

Tire Tread Performance Modification Utilizing Polymeric Additives

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ABSTRACT

Tire manufacturers have long grappled with the challenge of balancing the conflicting tire attributes of traction, rolling resistance, and treadwear. Improvements to one of these “magic triangle” attributes often comes at the expense of the other attributes. Recent regulations have further increased the pressure on manufacturers to produce optimized tires with minimal performance compromises. In order to meet this challenge, the tire industry is looking to new material systems beyond the traditional tire tread components. Polymeric materials beyond the base elastomers and processing oils used in tread provide opportunities to modify the physical and viscoelastic properties of tread. In this study, various polymeric materials were evaluated as additives in a model tire tread formulation. Hydrocarbon resin, high styrene resin, and thermoplastic styrene elastomers were added to the model formulation at various loading levels and through various addition strategies. The thermal behavior of the raw polymeric additives was characterized utilizing differential scanning calorimetry (DSC). The impact of the polymeric additives on the tread compound was assessed by evaluating the cure kinetics, physical properties, and viscoelastic properties of the experimental compounds. The viscoelastic properties, as measured by dynamic mechanical analysis (DMA), were utilized to predict the relative tire tread performance attributes. Each polymeric additive evaluated in this study was predicted to modify the tire tread performance in a unique way. The potential advantages and challenges of utilizing the polymeric additives to optimize tire tread performance will be discussed.

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INTRODUCTION

The tire industry faces increasing pressure to produce optimized tires that are fuel efficient, safe, and durable. As tire rolling resistance can have a significant impact on vehicle fuel economy, vehicle manufacturers select tires that help achieve fuel economy targets. At the same time, these fuel-efficient tires must meet safety, handling, and durability requirements in order to be selected by vehicle manufacturers. Customers are also being made aware of aftermarket tire performance through regulated tire labeling [1]. However, simultaneously optimizing all tire performance attributes is not an easy task. Improvement in one attribute often comes at the expense of the other attributes; this trade-off is classically described as the “magic triangle” of tire technology.

The rubber compound constituting the tire tread has a significant impact on overall tire performance. Tread compounds are composed of base elastomers like styrene butadiene rubber (SBR) and natural rubber (NR), fillers like carbon black and silica, processing oils, and other additives. As the elastomers, fillers, and oils typically make up the majority of the tread composition, these components are often adjusted to alter the tire tread performance. However, in order to push tire performance further, alternative materials are being investigated to optimize the properties of the tread compound. Various polymeric additives have been cited in literature for improving tread performance. These polymeric materials vary widely in composition and function within the tread rubber compound. Hydrocarbon resins

with varying aromatic and aliphatic character have been used to replace processing oil in the tread and improve the balance between rolling resistance and wet traction [2]. Multiple authors have cited the use of polymer resins derived from styrene and alpha-methylstyrene for increasing wet traction [3, 4, 5]. Sandstrom et al. combined multiple resins with spaced-apart softening points in a tread formulation to increase the predicted tread traction over a wide operating temperature range [6]. Thermoplastic styrene elastomers (TPS) are reported to improve tire handling when substituted for SBR elastomer or added to the tread formulation [7, 8].

Given the wide range of polymeric additives cited for use in tread formulations, the aim of the present study was to evaluate a selection of differing polymeric additives in a model tire tread formulation and compare the relative advantages and disadvantages for optimizing tire tread performance. Three types of polymeric additives were selected and assessed in three evaluations. The first evaluation examined an aliphatic hydrocarbon resin as a replacement for processing oil at three loading levels. The second evaluation examined a high styrene resin as both a substitute for processing oil and as a formulation additive. The final evaluation investigated two types of thermoplastic styrene elastomers as both substitutes for styrene butadiene rubber and as formulation additives. In each evaluation, the polymeric additive was compounded into a model tire tread formulation. The rubber cure kinetics, physical properties, and viscoelastic properties

were evaluated and compared to the control formulation to assess the impact of the polymeric additives on the predicted tire tread performance.

