natural rubber

technically specified & specialty grades

***Depth and Understanding:** Natural rubber is the oldest elastomeric material; its use predates even its "discovery" by Christopher Columbus on his second voyage to the New World. Since many compounders have been schooled in rubber chemistry while working with natural rubber formulas, there is usually a certain comfort level with natural rubber. Therefore, this Solutions brochure will discuss less of the compounding of natural rubber and focus more on the natural rubber products that Akrochem offers – both the general purpose, technically specified types as well as the specialty grades that help solve unique compounding problems.*

Akrochem's natural rubber line includes two broad groupings:

1) Technically specified rubber (TSR) for the myriad of typical mechanical good applications of the rubber industry. Unlike older natural rubber types that were graded by visual inspection, TSR is graded by the source of the rubber as well as measured properties. This has made a more consistent natural rubber available to the compounder. Akrochem carries those types that are used primarily by the molded goods industry – SMR L, SMR CV60, SMR GP.

2) Specialty natural rubbers that find their niche in unusual applications that require a novel approach to a compounding problem. These include precrosslinked rubbers, deproteinized rubber and methyl methacrylate grafted copolymers. We'll discuss in detail the unique properties each rubber offers a formulator.

technically specified rubber (TSR)

Grading of conventional forms of natural rubber has always been by visual examination. While the premium grades like Pale Crepe and RSS #1 have visually lower dirt content and excellent properties, these visual properties have no technological basis. Technically specified rubber (TSR) classifies natural rubber by basic rubber test specifications that are guaranteed. These tested properties include content of dirt, ash, nitrogen, and volatile matter; plasticity retention index (a measure of a rubber's thermal stability and aging resistance which can be directly related to the cleanliness of the rubber); mooney viscosity of controlled-viscosity (CV) grades and color of color-controlled grades.

The establishment of technically specified products by Standard Malaysian Rubber (SMR) has revolutionized the manufacturing of natural rubber. Rubber is now prepared in crumb form rather than sheets or crepes to improve the cleaning process. Mechanized methods have been adapted for automating the process. The result is a much cleaner, more consistent product. As other producers of natural rubber have come on-stream, the need to meet these requirements resulted, for the most part, in the same good quality natural rubber from Indonesia and Thailand, among others.

TECHNICALLY GRADED SPECIFICATIONS:

Grades:	*SMR CV(60)*	*SMR L*	*SMR GP*	*SMR 10**
Color Limit-Lovibond Scale, max	-----	6.00	-----	-----
Dirt Content, less than	0.02	0.02	0.08	0.10
Ash Content, less than	0.50	0.50	0.75	0.75
Nitrogen Content, less than	0.60	0.60	0.60	0.60
Volatile matter, less than	0.80	0.80	0.80	0.80
Plasticity Retention Index, %	60.0	60.0	50.0	50.0
Wallace Rapid Plasticity Po, min.	-----	35.0	-----	30.0
Mooney Viscosity: ML 1+4, 100 °C	55-65	-----	60-72	-----

* for illustrative purposes only. Akrochem does not carry SMR 10 at this time.

SMR L: This is a very clean, light-colored rubber. To prevent enzyme darkening of the rubber, 0.05% of sodium metabisulfate is added at the latex stage. SMR L's primary use is in colored compounds, especially light or bright colors. The clean, consistent rubber allows less colorant to be used as well as improving the batch-to-batch uniformity of the color (this week's color will match one made 6 months from now. Non-color-specified rubber does not lend itself to this consistency). The low dirt, etc. also results in high quality physical properties as well. For strictly physical properties, most compounders might choose the slightly less expensive SMR 5 which is clean but not as good a color. However, it doesn't make sense to carry two forms of the same product if SMR L will cover all requirements.

