixed into a model compound test recipe. In the baseline study, no recipe adjustments were made at this point to demonstrate the impact of the recycled rubber powder as a "drop-in" on physical and rheological properties [15]. Later subsections will discuss some recipe optimizations, or countermeasures, as a way to improve target properties when using recycled rubber powder [22,23]. The need for this work arose out of two situations concerning recycled rubber powder, RRP. The first situation is the most critical and that is the impact on the rubber rheological and physical properties when RRP is added to the mix. The second is the realization that many users do not modify their base recipes when incorporating RRP. The goal of the optimization protocols is to suggest formula modifications when using RRP in new rubber compounds to achieve targeted performance properties.

11.6.1 RRP Baseline Study

The model compound recipe is shown in Table 11.10, which is a generic emulsion SBR and BR polymer blend with all carbon black. The recipe is followed by the sources of the raw materials. Any modifications to this recipe are discussed in the separate sections on each study. Table 11.11 provides the particle size distribution of the 177 μm cryogenic recycled rubber powder, RRP, Class 80-3, sourced from truck tire tread buffings. Table 11.12 displays the mixing procedure for the two pass mix, which shows the RRP being added with the carbon black. Table 11.13 exhibits the standard cure times and temperature for the test specimens.

All experiments were conducted in the rubber laboratory of Lehigh Technologies, Inc., Application and Development Center, unless otherwise indicated. All mixes were performed in a 1.6 liter Farrel Banbury four speed internal mixer. Milling was performed on a Kobelco Stewart Bolling 2-roll mill 33 cm × 15 cm. Both machines are connected to two identical Sterlco temperature control units. The first master mix times were 7 minutes while all finish mixes were 2 minutes long in the Farrel Banbury and used the after mixing milling method recommended in ASTM D3182 Section 7.2.8 and 7.2.9. For each of the four major steps in the laboratory procedure, material weigh-up, mixing, curing, and testing, a unique random batch processing order was employed to reduce or eliminate bias scatter of the data. The experimental designs used replication of batches as discussed in the results section on the separate studies. Some of the designs with replicated batches used a procedure of blending the masterbatches for reducing variation.

Molding and curing were performed using a Wabash compression molding press. Standard curing was performed as per Table 11.13. Uncured specimens for the Drum Abrader, Flexometer, and Zwick Rebound tests were prepared by cutting disks from flat sheets and plying up sufficient layers to fill the cavities in multi-cavity molds for curing.

Per each test plan, as discussed in the results section on the separate studies, rubber specimens were tested according to the following methods: cured test specimens for tensile, elongation, modulus, trouser tear, and outdoor exposure were cut from flat sheets using the respective dumbbell Die C, Die T, and rectangular shaped die cutters on a hydraulic clicker press.

1. MDR2000 Rheometer ASTM D5289 at 160 °C
2. Tensile, Elongation, and Modulus, ASTM D412, unaged and oven aged
3. Trouser Tear Resistance, ASTM D624 T, unaged and oven aged
4. Hardness tested with Rex Digital Durometer, ASTM D2240 Type A on rebound specimens
5. BF Goodrich Flexometer ASTM D623, Method A
6. Zwick Rebound ASTM D7121
7. Zwick Rotary Drum Abrader ASTM D5963, Method A
8. Static Outdoor Exposure (20% Strain) ASTM D518, Method A

Table 11.10 Model Compound Base Recipe

Addition Sequence	Ingredients	Base Compound
		phr
First Pass	ESBR1500 (Non-oil extended)[a]	70.00
First Pass	High Cis Polybutadiene Rubber[b]	30.00
First Pass	Recycled Rubber Powder (RRP)[c]	As Per Studies
First Pass	N339 Carbon Black[d]	65.00
First Pass	Heavy Naphthenic Process Oil[e]	25.00
First Pass	Homogenizing Agent[f]	1.00
First Pass	Alkyl Phenol Formaldehyde Novolak Tack Resin[g]	3.00
First Pass	6PPD Antidegradant[h]	2.50
First Pass	TMQ Antidegradant[i]	1.50
First Pass	Microcrystalline and Paraffin Wax Blend[j]	2.50
First Pass	Zinc Oxide Dispersion (85% ZnO)[k]	3.53
First Pass	Stearic Acid[l]	2.00
Finish Pass	BBTS (TBBS) Accelerator[m]	1.00
Finish Pass	Sulfur Dispersion (80% Sulfur)[n]	2.50

Addition Sequence	Ingredients	Base Compound
		phr
Finish Pass	Retarder N-(cyclohexylthio) phthalimide[o]	0.10
	Total phr Finish Batch	209.63
	Density, kg/l	1.126

Notes for the recipe:
[a] Lion Copolymer Copo® 1500
[b] Lanxess Buna CB 1220
[c] PolyDyneTM from Lehigh Technologies, Inc.
[d] Sid Richardson Carbon Co.
[e] Nynas Nytex 4700
[f] Struktol® 40MS
[g] Akrochem® P90 Resin
[h] Akrochem® PD-2 Pellets
[i] Akrochem® DQ Pastilles
[j] Akrochem® AkrowaxTM 5084 Beads
[k] Akro-Zinc® Bar 85
[l] Akrochem® Stearic Acid – Rbrgrade
[m] Akrochem® supplied Emerald Performance Materials Cure-rite® BBTS (TBBS)
[n] Akroform® Sulfur PM (80%)
[o] Akrochem® Retarder CTP