EXPERIMENTAL

Materials

The polymeric additives were evaluated within model tire tread formulations. Table 1 lists the loading of each material in the model formulation in phr, parts per hundred rubber. Two internal model formulations were utilized among the three evaluations, with slight differences in the polymer blend and naphthenic oil loading. The model and experimental compound differences are specified in the discussion section of each evaluation.

Table 1. Model tire tread formulation.

Component	phr
Solution styrene butadiene rubber (sSBR)	75
Butadiene rubber (BR) or natural rubber (NR)	25
N234 carbon black	10
Precipitated silica	60
Silane coupling agent	4.8
Naphthenic oil	23.12 or 33.12
Zinc oxide	1.9
Stearic acid	1.5
Processing aid	2
Microcrystalline wax	2
Antioxidant	0.5
Antiozonant	2
Sulfur	1.5
Sulfenamide accelerator	1.3
Guanidine accelerator	1.5
Total	212.12 or 222.12

Table 2. Polymeric additives selected for evaluation.

Polymeric Additive	Description
Hydrocarbon resin (HC resin)	C5-C9 hydrocarbon aliphatic resin
High styrene resin (HSR)	High styrene resin, 63% styrene content
Thermoplastic styrene elastomer 1 (TPS-1)	Hydrogenated styrenic block copolymer, 30% styrene content, soft block type 1
Thermoplastic styrene elastomer 2 (TPS-2)	Hydrogenated styrenic block copolymer, 30% styrene content, soft block type 2

Table 2 describes the polymeric additives selected for evaluation in the model tread formulations. The loading levels and addition strategies for each polymeric additive are detailed in the discussion section. The hydrocarbon resin was a C5-C9 aliphatic resin, with C5 and C9 describing the carbon numbers of the derivative monomers. The high styrene resin had a high aromatic character, with 63% styrene. Two thermoplastic styrene elastomers, TPS-1 and TPS-2, were evaluated. Thermoplastic styrene elastomers are block copolymers of polystyrene and various polydienes. The TPS materials selected for evaluation had differing hydrogenated polydiene soft blocks. Examples of representative thermoplastic

styrene elastomers include SEB, SEP, SEEP, SEBS, SEPS, SEEPS, SIB, and SIBS, with (S) representing styrene monomer, (E) ethylene, (B) butylene, (P) propylene, and (I) isobutylene.

Processing

Mixing

The experimental tread compounds were prepared by mixing the formulations in a Farrel Model 2.6 BR Banbury mixer according to a three-pass mixing procedure, presented in Table 3. The elastomers, fillers, silane coupling agent, oil, and any polymeric additives were added in the first non-productive pass. After component addition, the rotor speed was increased to raise the batch temperature to 150-160°C to facilitate silanization. The activators, processing aid, wax, and antidegradants were added in the second non-productive pass. The rotor speed was again raised after component addition to achieve a batch temperature of 140-145°C. The sulfur and accelerators were added in the third productive pass. The Banbury fill factor ranged from 68-70% and a ram pressure of 50 psi was used during mixing. After each mix pass, the rubber compounds were sheeted out on a Farrel two-roll mill.

Table 3. Tread compound mixing protocol.

Non-Productive Pass 1		
Start temperature		65.6°C
Starting rotor speed, rpm		65
Fill factor		70%
Ram pressure, psi		50
Mix sequence (min)	0'	Add elastomers
	1'	Add 2/3 silica, coupling agent
	2'	Add 1/3 silica, carbon black, oil
	3'	Sweep
	3.5'	Adjust rotor speed to hold at 150-160°C
Dump conditions		Hold 6' for total mix time of 9.5'
Non-Productive Pass 2		
Start temperature		65.6°C
Starting rotor speed, rpm		65
Fill factor		68%
Ram pressure, psi		50
Mix sequence (min)	0'	Add Pass 1 masterbatch
	0.5'	Add zinc oxide, stearic acid, processing aid, wax, antioxidant, antiozonant
	1'	Sweep
	1.5'	Adjust rotor speed to hold at 140-145°C
Dump conditions		Hold 4' for total mix time of 5.5'
Productive Pass 3		
Start temperature		50°C
Starting rotor speed, rpm		65
Fill factor		68%
Ram pressure, psi		50
Mix sequence (min)	0'	Add 1/2 Pass 2 masterbatch
	0.25'	Add sulfur, accelerators
	0.5'	Add remaining Pass 2 masterbatch
	1'	Sweep
Dump conditions		Hold 4' for total mix time of 5.5'

