TECHNICAL UPDATE

CRAY VALLEY

Cleartack® W Resins for Tire Tread Compounds

BENEFITS

- Compatible with a variety of common elastomers
- Wide selection of softening points and glass transition temperatures
- Low molecular weight
- Low viscosity
- Excellent process aid, diluent, tackifier, and compatibilizer
- Colorless
- Low odor
- Non-reactive and hydrophobic character

TARGET MARKETS/ APPLICATIONS

- Tire tread compounds
- Other rubber compounds

ADDITIONAL INFO

- SDS/TDS: Cleartack® W

Introduction

Cleartack® W-Series resins are "water white" resins manufactured from pure aromatic monomers. Colorless and low odor, these have been typically used as tackifying and reinforcing resins in adhesives. They are now finding increased use as additives which improve the wet traction properties of solution styrenebutadiene rubber (SSBR)-based tire tread compounds. The compatibility of these resins in tread elastomers is a function of the molecular weight of the resin. The softening points (SP) and glass transition temperatures (T_g) of the resins increase proportionally with the molecular weight of the resin. Typically, higher T_g resins give improved traction, however an optimum of traction and rolling resistance can be achieved with resins having lower SP and lower T_g.

Materials and Tread Compound Preparation

Cleartack resins of varying SP and molecular weights are shown in Table 1. Carbon black (CB) and silica-filled tread compounds were prepared using a Banbury internal mixer and calendered via a two-roll mill between mixing stages; recipe and preparation conditions are shown in Table 2. Aromatic process oil was used in lieu of resin as a benchmark for comparison.

TotalEnergies

Table 1: Cleartack W Pure Monomer Resins.

Resin	Softening point[1], °C	T_g, °C	Mn, g/mol	Mw, g/mol
Developmental Resin A	52[2]	6.1	341	448
Developmental Resin B	60[2]	19.5	406	592
Cleartack® W85	85	42.4	547	926
Cleartack® W90	90	44.0	575	1032
Cleartack® W100	100	53.2	630	1094
Cleartack® W120	120	77.0	922	1625

[1] Literature value unless noted.
[2] Measured value.

Certified renewable feedstock available

Table 2: Tire Tread Test Formulations and Preparation Conditions.

Carbon black		Silica	
First stage: 60-120 °C / 5 minutes		**First stage: 160 °C / 6 minutes**	
SSBR (Buna® VSL 5025-0 HM, ARLANXEO	75	SSBR (Buna® VSL 5025-0 HM, ARLANXEO)	75
High cis BR (Buna® CB22, ARLANXEO)	25	High cis BR (Buna® CB22, ARLANXEO)	25
Carbon Black N330	80	Amorphous Silica (Zeosil® 1165MP, Solvay)	65
Zinc Oxide / Stearic Acid	3 / 2	Silane coupling agent on CB (Z-6945, Dow Corning)	10.4
Resin*	20	Resin*	20
		Second stage: 60-100 °C / 5 minutes	
		Stearic Acid	1
		6PPD	2
Productive stage: 60-100 °C / 5 minutes		**Productive stage: 60-100 °C / 5 minutes**	
6PPD	1.5	Zinc Oxide	2.5
S / TBBS / TMTD	1.8 / 1.6 / 0.3	S / TMTD / CBS / DPG	1.4 / 1 / 1.7 / 2
Curing: 160 °C / 20 minutes in heated press		**Curing: 160 °C / 20 minutes in heated press**	

* Cleartack W Resins (see Table 1) or Process Oil (Sundex 790, Sun Chemical)

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Tread Compound Evaluation

Tan δ curves of the cured CB and silica-based rubber specimens were obtained via dynamic mechanical analysis (DMA, Q800, TA Instruments) and are shown in Figure 1. It is common to associate a high value of tan δ at 0 °C with improved wet traction, and a low value of tan δ at 60 °C with lower rolling resistance.

Values of tan δ at 0 °C are highest for the CB compounds with resins softening below 90 °C, and for the silica compounds with resins softening below 100 °C. The tan δ curves of specimens with these lower softening point resins are narrow, and along with higher peak height, indicate better compatibility along with improved wet traction.

In general, values of tan δ at 60 °C are lower for both compounds comprising resins with 90 °C SP and below, indicating lower SP resins can provide better rolling resistance.

