Precipitated Silica for Rubber Products

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Typical rubber compounds used to anufacture industrial rubber products such as tyres, hoses and conveyor belts contain up to 8 classes of additives. They include curing agents, accelerators, activators, processing aids, antidegradans and fillers. Fillers improve the physical and mechanical properties such as tear, abrasion resistance, hardness and tensile strength. Choice of filler thus has a major influence on the service life, performance and durability of rubber products. Particulate fillers used in rubber industry in general can be classified as “Black” and “Non black” , depending on their origin, the former being produced from petroleum feedstock and the latter from mineral sources. The most important particulate reinforcing fillers being used in rubber industry are carbon black and precipitated silica. Carbon Black historically was the first reinforcing filler used in the tire industry. Since the early nineteen forties, carbon blacks have been complemented by the group of highly active silicas. Technological reasons have long prevented silicas from being used in tyre compounds. Conventionally, carbon black is considered to be more effective reinforcing filler for rubber tyre treads than silica if the silica is used without a coupling agent. Precipitated silicas are traditionally used in shoe soles of athletic footwear, where these white reinorcing fillers give an improved resistance to wear and tear with the option of using all possible colours. The great advantages of light-colored reinforcement vis-a-vis carbon black is the possibility of satisfying practical requirement, whether they be that of shoe soles be non-marking, transparent, or a particular color or whether it be necessary for applications in rubber rice rollers, conveyor belts, transmission belts, hoses, footwear, rubber sheets, railway pads etc. The addition of 20 - 100 parts by weight of precipitated silica to 100 parts by weight of natural or synthetic rubber improves the tensile strength, hardness, tear strength, and abrasion resistance of the vulcanized material. Precipitated silicas are also used as reinforcing agent in silicone rubber, where they replace the more expensive pyrogenic silicas in certain formulations. Precipitated silicas have been used in tire compounds for many years, typically as a minor portion of the filler owing to its hydrophilic nature, in combination with carbon black as the major filler. In the tread area the primary usage of silica has been in large off-the-road tires to promote high tear, cut growth, and chunking resistance. In tire wire compounds silica promotes good brass coated wire to rubber adhesion. Silica is also reported to be used in tire sidewall for increasing tear strength, cut growth resistance and resistance to ozone ageing.

The major breakthrough in silica technology came with the discovery of silane coupling agents. Sulfur functional organosilanes are utilized as coupling agents that modify the surface chemistry of silica and enhance its compatibility and reinforcement capabilities. The fillersystem based on silica and the silane coupling agent in winter tire tread compounds which led to an improvement in winter performance never seen before. Compounds using silica are more elastic and flexible at lower temperatures, allowing better grip and braking during wintry weather. Silanes turned silica into an active chemical reactant in the rubber compound. Another major improvement of the precipitated silica came with development of highly dispersible silica, an innovation that has proven to be a breakthrough for the tire industry. On account of its excellent dispersion capacity, the newgeneration silica has permitted to develop the green tires (replacing carbon black by silica in car tire tread compound) which have a low rolling resistance, improved wet grip and maintained longevity.

Demands for lower rolling resistance, with its resultant reduction in fuel consumption and lowering of combustion gas emissions, created the need for a new balance of tire tread properties that were beyond the capabilities of traditional carbon black !ill er approaches.

Precipitated silicas are manufactured using a wet process that involves chemical reactions and precipitation, achieved by neutralizing a solution of sodium silicate (water glass). The process steps

include precipitation, filtration, washing, drying, milling and granulation, followed by packing and shipping

of the product. The size of the primary particles and the amount of aggregation and agglomeration are determined by the manufacturing processes, reaction conditions, e.g. pH, temperature, concentration and amount of agitation. Precipitated silica thus produced has its use in manifold applications. Among all, the use of precipitated silica as a reinforcing agent in rubber & tires is the largest single application. At present, precipitated silica manufacturers supply products that can be divided into three groups 1.
Products that can be described as first-generation, standard, or conventional (CV) silica.