Cure

Cure kinetics of the rubber compounds were determined utilizing an oscillating disc rheometer (Monsanto Rheometer ODR 2000) according to ASTM D2084 [9]. The time at which the ODR measured 90% of the maximum torque, t_{90} , was used to determine the rubber cure time. Rubber charges were compression molded into 2 mm-thick test plaques with a curing temperature of 160°C and a molding time of $t_{90} + 5$ minutes.

Material Properties

Thermal

The thermal behavior of the raw polymeric additives was characterized utilizing differential scanning calorimetry (DSC). The polymeric materials were tested with a Mettler Toledo DSC1 equipped with a Thermo Scientific EK90 IntraCooler. The samples were first heated from room temperature to 200°C at 10°C/min to remove any thermal history. The samples were then cooled to -50°C at 10°C/min. Heat flow data was reported for a final heating segment from -50°C to 200°C at 10°C/min.

Physical

Rubber tensile and tear properties were evaluated utilizing an Instron dual column testing system equipped with a 5 kN load cell and a long-travel extensometer. Tensile properties were tested according to ASTM D412, Test Method A, Die C [10]. A hydraulic die press was used to die-cut five dumbbell-shaped tensile specimens per compound from 2 mm-thick test plaques. Rubber tear resistance was measured according to ASTM D624, Die B, razor-nicked method [11]. For both tensile and tear test methods, the Instron cross-head speed was 500 mm/min and the gage length was 25 mm. Rubber hardness was measured with a Shore A Durometer according to ASTM D2240 [12].

Viscoelastic

Dynamic mechanical analysis (DMA) was used to evaluate the viscoelastic properties of the rubber compounds. Rubber samples were tested in tension in a Rheometrics Solids Analyzer RSA II. The samples were oscillated at a frequency of 1 Hz through temperature sweeps from -100°C to 100°C.

RESULTS AND DISCUSSION

Hydrocarbon Resin Study

Hydrocarbon resins can be utilized as processing aids and plasticizers in rubber formulations [2, 13]. With the ban on processing oils with high polycyclic aromatic hydrocarbons (PAH), hydrocarbon resins can serve as alternative plasticizers in rubber formulations [14]. In addition, improvements in rubber viscoelastic properties have been cited with the use of hydrocarbon resins as plasticizers [2]. In this study, a C5-C9 hydrocarbon aliphatic resin was investigated as a replacement for naphthenic processing oil at 5, 10, and 20 phr loading levels. Table 4 compares the naphthenic oil and hydrocarbon resin

(HC resin) loading levels for the control compound and 3 experimental compounds. The base polymer system in this study was 75 phr sSBR with 25 phr BR.

Table 4. Hydrocarbon resin study control and experimental compounds.

	Control	5 phr HC resin	10 phr HC resin	20 phr HC resin
sSBR phr	75	75	75	75
BR phr	25	25	25	25
Naphthenic oil phr	33.12	28.12	23.12	13.12
Hydrocarbon resin phr	0	5	10	20
Total phr	222.12	222.12	222.12	222.12

The thermal behavior of the raw hydrocarbon resin is presented in Figure 1. At a heating rate of 10°C/min, a single glass transition temperature is observed around 41°C.