Table 11.11 Particle Size Distribution by Sieve Analysis of Recycled Rubber Powder (RRP) Used in Baseline Study

Test	Method	Screen Size, µm	177 µm Class 80-2
Sieve Analysis	ASTM D5644-01		**% Retained**
		250	0.0
		177	1.9
		149	13.6
		125	17.8
		105	14.4
		Pan	52.3
		Total	100.0

Table 11.12 Mixing Procedure for Baseline Study

	First Master Mix
	Mixer and mill temperature control units set to 82 °C
	Exhaust system is on 1/2 draw
	Mixer rotor set to speed #1-77 rpm
Time	Procedure
0’	1. Load rubber, start timer and temperature recorder
1.0’	2. Load 1/2 carbon black and 1/2 RRP
2.0’	3. Load all oil, 1/2 carbon black, rest of RRP

Table 11.12 Mixing Procedure for Baseline Study *(continued)*

3.0’	4. Raise and scrape ram
4.0’	5. Load rest of chemicals
6.0’	6. Raise and scrape ram
7.0’	7. Stop mixer and discharge batch
	Finish Pass Mix
	Mixer temperature control unit set to 46 °C
	Mill temperature control unit set to 66 °C
	Exhaust system is on 1/2 draw
	Mixer rotor set to speed #1-77 rpm
Time	**Procedure**
0’	1. Load 1/2 of masterbatch rubber, chemicals, rest of masterbatch, start timer and temperature recorder
1.0’	2. Raise and scrape ram
2.0’	3. Stop mixer and discharge batch

Table 11.13 Specimens Standard Cure Times and Temperature for Baseline Study

Specimens	Cure Time	Temperature
Tensile sheets 150 mm × 150 mm × 2 mm	20’	160 °C
Drum Abrader (Diam. × Height) 15.8 mm × 10.0 mm	30’	160 °C
Flexometer (Diam. × Height) 17.9 mm × 23.5 mm	40’	160 °C
Zwick Rebound (Diam. × Height) 37.2 mm × 18.7 mm	45’	160 °C

Newly mixed unvulcanized rubber with recycled rubber powder will appear “dry and grainy” and rubber stocks with large quantities, greater than 15% by weight or more, may appear “crumbly,” and may have difficulty knitting together. Mill handling and appearance may also be an issue as newly mixed unvulcanized rubber with large quantities of recycled rubber powder may tend to “bag and sag” on the mill, tending not to form a tight band on the mill at the same mill nip, or opening, as uncured rubber without recycled rubber powder. Also, working with newly mixed unvulcanized rubber with recycled rubber powder, one may notice a viscosity increase, as evidenced by a higher power usage in the mixer or higher stiffness of the slab rubber on the mill. These effects are duplicated in the cement industry, with higher solids content cement, and in the food processing industry, with a cook adding too much flour to a cake mix. Recycled rubber powder particles are composed of fully crosslinked polymer chains that do not have the flexible polymer

chains of uncrosslinked rubber and adding these crosslinked particles will increase compound viscosity, as reported by a number of researchers [19,24]. This effect is demonstrated in Figure 11.13 on the MDR Rheometer minimum torque, which is consistent with viscosity.

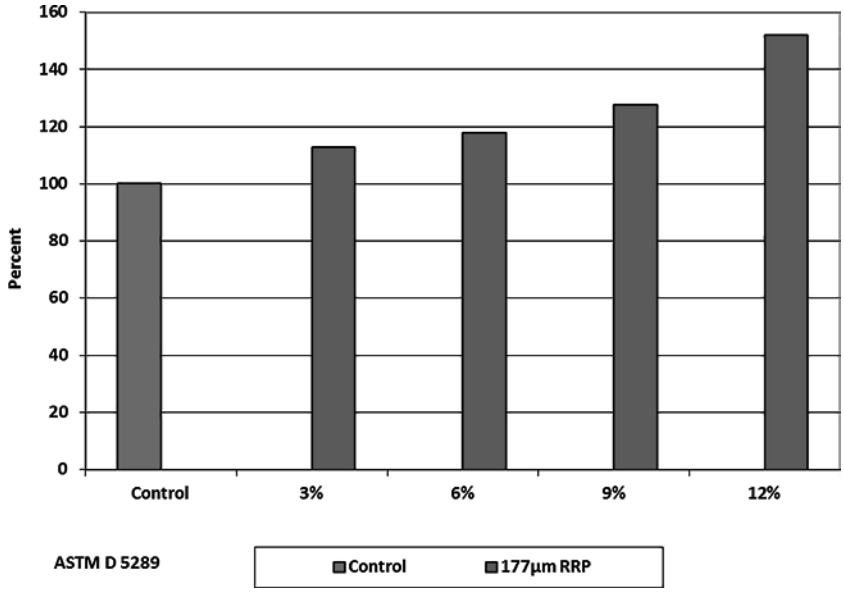


Figure 11.13 MDR Rheometer minimum torque, consistent with viscosity, of the model compound when 3% to 12% 177 µm RRP has been incorporated.

Many researchers have provided theories of the unvulcanized rubber properties of tack and green strength, which are necessary for plied up rubber products, such as tires and conveyor belts. For example, Hamed, [29], described the necessary conditions that must be met for development of high tack between two unvulcanized rubber surfaces, intimate molecular contact, interdiffusion of molecular segments, and good green strength. However, newly mixed rubber with large quantities of recycled rubber powder will exhibit poor tack and green strength. This is explained by the fully crosslinked inflexible particles of the recycled rubber powder interfering with molecular contact, interdiffusion of the molecular segments, and disrupting the ability of the unvulcanized polymers to generate green strength, such as interfering with the natural rubber's ability to generate green strength through strain induced crystallization [29].