SMR CV60: This is a viscosity-controlled natural rubber. To prevent the raw rubber stiffening that normally occurs with storage, 0.15% of a hydroxylamine is added to the latex stage. Thus, the original mooney viscosity of approximately 60 is maintained even over several years. By contrast, uncontrolled rubber (SMR L, 10, 20, RSS) starts out at approximately 60 mooney but will stiffen to between 90 and 120 mooney by the time it has arrived in North America. As a result, most non-viscosity controlled rubber has to be premasticated and/or peptized to make it serviceable. This leads to extra mixing time and erratic viscosity results. Most molded goods manufacturers have found CV60 able to replace RSS and SMR 5 and 10 while freeing up mixer time and gaining more consistency in processing. Remember when you compare SMR CV60 to an uncontrolled viscosity material, you have to compare properties at a similar viscosity. The higher starting viscosity of natural rubbers like RSS#1 will give them a slight advantage in physical properties over the CV60. But if compared at realistic processing parameters (where the higher viscosity rubber has been masticated or peptized), CV60 will match up well with these rubbers.

Note: Be very careful about lab comparisons of natural rubbers. For that matter, be careful about any lab-mixed natural rubber formula. Typically, the much greater shear from tighter clearances in the lab mixer and tighter mill nips in the lab will lower the molecular weight of any natural rubber causing poorer physical properties than one would expect. Use lab mixes for initial compound development, cure studies, etc., but don't rely on tensile, abrasion and tear properties until a factory batch is made. Another alternative is to "baby" the lab batch by mixing at much slower speeds, dumping at lower temperatures and milling on as wide open a mill as possible. Also, remember that natural rubber develops maximum physical properties with a cure around 280 °F. Development work should be done at these temperatures, not your "standard lab cure temperature" of 320 °F or 340 °F.

SMR GP: This is another viscosity-controlled natural rubber (66 +/- 6 mooney viscosity) that is extremely price competitive with specifications similar to SMR 10. Thus, using the SMR GP eliminates the price advantage of SMR 10 over SMR CV60. You then have the cost of SMR 10 with the processability of a CV60.

One-pass mixing with SMR GP bale rubber is excellent compared to bale SMR 10 one-pass mixed. Carbon black dispersion is much better; mooney viscosity is lower; and mooney scorch is lengthened. A single-passed batch was run using SMR GP and one with SMR 10 with the following results:

Rubber	Compound Viscosity ML 1+4/100 ℃	Scorch 120 ℃, min	Black Dispersion Cabot Rating **	Tensile / Elong MPa / %
SMR GP	58	18.0	C 1-3	26.0 / 545
SMR 10	72	16.0	H 1-3	24.5 / 510

Rubber, 100; N762 Black, 50; Naphthenic Oil 2.5; ZnO, 5; Stearic, 2; Antx DQ, 2; sulfur, 2.25; CBTS, 0.5
** lower letter designates better dispersion

The processing advantages are obvious. If you're trying to reduce costs by one-pass mixing SMR 5, SMR 10, SMR 20, RSS #1 or #3, try SMR GP to upgrade the compound processability without cost penalty. Or conversely, if you are 2-pass mixing these rubbers with uncontrolled viscosity, try single passing with a viscosity-controlled polymer.

specialty natural rubber

Precrosslinked Natural Rubber: By introducing some crosslinking (essentially a light cure) into natural rubber latex, a uniquely useful product results. Crosslinked natural rubber is an outstanding way to improve processing in many rubber articles. The standard curing system is:

	PHR
Natural Rubber	100.00
Mercaptobenzothiazole (MBT)	0.32
Accelerator EZ	0.16
Sulfur	1.60
ZnO	1.20
	103.28

After vulcanization, the cured latex still has a fine enough particulate size that the latex is passed through a 325 mesh screen. The cured latex is then intimately blended with unvulcanized natural rubber latex. Akrochem offers 5 versions of precrosslinked natural rubber:

Product	Vulcanized Portion, %	Unvulcanized Portion, %	% Oil
PA-80	80	20	----
PA-57	57	14.4	28.6
Superpoly 50	50	50	----
Superpoly 40	40	60	----
Superpoly 20	20	80	----

PA-80 is the traditional precrosslinked natural rubber. Typically, using 20 phr of this highly crosslinked rubber will make significant improvements in a stock's processability. PA-57 is PA-80 with 40 phr of a naphthenic oil added. The PA-57 allows smoother processing of low durometer stocks, higher viscosity in compression molded rubber, as well as improved blending with other rubbers [In certain situations PA-80 can be a problem blending with unvulcanized rubber. Small "nibs" of cured rubber will sometimes show up in softer mixes due to insufficient shear. PA-80 should be premasticated before blending. PA-57, as well as the other crosslinked versions, permits blending without premastication]. The Superpolys are different levels of precrosslinking allowing optimizing of the vulcanized portion. They can be used at 100 rhc without any blending issues.