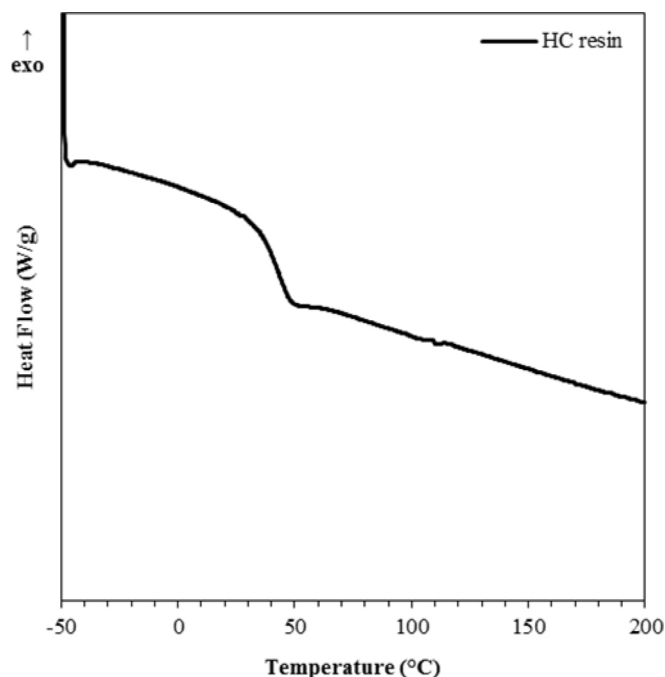


Figure 1. Hydrocarbon resin thermal behavior as characterized by DSC. Resin sample was heated from -50°C to 200°C at 10°C/min.

The cure kinetics of the control compound and experimental HC resin compounds are presented in Table 5. All compounds had similar scorch times (t_{s2}). Replacing naphthenic oil with hydrocarbon resin increased the cure time (t_{90}). The cure time of the experimental compound with 20 phr HC resin was 1 minute longer than the control compound. Replacing naphthenic oil with hydrocarbon resin also increased ML, the minimum torque during cure, which is an indication of uncured compound viscosity and processability. Hydrocarbon resin substitution only slightly increased MH, the maximum torque, which is an indication of cured compound stiffness.

Table 5. Cure kinetics of hydrocarbon resin study compounds.

	Control	5 phr HC resin	10 phr HC resin	20 phr HC resin
ts2 (min)	4.08	4.28	4.24	3.90
t90 (min)	11.15	11.44	11.71	12.16
ML (lb-in)	6.28	7.38	7.69	8.98
MH (lb-in)	45.23	46.61	45.89	47.37

Tensile, tear, and hardness properties of the control and HC resin compounds are presented in Table 6. The physical properties of the compounds exhibited slight variations, but overall, replacing naphthenic oil with hydrocarbon resin did not significantly impact the compound physical properties.

Table 6. Physical properties of hydrocarbon resin study compounds.

	Control	5 phr HC resin	10 phr HC resin	20 phr HC resin
Tensile Strength (MPa)	18.23 (0.75)	18.93 (1.41)	19.79 (0.59)	19.88 (0.59)
Elongation (%)	570.6 (18.8)	525.8 (31.4)	589.4 (13.9)	525.4 (12.8)
100% Modulus (MPa)	1.49 (0.03)	1.56 (0.04)	1.40 (0.01)	1.54 (0.05)
300% Modulus (MPa)	7.08 (0.13)	8.20 (0.12)	6.84 (0.10)	8.51 (0.21)
Tear Resistance (kN/m)	30.78 (3.46)	28.24 (1.38)	29.37 (2.71)	27.59 (1.83)
Shore A Durometer (pts)	59.8 (0.5)	58.6 (0.3)	57.5 (0.3)	58.9 (0.5)

Replacing the naphthenic processing oil with hydrocarbon resin impacted the tread compound viscoelastic properties, as evidenced by the compound tan delta and storage modulus (E') curves presented in Figures 2 and 3, respectively. The tread compound glass transition temperature (T_g) increased linearly with increasing HC resin loading (Table 7). This trend is consistent with the Fox equation, which predicts the resulting glass transition temperature when mutually soluble components are mixed (Eq. (1)):

$$\frac{1}{T_{gmix}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where w_i is the weight fraction of component i in the mixture, and T_{gi} is the glass transition temperature of component i [15]. The increasing substitution of higher- T_g hydrocarbon resin for lower- T_g naphthenic oil increased the overall compound T_g . In addition to the increase in compound T_g , the presence of a single glass transition in the compound tan delta and E' curves suggests that the hydrocarbon resin was compatible with the polymer components in the rubber compound. Compounds with incompatible components do not follow the Fox relationship, and exhibit multiple transitions corresponding with the individual component T_g s.