The impact on the rubber's rheological and physical properties when RRP is added to the mix has been investigated and reported in published literature. Many researchers, including the author, have reported losses in physical properties when incorporating RRP into new rubber [19,24–28]. In the model compound recipe

given above, Figure 11.14 to Figure 11.19 show some of the key properties of new rubber when 177 μm RRP has been incorporated in increasing levels from 3% to 12% by weight [15,22,23].

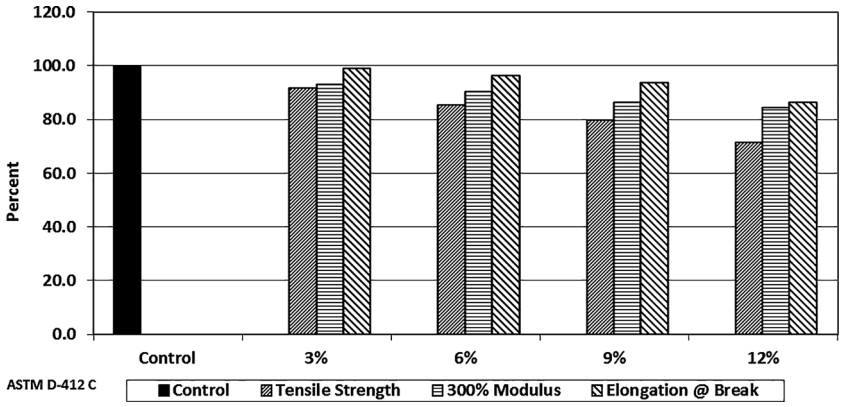


Figure 11.14 Physical properties of the model compound when 3% to 12% 177 μm RRP has been incorporated.

In Figure 11.14 we see that, compared to a control compound without RRP, adding 3% to 12% 177 μm RRP causes a gradual decline in physical properties and in Figure 11.15, Figure 11.16, and Figure 11.17, we see increases in heat build-up and compression set, declines in rebound, and reduced abrasion resistance. The previously mentioned literature references offer explanations for most of these property losses. Gibala, Thomas, and Hamed [26] postulated that RRP particles in new cured rubber are discontinuities and act like stress-raising flaws.

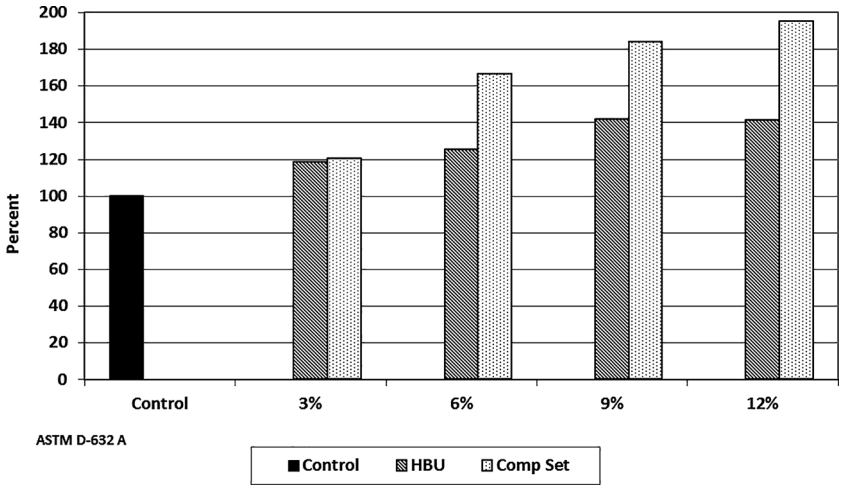


Figure 11.15 Flexometer heat build-up and compression set of the model compound when 3% to 12% 177 μm RRP has been incorporated. Lower is better.

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■ 13.3 Synthetic Silica

Synthetic amorphous silica (SAS) is a form of silicon dioxide (SiO_2) that is generally manufactured by one of two processes: (1) a wet process, which is used to produce precipitated silica and silica gel, and (2) a thermal process for making pyrogenic silica. Precipitated silica is synthesized in a heated reactor by neutralizing a stirred alkaline solution of sodium silicate with sulfuric or carbonic acid. Amorphous silica particles are precipitated out of the salt solution forming a low-solids slurry. Particle size and structure can be controlled by the rate and order of addition of reactants, reactant concentration, and reaction temperature. Primary silica particles fuse together to form aggregates, which in turn form loose agglomerates. After filtering and washing the precipitate, the product is typically spray dried to a near neutral pH. The dried silica is milled to reduce the average agglomerate size. Primary particle size ranges from 10 to 30 nanometers, whereas the resulting aggregates are usually 30 to 150 nanometers. The final product is

classified by aggregate size, shape, pore volume, and the Brunauer–Emmett–Teller (BET) and cetyltrimethylammonium bromide (CTAB) surface area. More than two-thirds of the precipitated silica production is used in elastomer compounding of products such as rubber, plastics, adhesives, and sealants [1].