Figure 2 shows tan δ values at 60 °C vs 0 °C and demonstrates that the best balance of wet traction and rolling resistance can be found with resins of lower molecular weight and SP. This result is counterintuitive, as conventional wisdom suggests higher SP resins would maximize the compound T_g, and thus wet traction. However, compounds containing resins with SPs greater than 100 °C show broader tan δ peaks with decreasing height and no further temperature shift, indicating that compatibility decreases as the molecular weight (and SP) of the resin increases.

Figure 1: Tan δ curves via DMA for CB (left) and silica-filled (right) tread compounds comprising Cleartack W resins of varying SP.

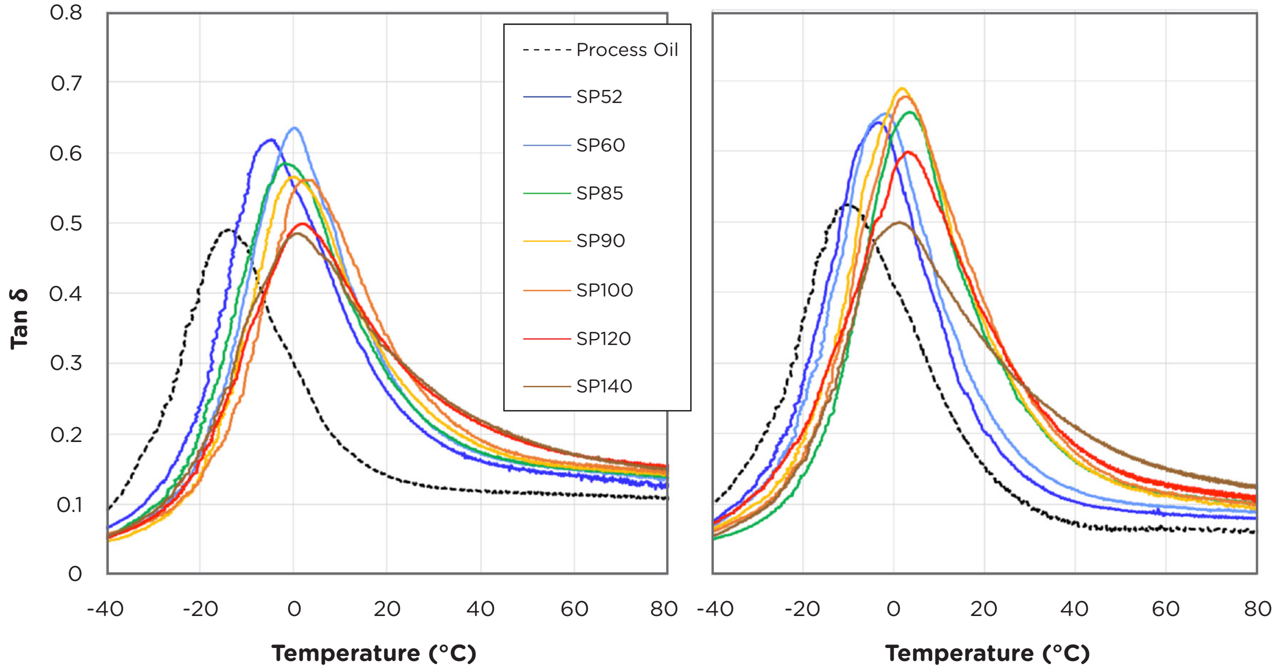
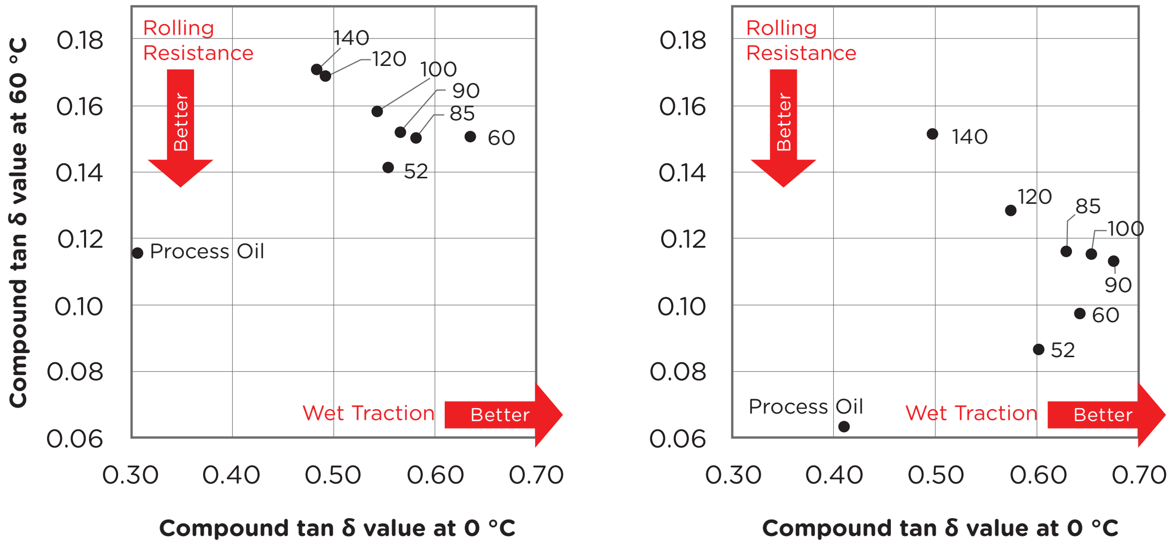