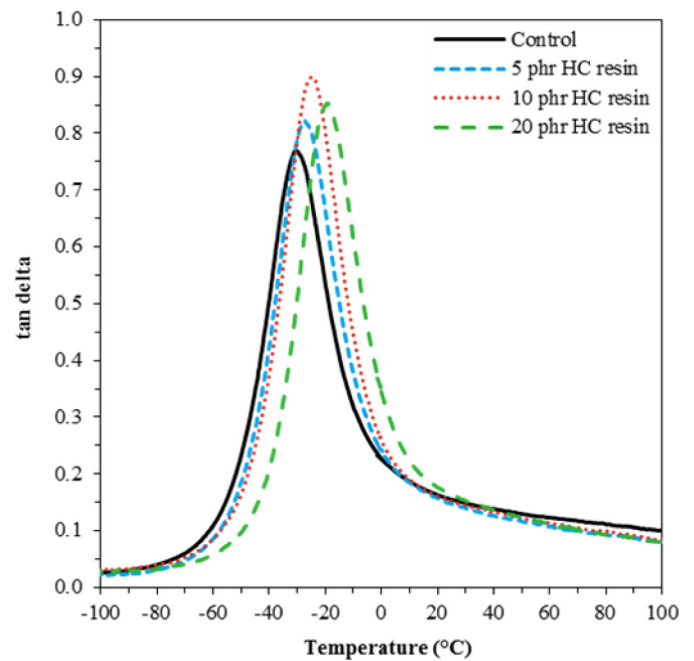
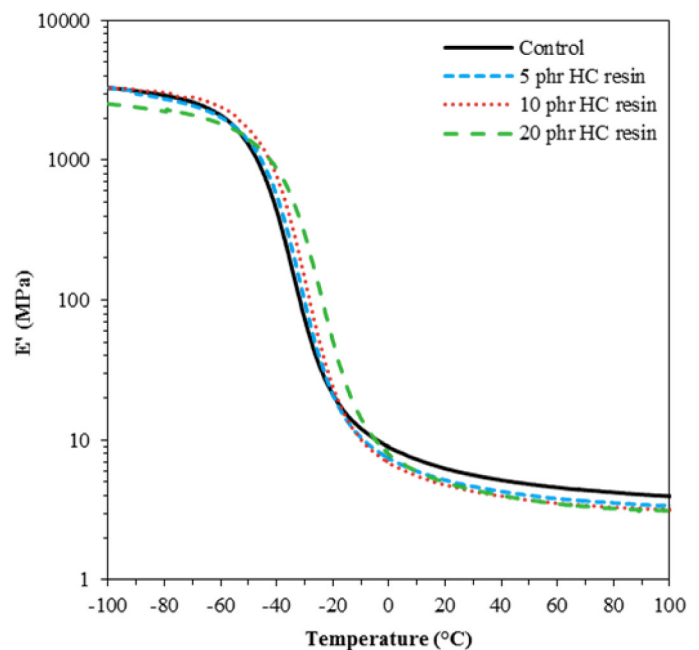


Figure 2. Tan delta vs. temperature curves of hydrocarbon resin study compounds.

Table 7. Glass transition temperatures (T_g) of hydrocarbon resin study compounds.

	Control	5 phr HC resin	10 phr HC resin	20 phr HC resin
T_g (°C), tan delta max	-30.5	-27.5	-25.0	-19.3

Figure 3. Storage modulus (E') vs. temperature curves of hydrocarbon resin study compounds.

In addition to increasing the compound T_g , the substitution of HC resin for naphthenic oil also increased the compound tan delta peak heights and lowered the storage modulus (E') and tan delta values at higher temperatures. This result could potentially indicate a reduction in crosslink density.