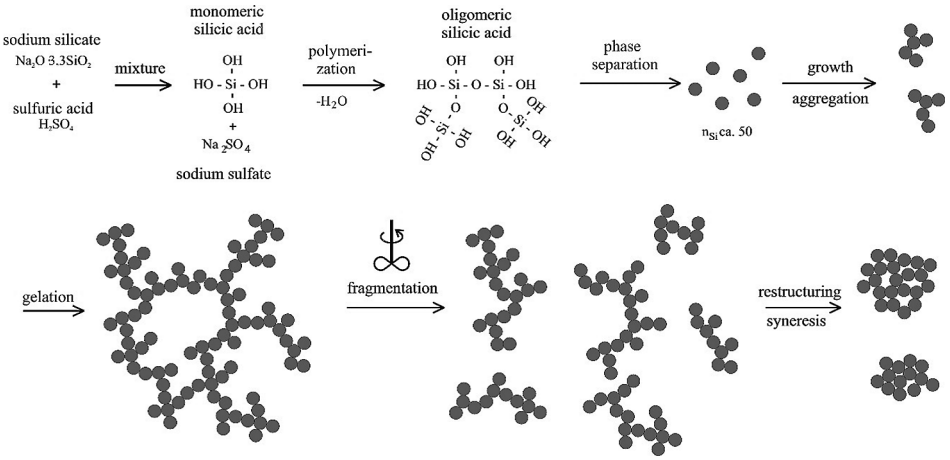

Figure 13.5 Precipitation process of silica [2,3].

In contrast to precipitated silica, silica gel is made by reacting a sodium silicate solution with sulfuric acid under acidic conditions. The silica properties are controlled by reaction rate, order of reactant addition, reactant concentration, reaction temperature, and mixing conditions. During the reaction, a hydrosol is formed, which is aged to form a rigid transparent gel. The gel is fragmented into small pieces, washed, and dried. A dry silica xerogel is formed when water is removed slowly from the gel. Conversely, if water is removed quickly, the colloidal silica structure is preserved as a dry silica aerogel with lower density and higher pore volume. Aerogels have a neutral pH, while xerogels are acidic (4 to 5 pH). Particle size distribution is controlled by milling, but the reported particle size measurement is reflective of aggregate size rather than primary particle size. Certain surface-treated grades are available, which provide improved organic matrix compatibility [1].

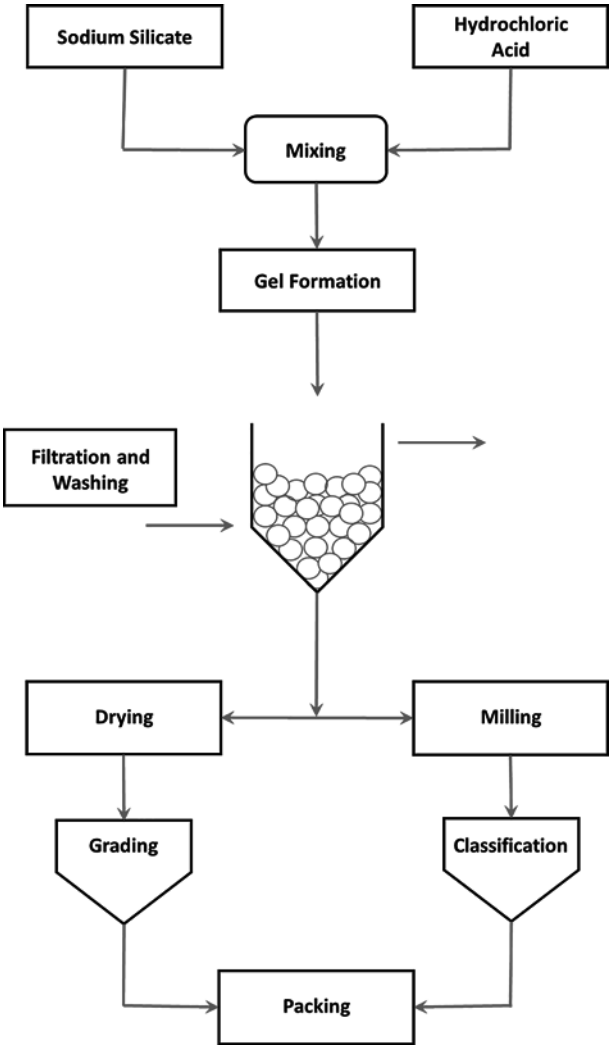

Figure 13.6 Silica gel process.

Pyrogenic or fumed silica is prepared by the hydrolysis of silicon tetrachloride ($SiCl_4$) in a hydrogen and oxygen flame. Particle size and surface area are controlled by varying the ratio of these reactants. Primary silica particles are spherical and approximately 7 to 40 nm in diameter. The primary particles fuse together to form branched or chain-like clusters. Fumed silica aggregates average about 1 µm and form agglomerates with a pH of approximately 4 in aqueous dispersions. Fumed silica is produced and sold in a hydrophilic form but can be surface-treated with silane to produce a hydrophobic form [4].