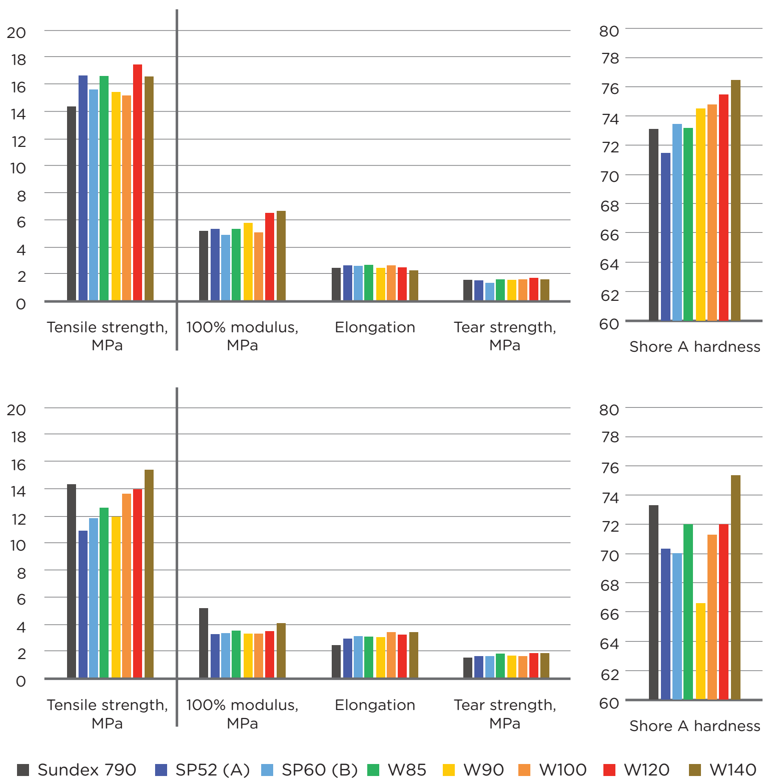
Figure 2: Tan δ values at 60 °C vs. 0 °C via DMA for CB (left) and silica-filled tread compounds comprising Cleartack W resins of varying SP (noted).



Physical Properties

The CB and silica-based compounds were evaluated for tensile, tear, and hardness; results can be seen in Figure 3. For both compounds, tensile strength, modulus, and hardness increase with increasing SP, T_g, and molecular weight of the resin. Tear strength increases slightly as well.

Figure 3: Tensile, tear, and hardness properties of CB (top) and silica-filled (bottom) tread compounds.



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Summary

A balance of high wet traction and low rolling resistance can be achieved with pure monomer resins of low molecular weight due to higher compatibility with an SSBR elastomer system, despite these resins having lower T_gs than higher molecular weight grades. This is unexpected, as generally higher T_g resins maximize the T_g of the compound and thus maximize wet traction indicators. Resins with lower T_g (and molecular weight) can also decrease the tensile properties and hardness of tread compounds, as would be expected with resins of lower T_g. However, by understanding the structureproperty relationships of pure monomer resins, formulations can be designed to acheive specific property requirements.

Appendix: Test Methods

Property	ASTM Method	Comments
Dynamic Mechanical Analysis	N/A	Tension: Film Clamp, 14 Hz frequency, 6 micron oscillation amplitude, 110% force tracking, 0.05 preload force
Tensile Strength and Elongation at Break	D 412	Method A, Die C
Tear Strength	D 624	Method A

About Cray Valley

Cray Valley is a global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings, and other materials. Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacturing, electronics, and other demanding applications.

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