2. Products belonging to the second generation of silica. Today, such products are frequently termed easily dispersible silica or semi-highly dispersible (SD)silica. 3.The third and latest generation of silica comprises a productgroupcharacterizedbyexcellentdispersion.These products are described as highly dispersible (HD) silica. An easy incorporation of the silica into the rubber mixture and its good dispersion are crucial because they have a considerable effect on the processing costs and on the rubber product's performance. Table 1 indicates some of the rubber grade silicas available from Madhu Silica.

Table 1 : Rubber Grade Precipitated Silica offered by MSPL in Granular Form\

Silica Grade	BET Surface Area, $m^2/_g$	CTAB Surface Area, $m^2/_g$	pH (5% in Water	Loss on Drying,%	Bulk Density, g/l	Type
MFIL-150(G)	125	115	6.9	5.5	333	CV
MFIL-200(G) LG	160	145	6.5	5.5	330	CV
MFIL-200 (G) RG	180	170	6.5	5.5	330	CV
MFIL-200 (G) HG	220	200	6.5	5.5	330	CV
MFIL-210(G)	205	155	6.2	5.5	312	SD
MFIL-125(G)	125	120	6.9	5.5	300	SD
MFIL-100 (G)	115	110	6.5	6.0	300	HD
MFIL-200(HDS-G)	175	170	6.5	6.0	300	HD
MFIL-210(HDS-G)	210	200	6.5	6.0	300	HD

*All corresponding grades are also available in pow:ier and micro-pearl forms.

Highly dispersible silica (HDS) has become the worldwide benchmark, enhancing low rolling resistance and high wet-grip properties when compared to carbon black compounds. HDS, compared to conventional (CV) silica, provides substantially better dispersibility and higher loadability in rubber compounds due to its specific structure. Proper understanding of silica's morphology and surface chemistry is necessary to understand the behaviour of silica in rubber. Characterizing silica morphology include the ratio between the inner and outer surfaces, the size and shape of pores, the absorption capacity, the surface roughness, the primary particle size, the formation of aggregates from these primary particles with the development of siloxane bonds, and the combination of aggregates to form agglomerates held together by van der Waals forces.

However, in recent times synthetic precipitated silicas have also proved to be beneficial to rubber properties, and are replacing blacks in many applications. Partial replacement of carbon black by precipitated silica in rubber formulation (e.g. tread, footwear, conveyer / transmission belt, seal and hoses compounds) is one such example, wherein it has been reported to have reduced rubber compound cost, optimised process-ability and achieved desired end application properties. Table 2 gives an example of such a guideline compound formulation which is commonly used for partial replacement of carbon black by low surface area silica grade, MFIL-1oo(G) in combination with regular surface area grade, MFIL-2oo(G) and where the silica/ black ratio varies from 5/55 to 25/ 35; as seen in the table compound costs decrease in proportion to silica content.

Table 2 : Compound Formulation

SI. No.	Ingredients	PHR				
		C1	C2	C3	C4	C5
1	Natural Rubber	49.50	49.50	49.50	49.50	49.50
2	Poly Butadiene Rubber	50.5050	50.50	50.50	50.50	50
3	Peptiser	0.07	0.07	0.07	0.07	0.07
4	Process Oil	12.00	12.00	13.00	13.00	14.00
5	**Carbon Black**	**55.00**	**50.00**	**45.00**	**40.00**	**35.00**
6	**Precipitated Silica, MFIL-200(G)**	**5.00**	**5.00**	**5.00**	**5.00**	**5.00**
	Precipitated Silica, MFIL-l00(G)		**5.00**	**10.00**	**15.00**	**20.00**
7	Anti-oxidant	2.25	2.25	2.25	2.25	2.25
8	Stearic Acid	2.50	2.50	2.50	2.50	2.50
9	Microcrystalline Wax	1.75	1.75	1.75	1.75	
10	Zinc Oxide	2.60	2.60	2.60	2.60	2.60
11	Soluble Sulphur	1.64	1.64	1.64	1.65	1.70
12	Accelerator	1.03	1.03	1.03	1.05	1.10
	Compound Cost/ Kg {Rs)	**X**	**X_**	**X--**	**X---**	**X----**

A detailed rubber compound properties evaluation based on this partial replacement of carbon black by low surface area silica, in Table 3, also shows its superiority as far as hysteresis, reinforcement and processing characteristics are considered.