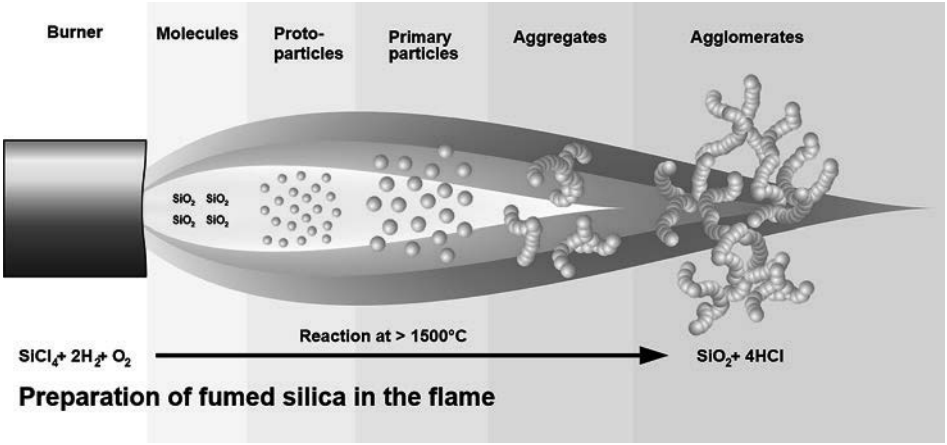

Figure 13.7 Fumed silica is made from flame pyrolysis of silicon tetrachloride or from quartz sand vaporized in a 3000 °C electric arc [5].

Synthetic amorphous silica is often mistakenly identified as the crystalline form of silica simply because it contains the same name and chemical formula. Although SAS and naturally-occurring silica variants have the same chemical composition, these materials are classified under very different health and environmental risk categories. Naturally-occurring silica is crystalline quartz that has been shown to increase the risk of silicosis, a form of occupational lung disease caused by inhalation of crystalline silica dust that results in inflammation and scarring in the form of nodular lesions in the upper lobes of the lungs [6]. To help clear up any misconceptions regarding these two variants, SAS has been widely tested in numerous toxicological and epidemiological studies over several decades and determined to be a non-hazardous substance [7,8]. Inhaled SAS has a short retention time, which produces transient, reversible pulmonary effects in humans and animals. SAS is of low toxicity and does not meet any classification criteria of a hazardous material under European Regulation (EC) No 1272/2008 (CLP Regulation) or the Globally Harmonized System (GHS) of Classification and Labelling of Chemicals. Under such regulations, synthetic amorphous silica is generally considered a safe product that is highly utilized in a wide range of applications [9]. The three primary forms of SAS and their physical/chemical properties are listed in Table 13.12.

13.3.1 Precipitated Silica

Precipitated silica was developed in the early 1940s as a white, submicron-size reinforcing filler for rubber. However, this inexpensive commercial material has many different industrial applications, including use as an adsorbent, pigment, catalyst support, electric insulator, acoustic insulator, optical material, and filler

for polymers that include rubber. Its usage has constantly increased, and an estimated 75% of the total production is used in rubber (e.g., tires, shoe soles, belts, and engine mounts) [10]. The primary application for precipitated silica is in tire compounds either as a minor portion of the filler in combination with carbon black or as the major filler component. Substituting low levels (5 to 10 phr) of silica for carbon black in certain components of the tire can enhance tear resistance, cut growth resistance, and adhesion properties.

Table 13.12 Physical and Chemical Properties of the Three Types of Synthetic Silica [8]

Property (units)	Pyrogenic	Precipitated	Gel
Purity, % SiO_2 (by weight)	>99.8	>95	>95 (dry)
Color	White	White	White
Specific surface area (BET, m^2/g)	50-400	30-500	250-1,000
Loss on drying (% by weight)	<2.5	5-7	2-6
pH	3.6-4.5	5-9	3-8
Tapped (bulk) density (g/l)	30-250	30-500	500-1,000
Ignition loss (% by weight)	<2	3-14	2-15
Particle size			
Primary particle (nm)	5-50	5-100	1-10
Aggregate (µm)	0.1-1	0.1-1	1-20
Agglomerate (µm)	1-250*	1-250*	NA
Porosity			
Mean pore size (µm)	None	>0.03	0.0001-1
Pore size distribution	None	Very Wide	Narrow
Specific gravity (g/cm^3)	2.2	1.9-2.2	1.8-2.2
Structure, DBP absorption (ml/100 g)	250-350	80-320	80-350

*Agglomerate particle size is typically 100 µm

Prior to the 1970s, silica usage was not so popular [11]. This was principally the case because the polar nature of the silica surface made it difficult to disperse significant volumes in rubber compounds, resulting in reduced reinforcement and poor performance. The major breakthrough in silica technology came in 1972 when Degussa introduced Si69 silane coupling agent silica-filled rubber as a way to improve reinforcement properties [12–14]. In the early 1990s, Michelin introduced silica-filled tires [15] and, since then, precipitated silica has been primarily used in tire treads. Increased demand for what the tire industry refers to as the "magic triangle" of tire properties – rolling resistance, wet traction, and wear – has resulted in tire manufacturers incorporating more silica in tread compounds and driving the continued improvement of silica surface modification techniques.

The optimization of silica technology requires an accurate characterization of the precipitated silica product, which has not been fully identified in the industry. The characterizing of silica is principally rooted in accurately describing its morphology, which includes its inner and outer structure, surface chemistry, specific sur-

face area, pore volume and distribution, intra-aggregate structure, and void volume. These properties can be manipulated during the silica manufacturing process to deliver an extremely versatile material having a wide range of performance-enhancing properties [10]. Today, as a result, numerous silicas with varying specifications for specific purposes have been created.

In the case of precipitated silica, it is currently used in tire sidewalls [16,17] to increase tear strength and cut growth resistance and ozone aging resistance [18]. Precipitated silica technology has been credited with reducing rolling resistance in tires approximately 20% over the last 27 years, corresponding to a vehicle fuel savings of 3 to 4%, as compared to carbon black tread compounds [19]. SAS is also being used as a filler in truck tires, where carbon black was historically the staple filler. Amorphous precipitated silica is an inexpensive and easily available commercial material that has presented both environmental and economic advantages [20].