As most compounders know, use of a precrosslinked rubber, whether synthetic or natural, offers a variety of processing advantages. Precrosslinked natural rubber improves processing without impairing the finished physical or functional properties. In fact, blends with SBR will have improved physicals as is typical with NR addition to SBR while providing the smoother processing.The table below shows varying levels of PA-80 mixed with SMR L. Physical properties are consistent throughout. At 40 phr of PA-80, the extruder die swell has been reduced by 67%.

Minor adjustments in the cure system should be made since as the precrosslinked level gets higher, scorch will decrease. Retarder CTP [N-(cyclohexylthio)phthalimide] or PX (phthalic anhydride) can be added or a sulfenamide like CBTS, BBTS or OBTS could replace a thiazole to restore scorch to normal. No adjustment for scorch was made in this study. Also, the total cure should be reduced in proportion to the amount of precrosslinked rubber added to maintain the same crosslink density.

			Parts Per Hundred			
SMR L	100	80	60	40	20	0
PA-80	0	20	40	60	80	100
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1
MBTS	1	0.92	0.84	0.76	0.68	0.60
DPG	0.10	0.09	0.08	0.07	0.07	0.06
Sulfur	3	2.76	2.52	2.28	2.02	1.80
Mooney Viscosity [ML 1+4@ 100 ℃]	36	40	46	52	63	78
Mooney Scorch [t_2, 120 ℃, min]	25	24	21	16	12	8
Die Swell, %	150	91	49	25	15	11
Durometer, IRHD	44	44	45	45	46	44
Tensile Strength, MPa	26	28	28	26	26	25
Elongation at Break, %	735	745	750	740	750	735
Modulus at 300%, MPa	1.7	1.7	1.7	1.8	1.6	2.1
Compression set, 24 hrs/70 ℃	18	20	18	19	21	22

The processing advantages are most profound in extruded or calendared stocks. Dimensional stability of the processed rubber is dramatically improved. This is especially critical in lightly loaded or gum recipes. Below are the results of a high quality tubing compound:

Compound: Rubber 100, precipitated whiting 40, ZnO 5, TiO_2 5, color 0.75, Antioxidant 235 1.0, Sulfur 1.5, MBTS 1.0, TMTD 0.25 (accelerators and sulfur reduced 40% for Superpoly 40)

Pale Crepe	100	----
Superpoly 40	----	100
Compound Mooney Viscosity	45	58
Mooney Scorch (min)	9	7
Extrusion Rate (cm/min)	98	154
Die Swell %	108	29
Surface Appearance	rough	smooth
Degree of collapse	nearly complete	very slight

Below is a summary of the improved processing effects of precrosslinked natural rubber. Take a moment to visualize a problem that you may have in-house and how these factory-proven problem-solvers can help that problem.

- Swell of material passing through a calendar nip or an extruder die is greatly reduced.
- Precrosslinked rubber's higher green strength improves resistance to collapse, distortion or stretching.
- Smooth surfaces, sharper profiles and edges. Calendared sheets aren't full of "crows feet" that can be a source of trapped air.
- Gauge is consistent due to less surging, swelling and stretching.

- Less air trapping, porosity and blisters due to higher viscosity. Salt bath curing is dramatically improved (e.g., extruded windshield wiper blades).
- Increased throughput and productivity. An example starting with a simple natural rubber extruded stock:

calcium carbonate, phr	Throughput, g/min	
	RSS #1	Superpoly 20
0	200	1000
20	320	940
50	420	600

- Processed stock is easier to handle due to green strength, viscosity, less stickiness.
- Repeated milling of stock has less effect on processability. Sticky, overmasticated rubber is seldom a problem.
- Reduced nerve of rubber prevents preforms from "pulling apart." Tank linings tend to stay in place and don't pull away. Less air is built into a part.
- Molded parts exhibit less air-trapping and stronger knit lines due to less stock turbulence; smoother cavity fill and less excessive flow out of the cavity (which can leave the cavity starved of rubber and not filled). This is especially critical in low duro, compression molded stocks. As stated earlier, PA-57 is an excellent choice for this type application.
- Open steam-cured parts resist distortion, sagging and exhibit less water marking.