Table 3 : Compound Properties

Compound Properties		C1	C2	C3	C4	C5
A	**Cure Characteristics (150 deg C / 30 Min) MOR**					
	ML(lb-in)	2.46	2.47	2.24	2.12	2.33
	MH(lb-in)	15.59	15.91	14.41	13.11	12.72
	MH - ML(lb-in)	13.13	13.44	12.17	10.99	10.39
	TSl (min)	4.6	4.75	5.23	5.8	5.52
	TS2 (min)	5.52	5.2	6.3	7.02	6.82
	Tel0 (min)	4.98	4.75	5.57	5.98	5.55
	Tel5 (min)	5.5	5.73	6.17	6.7	6.35
	Tc25 (min)	6.02	6.25	6.77	7.48	7.23
	TcS0 (min)	7.07	7.22	7.87	8.77	8.63
	Tc90 (min)	11.65	11.47	12.45	13.77	13.47
B	**Mooney & Mooney Scorch**					
	Mooney@ 135	51.66	52.24	49.06	49.13	53.29
	MS@135					
	ts	12.34	12.75	13.79	1457	13.99
	t10	13.2	13.66	14.87	15.9	15.31
	t35	14.6	15.08	16.57	18.04	17.54
C	**Dispersion Rating of Cured Sample, lOOX Magnification, G Scale**					
	x	10	10	10	10	9.5
	y	9.5	9.5	9.5	9	9

D	Unaged Physical Properties (cure 150c/30m)					
	M100 (Mpa)	1.91	1.84	1.73	1.53	1.31
	M200 (Mpa)	4.54	4.2	4.19	3.26	2.67
	M300 (Mpa)8.61	8.13	8.13	6.16	5.01	
	TS (Mpa)	21.7	21.04	22.4	20.95	20.98
	EB(%)	592	580	608	678	754
	Abrasion loss (mm3)	122	116	118	128	131
	Hardness (Sh-A)	61	61	61	57	56
	Work up to break (J/mm2)	1.38	1.27	1.42	1.46	1.6
	Tear Strength (N/mm)	85	78	84	80	79
	Tear Energy (J)	21.35	19.73	19.04	19.77	22.66
E	De-Mattia Cut Growth Resistance: Samples Cured at 141.7 deg C for 60 min					
	Crack Length after SK Cycles	11.7	11.9	10.5	10.3	9
	Crack Length after 10K Cycles	17.5	18.4	16.3	17.1	13.3
	Crack Length after 25K Cycles	21.9	22.6	21.5	22.1	20.3
F	Dynamic Mechanical Properties (cure 150 C / 30 m) : 10 hertz, 0.25%, dynamic strain					
	Storage Modulus at 60 degC (Mpa) rr-	14.9	13.3	14	11.1	10.3
	Loss Modulus at 60 degC (Mpa) E”	2.44	2.1	2.13	1.77	1.7
	Tan delta at 60 degC 0.164	0.159	0.152	0.159	0.165	
	Loss Compliance at 60 degC (Mpa-1)	0.0108	0.0115	0.0106	0.0139	0.0156

This highly dispersible, low surface are silica grade, MFIL-10o(G), is specially introduced for higher load-ability, partial replacement of carbon black in the formulation to prove its feature in mechanical rubber goods. As demonstrated, around 10 to 12 phr replacement of carbon black by silica in compound formulation woks well and thus reducing compound cost is gaining considerable attention in rubber industries.

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