13.3.2 Precipitated Silica Characterization

13.3.2.1 Structure and Surface Chemistry

Precipitated silica surface structure and chemistry has been the subject of intense studies for more than 60 years [21]. Structural properties such as primary particle size, silica surface area, porosity, siloxane bond development, aggregate, and agglomerate formation are a few of the attributes used to characterize silica surface morphology. Silica surface chemistry is characterized by the concentration and distribution of different types of OH groups and siloxane bridges, percent of physically absorbed water, and pH [22]. Because of the importance of these properties in determining the practical applications of silica, numerous physical and analytical techniques have been utilized to elucidate the complexity of the amorphous silica surface [22–25].

Precipitated silica consists of silicon dioxide monomers to form an inorganic polymer $(SiO_2)_n$. Silicon atoms are covalently bonded to four oxygen atoms in a tetrahedral arrangement (see Figure 13.8a). Each of the four oxygen atoms is bonded to at least one silicon atom to form either a silanol (≡Si-OH; Figure 13.8b) or a siloxane bridge (≡Si-O-Si≡; Figure 13.8c) functionality. The bulk structure is determined by random packing of the $[SiO_4]^{4-}$ units, which results in a nonperiodic structure [21]. Silanol groups are formed during the synthesis process. The condensation polymerization of the acid forms spherical colloidal particles containing silanol groups on the surface. Yaroslavsky and Terenin proved the existence of the surface hydroxyl groups in the late 1940s [26]. An investigation of silica surface chemistry by Kiselev and Zhuravlev two decades later determined that surface properties, an

oxide absorbent, depend on the presence of these silanol groups. Using a deuterium exchange method developed by L.T. Zhuravlev, Kiselev and Zhuravlev ascertained that the surface hydroxyl group concentration was fairly consistent over a wide range of amorphous silicas independent of the surface area. The numerical value of hydroxyl groups per unit surface area was $\alpha_{OH,AVER}$ = 4.6 nm^{-2} (least-squares method), known today as the Kiselev–Zhuravlev constant [22,27]. Another decade would pass before Maciel and Sindorf, using CP MAS NMR, would discover that the silica surface not only contains single silanols, but has a population of germinal silanols (Figure 13.9a, two silanols bonded to the same silicon atom) [23]. The authors later observed that single silanols could be vicinal (i.e., silanols involved with the formation of intramolecular hydrogen bonding; Figure 13.9b) or isolated (silanols [28] that are separated from other adjacent silanols by a distance > 3.1 Å, which prohibits hydrogen bonding) [29]. The distribution of the silanol functionalities on the surface of any SAS is approximately 17–20% germinal and 80–83% single [24]. Specifically for precipitated silicas with surface areas around 175 m^2/g, germinal silanol population is 17.8% and single silanol population is 82.2% [30].

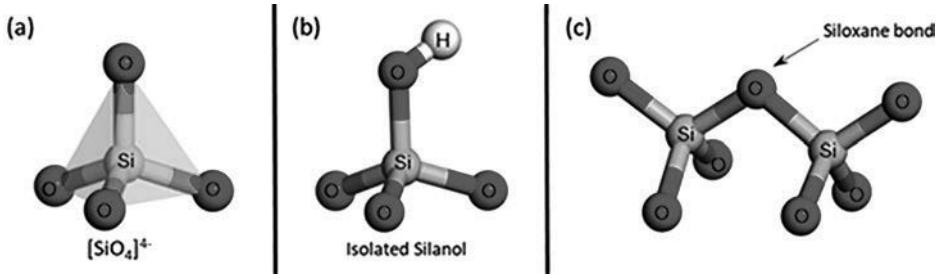

Figure 13.8 Silica surface structures: (a) $[SiO_4]^{4-}$ units in a tetrahedral arrangement; (b) isolated single silanol; (c) siloxane bond connecting two silicon atoms. Oxygens shown without hydrogens are bonded to silicon atoms forming siloxane bridges.

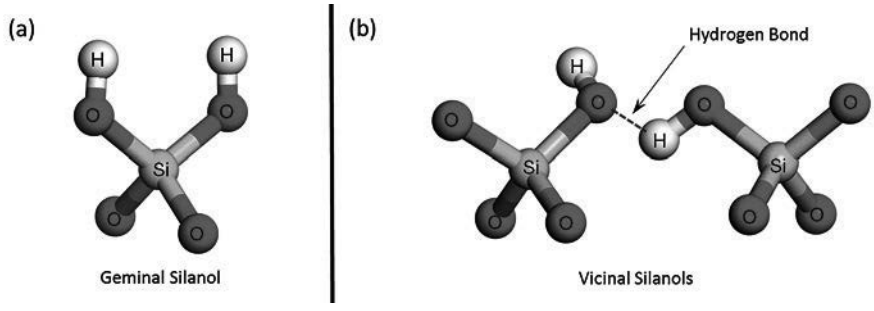

Figure 13.9 Reactive silica surface structures: (a) germinal silanol (two hydroxyl groups bonded to one silicon atom); (b) vicinal silanol (two isolated silanols hydrogen bonded to each other). Oxygens shown without hydrogens are bonded to silicon atoms forming siloxane bridges.