other applications

Adhesives – Superpoly 20 is used extensively in adhesives as well as printing inks. When dissolved in rubber solvents, Superpoly 20 (also known as Superpoly ADS in the Adhesive Industry) gives a lower solution viscosity when compared to regular unvulcanized rubber. The lower solution viscosity (see table below) allows higher solids content, which is critical to pressure-sensitive adhesives. The vulcanized phase in the adhesive provides better cohesion and heat stability of the rubber coating. The deposited adhesive film resists flow or wiping, especially when the adhesive is used at high temperatures.

Solution Viscosity	Raw Mooney Viscosity ML (1+4 @ 100 °C)	Brookfield Viscosity* cps, room temp
SMR L, masticated	59.5	443
Superpoly 20 (ADS)	56.5	220

* (5% concentration of rubber in toluene)

Case Study Using Precrosslinked Rubber: A high quality, 60 duro natural rubber compound was used for a large (approx. 4' x 6') compression molded, intricately-designed part. Calendared sheet stock was loaded into the mold in complicated patterns. The loading pattern changed with every run of calendared stock. Molding flaws were inherent in the part due to excess or insufficient flow (depending on the viscosity resulting from calendaring). Stock often had to be remilled over and over resulting in blisters and air traps; knit lines were weak from lack of pressure due to excess flow from the mold or because minute amounts of air were trapped in the knit line. Sticky preforms were hard to re-position once they were loaded. Scrap parts were ubiquitous to the product.

The solution to this molding problem was to substitute 50 phr of Superpoly 50 in place of 50 phr of the #1 RSS typically used. Calendared sheets now ran smoother; "crows feet" that would trap air were eliminated. Stock was not only higher viscosity, which helped remove air from the mold, but also remilling the stock had only a minor effect on the subsequent viscosity. Blisters that had once been attributed to water suddenly disappeared. Knit lines were stronger. What had been thought to be a flex-cracking problem was improved by the better knit. Plied-up preforms were tacky but could be pulled apart if needed. The mold-loading pattern was established and maintained. Physical properties and product performance were equal or better. Scrap, repairs and rework were all greatly reduced.

MEGAPOLY and MEGATEX: These specialty polymers are natural rubber with polymethylmethacrylate (PMMA) grafted into the polyisoprene backbone. The PMMA addition provides rubber that is self-reinforcing and, due to its dual polarity nature, is highly useful in adhesive products. As might be expected, the polarity of the Megapoly improves oil resistance of general-purpose rubbers. This modified rubber comes in both dry rubber form (Megapoly – for dry rubber compounds and solvent-based adhesives) as well as an aqueous form (Megatex – for latex addition and water-based adhesives).

PMMA Grafted Natural Rubber:

Latex	Dry	PMMA Content % (dry wt)
Megatex 15	-----	15
Megatex 30	Megapoly 30	30
Megatex 49LS	Megapoly 49	49

Megapoly – as this dry polymer is added to a natural or synthetic rubber formula, the cured product becomes harder and stiffer (higher modulus) in direct relation to the amount of PMMA present. Tear strength improves; adhesive properties show pronounced improvement to metal, fabric, polymers, and other dissimilar substrates. Crumb-form Megapoly available for easier solvation.

Megapoly can be used to raise the durometer of rubbers while providing excellent processing and physical/dynamic properties. High durometer, but highly flexible, impact-resistant materials can be made with improved viscosity and scorch compared to a highly loaded black compound. Bright colors, even translucent compounds, can easily be made in the 90+ duro range. Here are a few representative formulas:

Gum and Black-Loaded Comparisons:
ZnO - 4, Stearic - 2, Antx DQ - 1, CBTS - 0.5, Sulfur - 2.5