■ 18.2 Phenol-Formaldehyde Resins

Phenol-formaldehyde resins have long been used in the rubber industry as tackifiers, reinforcers, or curing agents. Phenolic tackifiers can be found in many compounds that require good tack for component building purposes. Phenolic reinforcing resins are found in the compounds where high stiffness and hardness are needed. Phenolic curing resins are used to cure butyl tire-curing bladders, air bags, TPE elastomers, and products that require high heat resistance.

Phenol-formaldehyde resins can be chemically classified into two major groups: novolaks and resols. The novolak resins are made from the reaction of phenol with formaldehyde under acidic conditions (see Figure 18.1). The phenol can be an alkylphenol or a combination of phenol and alkylphenol. The molar ratio of formaldehyde/phenol is less than one for novolaks. Novolak resins are thermoplastic resins that soften at elevated temperatures unless crosslinked with a methylene donor. Tackifying and reinforcing resins are variations of novolak resins.

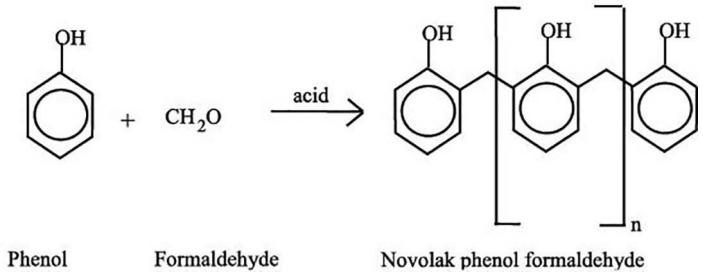

Figure 18.1 Formation of a novolak resin.

The resol resins are made from the reaction of phenol with formaldehyde under basic conditions (see Figure 18.2). The phenol is usually an alkylphenol. The molar ratio of formaldehyde/phenol is greater than one for resols. Resol resins are thermoreactive. Adhesive and curing resins are produced from different variations on resol resins.

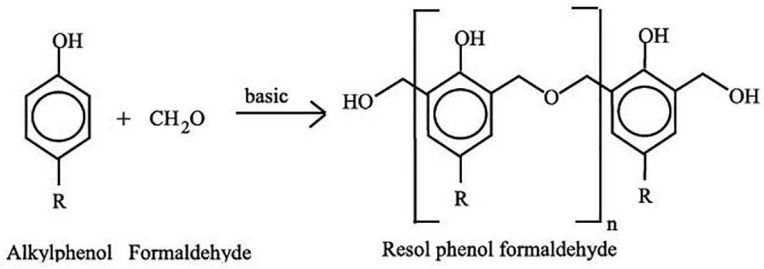

Figure 18.2 Formation of a resol resin.

18.2.1 Types of Phenol-Formaldehyde Resins

18.2.1.1 Reinforcing Resins

Reinforcing resins are novolak resins that typically have a branched structure. These resins are made from the reaction of a phenol and formaldehyde under acidic conditions to produce a branched novolak resin as shown in Figure 18.3.

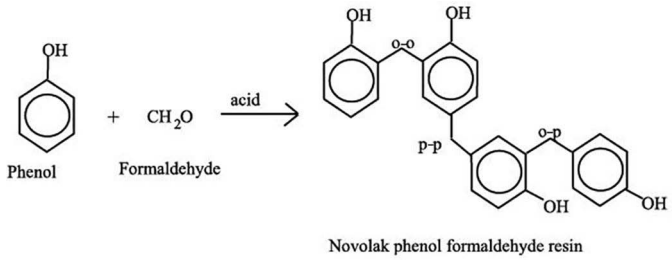

Figure 18.3 Formation of a reinforcing resin.

The ratio of ortho-ortho (o-o), para-para (p-p), and ortho-para (o-p) bonds is dependent on the type of catalyst.

Novolak reinforcing resins can be modified by the following:

- Part of the phenol in the reaction can be replaced by other phenolic or non-phenolic compounds
- Part of the formaldehyde can be replaced by other aldehydes
- Varying the type of catalyst during the polycondensation can form linear versus branched structures
- Common chemical modifications to reinforcing resins are made with cashew nut oil, cresol, or tall oil

Reinforcing novolaks are thermoplastic and must be crosslinked with a methylene donor such as HMT (hexamethylenetetramine) or HMMM (hexamethoxymethylomelamine) to make them thermosetting and reinforcing. The amount of methylene donor needed to crosslink novolak resins depends on the hardness level needed, the amount of novolak resin in the formulation, and whether the methylene donor is HMT or HMMM. Generally, the amount of methylene donor used is 8 to 15% of the total novolak resin in the formulation. Higher amounts of HMMM are used to get the same hardness level as HMT. Formulations with less than 10 phr of novolak resin may require larger amounts of methylene donor because of dilution by the overall compound formulation.

Reinforcing phenol-formaldehyde resins can be used to make a high hardness (90+ Shore A durometer) bead filler that has good processing properties. A model formulation is shown in Table 18.2.

Table 18.2 High Hardness Tire Bead Apex Compound

Ingredient	PHR
First stage (Banbury):	
Natural rubber SMR20	60.00
Butadiene rubber 1220	40.00
Carbon black HAF LS N326	80.00
Aromatic oil	5.00
Stearic acid	1.50
6PPD Antidegradant	1.00
Zinc oxide	7.00
Phenolic resin	15.00
Second stage (2-Roll Mill):	
HMT or HMMM methylene donor	1.50
MBS accelerator	0.80
Insoluble sulfur (95% active)	2.20
PVI scorch inhibitor	0.25

A high hardness tread compound with good flex properties, improved tear resistance and good processing properties is possible with phenolic reinforcing resins. Table 18.3 shows a model formulation.

Table 18.3 High Hardness Tread Compound

Ingredient	PHR
1st step	
SBR 1500	100.00
N339 carbon black	65.00
Silica	8.00
Phenolic resin	8.00
Wax	1.00
6PPD antidegradant	2.25
Zinc oxide	2.50
Stearic acid	2.00
Aromatic oil	21.00
2nd step	
HMMM methylene donor	1.20
Sulfur	1.60
TBBS accelerator	1.40

A hard subtread compound with low rolling resistance can be made with a phenol-formaldehyde reinforcing resin that gives good tire handling properties and low hysteresis in low rolling resistance tires, high performance tires, and truck tires, as shown in Table 18.4.

Table 18.4 Low Rolling Resistance Hard Subtread

Ingredient	PHR
First stage	
SMR- or SIR-20 NR	50.00
1203 High Cis BR	50.00
N650 carbon black	35.00
Aromatic oil	0
Naphthenic oil	0
Phenolic resin	10.00
Zinc oxide	3.50
Stearic acid	2.00
TMQ antioxidant	1.50
Wax	1.50
6PPD antioxidant	1.50
Final stage	
Sulfur	1.80
TBBS accelerator	2.00
DPG accelerator	0.25
HMMM methylene donor	1.20

In the automotive industry, EPDM rubber profiles are used to weatherproof windows, doors, and car hoods. Phenolic resins have been used to make weather-stripping profiles that are made of co-extruded dual hardness rubber compounds. These co-extruded profiles have replaced the traditional profile containing a soft rubber compound and a metallic insert. Table 18.5 lists the components of a high hardness EPDM model compound (50+ Shore D durometer) made with phenol-formaldehyde reinforcing resins.

Table 18.5 High Hardness EPDM Compound

Ingredient	PHR
Masterbatch	
EPDM	100.0
Carbon black N660	150.0
Calcium carbonate	20.0

Table 18.5 High Hardness EPDM Compound *(continued)*

Ingredient	PHR
Process oil	40.0
Poly ethylene glycol	3.0
Process aid	3.0
Stearic acid	2.0
Zinc oxide	8.0
High styrene resin	5.0
Phenolic resin	15.0
Calcium oxide	10.0
Final	
HMT methylene donor	1.5
Sulfur	1.5
MBT accelerator	1.5
TMTD accelerator	0.8
ZDBC accelerator	1.4
CBS accelerator	1.5

Phenolic reinforcing resins are compatible with the most common elastomers in the rubber industry; however, the degree of compatibility varies somewhat depending on the polarity of the elastomer. For example:

- NBR: Phenolic resins are very compatible with NBR polymers, and large amounts (25 to 100+ phr) of resin can be incorporated to form very hard, ebony type compounds. Lesser amounts (10 to 20 phr) of resin in NBR form softer and more flexible vulcanizates.
- EPDM: Phenolic reinforcing resins have good compatibility with EPDM polymers. Levels of up to 30 phr can be used. Reinforcing novolak resins can increase the hardness and abrasion resistance of EPDM compounds.
- SBR, BR, and NR: Phenolic resins are not as compatible with SBR, BR, and NR polymers. However, levels of 10 to 20 phr can increase hardness and abrasion resistance. NBR rubber at levels of 15 to 25 phr is often combined with SBR, BR, or NR to increase the compatibility of the resin, enabling resin levels greater than 20 phr to be incorporated.
- CR: Phenolic resins have the least compatibility with CR polymers. Levels of 5 to 10 phr are recommended. NBR rubber (15 to 25 phr) is often used in combination with CR rubber to increase the compatibility of the resin allowing for resin phr levels above 15.

18.2.1.2 Tackifying Resins

Tackifying resins are produced from different variations on novolak resins. Generally, they have a linear structure as shown in Figure 18.4. The alkyl group (R) is usually an octyl or *t*-butyl group.

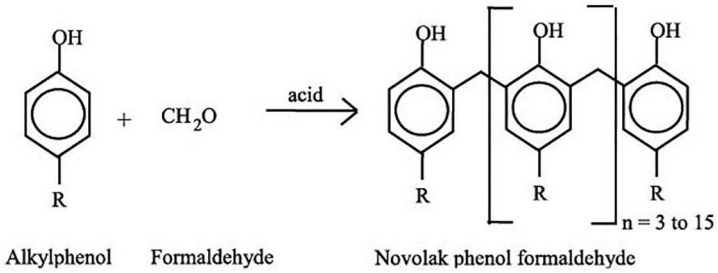

Figure 18.4 Formation of a tackifying resin.

Table 18.6 shows a model formulation with a phenol-formaldehyde tackifying resin. Generally, phenolic-formaldehyde resins with higher molecular weights and higher softening points have superior tack, especially after aging under conditions of high humidity and temperature.

Table 18.6 Tackifying Resin Compound

Ingredient	phr
SMR 20 natural rubber	45.00
BR 1220 BR	30.00
SBR 1500	25.00
N650 carbon black	50.00
Naphthenic oil	15.00
Stearic acid	2.00
Zinc oxide	2.50
6PPD antidegradant	3.50
Wax	3.00
Tackifying resin	5.00
Sulfur	1.75
MBTS accelerator	0.90

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1,1-di(t-amylperoxy)cyclohexane **624, 631**
1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane **617, 628**
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