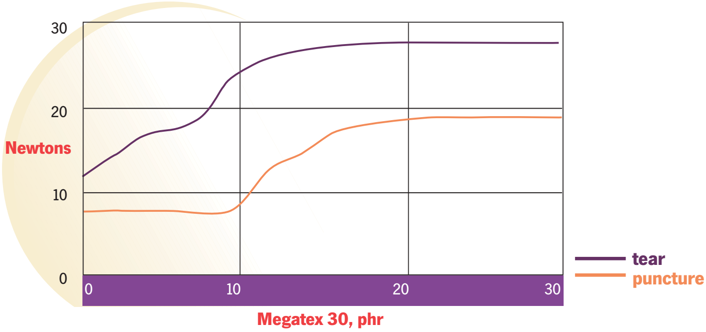
	1	2	3	4	5	6	7	8	9	10
Megapoly 49	0	20	40	60	80	100	0	20	50	70
SMR CV60	100	80	60	40	20	0	100	80	50	30
N326 Black	--	--	--	--	--	--	50	50	50	50
Duro, Shore A	42	52	66	78	88	96	65	75	89	97
Tensile, MPa	27	25	27	26	23	17	29	24	20	16
Elong, %	740	625	595	540	360	215	550	495	270	130

Compared to an HAF black-loaded tread stock, formula #3 above had similar physical properties but lower viscosity, longer scorch and a resilience of 75% vs. 57% for the tread stock. While #3 could not replace a tread stock (abrasion is not good enough for one thing), it can suggest the use of PMMA-modified natural in high durometer, dynamic compounds. For example, bonded bushings made from a Megapoly 49 blend had a two-fold improvement in fatigue life (when subjected to a cyclic twisting of ± 20° at a speed of 120 cycles/min) over conventional compounds. And, of course, adhesion bonds are tenacious.

90 Duro Translucent Compounds: are easy to make in either peroxide or sulfur cures. These can be used for fluorescent or metallic-look colors (use peroxide for fluorescents).

Adhesion Enhancement with PMMA Modified Rubber: Use of Megapoly in solvent-based adhesives and Megatex in aqueous-based adhesives will dramatically improve adhesion between dissimilar materials. Because the polar PMMA is grafted to the non-polar natural rubber, incompatible materials can be bonded. One example is pressure-sensitive rubber adhesives with various plastic backings (particularly PVC in electrical insulation tape). Where previously a primer adhesive had to be used with a second adhesive to achieve a good bond between rubber and PVC, use of Megapoly requires only a one-coat adhesive. Phenolic resins are excellent tackifiers for these systems and Superpoly 20 (as discussed here earlier) is used to minimize flow of adhesive on plastic surface and increase solids. A representative formula for masking, duct or PVC tape would be: Megapoly 30 – 10 phr, SBR 1502 – 40 phr, SP-20 – 30 phr, SMR L – 20 phr, terpene and/or phenolic resin – 115 phr, AO – 1.5 phr, 30-35% solids in toluene.

Use of Megatex in Latex Goods: The aqueous-based Megapoly can be added to latex products to improve their tear and puncture resistance. See chart below:



20 phr Megatex 30 effectively doubles the tear and puncture strength of this latex film. This is accomplished with minor effect on the elongation properties (905% in control; 840% with 20 phr Megatex 30).

deproteinized natural rubber (DP-Poly)

Deproteinized natural rubber or DP-Poly (not to be confused with depolymerized or liquid natural rubber which is known as DPR) is a highly purified form of natural rubber from which most of the ash and proteins have been removed. In addition, hydrophilic materials like inorganic salts are also removed. This results in a natural rubber with unique attributes that are valuable in specialized applications.

Specification Properties (SMR L and CV60 shown for comparison purposes):

	DP-Poly (CV)	SMR CV(60)	DP-Poly (S)	SMR L
Color Limit – Lovibond Scale, max	6.00	8.00*	4.00	6.00
Dirt Content, % wt, max	0.01	0.02	0.01	0.02
Ash Content, % wt, max	0.15	0.50	0.15	0.50
Nitrogen Content, % wt, max	0.12	0.60	0.12	0.60
Volatile Matter, % wt, max	0.30	0.80	0.30	0.80
Mooney Viscosity ML 1+4/100 °C	65±5	60±5	*	*

* Not a specified property

Deproteinized Rubber comes in two forms: standard (S) and controlled viscosity (CV) that would parallel SMR L and CV(60) as shown above. While some of the characteristics of the DP-Polys can be seen in the specifications, the important functional differences are summarized here:

- The removal of the non-rubber constituents (rhc of the DP-Polys is about 96% vs 93% for regular rubber grades) provides much lower water absorption in cured parts. Parts exposed to water, acids and bases exhibit less swell and deterioration. This property can be important to hydraulic mounts, marine parts, pump stators, electrical parts, and tank linings. Prior to curing, the rubber is also less sensitive to moisture pick-up resulting in more consistent cure times as well as consistent modulus development upon cure. This can be critical to precision parts.
- The higher rubber hydrocarbon content also improves long-term properties like creep and stress relaxation**. This is especially noticeable when a soluble cure and activation system is used. These attributes are important to bridge pads, earthquake building mounts, shock absorbers, anti-vibration parts, bearings, and joint rings.
- Low protein and low antigen content are useful in medical and pharmaceutical applications, stoppers, syringes, medical adhesives, baby pacifiers and nipples, and food contact articles. The low nitrogen content potentially results in less nitrosoamine generation in the cured rubber.

- Low dirt and light color are useful for bright colors and transparent items.
- The DP-Polys have a much lower tendency to crystallize compared to regular natural rubber. Most natural rubber users (especially in colder climates) have experienced crystallized raw natural rubber when exposure to cold makes rock-hard bales of rubber. While this is a reversible phenomenon through hot rooms or extra mixing, it can cause fluctuations in the mix quality. It is theorized that the fewer non-polymer materials in the DP rubber provides fewer sites for crystals to nucleate and thus slows crystal formation. This resistance to crystallization carries over to cured parts. Normally, natural rubber crystallization resistance is achieved through high sulfur cures. Parts like bridge pads that require long-term compression set and stress-relaxation resistance as well as crystallization resistance shouldn't be made with high sulfur cures. Use of deproteinized rubber allows low sulfur cures to be used.

**Creep and stress relaxation are really two sides of the same coin. Creep is the further deformation, with time, of a rubber part under stress (beyond the immediate deformation). Inversely, a rubber part under constant strain or deformation will exhibit a reduction in stress over time. This is stress relaxation.

Following is a series of 55 duro natural rubber compounds that vary the type of rubber and the type of curing system. The effects of both the deproteinized rubber as well as the soluble EV cure are evident:

Base Compound: Rubber - 100, N762 black – 50, ZnO – 5.0, Antioxidant DQ –2.0
Conventional cure system: Stearic – 2.0, Sulfur – 2.0, CBTS – 0.5
Soluble EV system: zinc 2-ethyl hexanoate – 2, Sulfur - 0.6, OBTS – 1.4, TBTD – 0.6

Polymer Cure	CV60 conventional	DP-Poly CV conventional	CV60 soluble EV	DP-Poly CV soluble EV
Durometer	56	55	54	54
Tensile, MPa	26	26	25	26
Elongation, %	545	555	525	515
Comp set 24/70 ℃	33	27	11	8
Wt Chg in Water 72/100 ℃, %	---	---	2.91	0.66
Resilience @ 50 ℃	82	84	83	86
Stress Relaxation (extension), rate	5.1	3.7	4.3	3.5
Stress Relaxation (compression), %	12.4	10.5	11.7	8.6
Stress Relaxation (thermocyclic**), %	14.0	8.0	7.0	1.0

** Rubber parts cycled through temperature changes (e.g., 20 ℃, 60 ℃, 20 ℃) will exhibit more stress relaxation than the sum of the stress relaxation at each individual temperature. This test result shows the additional stress relaxation caused by temperature cycling and the virtual elimination of this effect by DP-Poly and a soluble cure.

conclusion

Natural rubber continues to play an important role in the rubber industry. It has unique properties of high strength and tear, resilience, dynamic properties, tackiness in its uncured state, and (somewhat depending on the commodity market) an attractive price not tied to the price of oil (remember, NR is a *renewable* resource). Akrochem offers compounders access to a wide line of natural rubber products that can take care of general purpose molded, calendared and extruded goods as well as help solve unusual compounding problems.

AKROCHEM CORPORATION
SEVEN DECADES OF SUPERIOR SERVICE