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Sources of hysteresis in rubber compounds

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One useful property of cured elastomers is their ability to store energy when stretched, and to release some or most of that energy upon retraction.[1] In most cases, the deformations to which a rubber part is subjected are small with respect to its ultimate deformation at failure.

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In vibration isolation applications, the deformations are periodic, often sinusoidal, and generally less than 25 percent strain. In dynamic applications, dynamic properties are of more interest than static properties or single cycle failure properties such as ultimate tensile and elongation. At normal operating temperatures, rubber is neither purely elastic nor purely viscous in its behavior.

Fig. 1: Relationship between complex, storage and loss moduli.

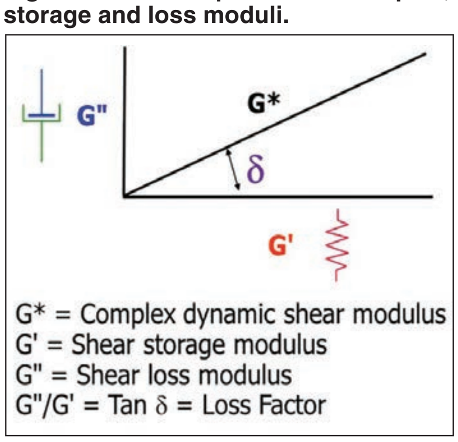


Fig. 2: A dynamic hysteresis loop for a 50 durometer natural rubber.

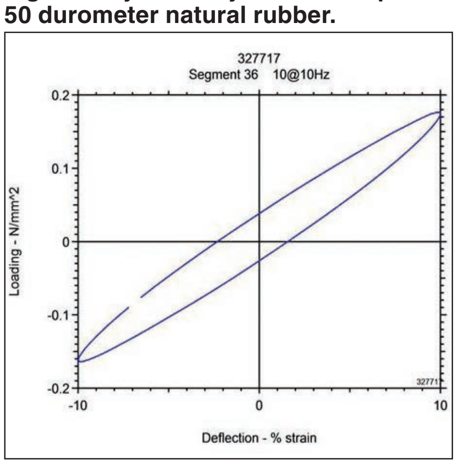


Fig. 3: Double lap shear specimen used for dynamic testing.

Executive summary

Hysteresis is a measure of the amount of energy lost per cycle during deformation of an elastomer. Tangent delta, or the loss factor, is a measure of hysteresis and is the ratio of the loss modulus to the storage modulus. Tangent delta is strongly influenced by the choice of polymer. The addition of carbon black significantly increases tangent delta in rubber compounds. Plasticizers may slightly increase tangent delta but in some cases, they can significantly reduce tangent delta. In natural rubber compounds, the choice of accelerator and the amount of sulfur in the cure system did not have much impact on damping.

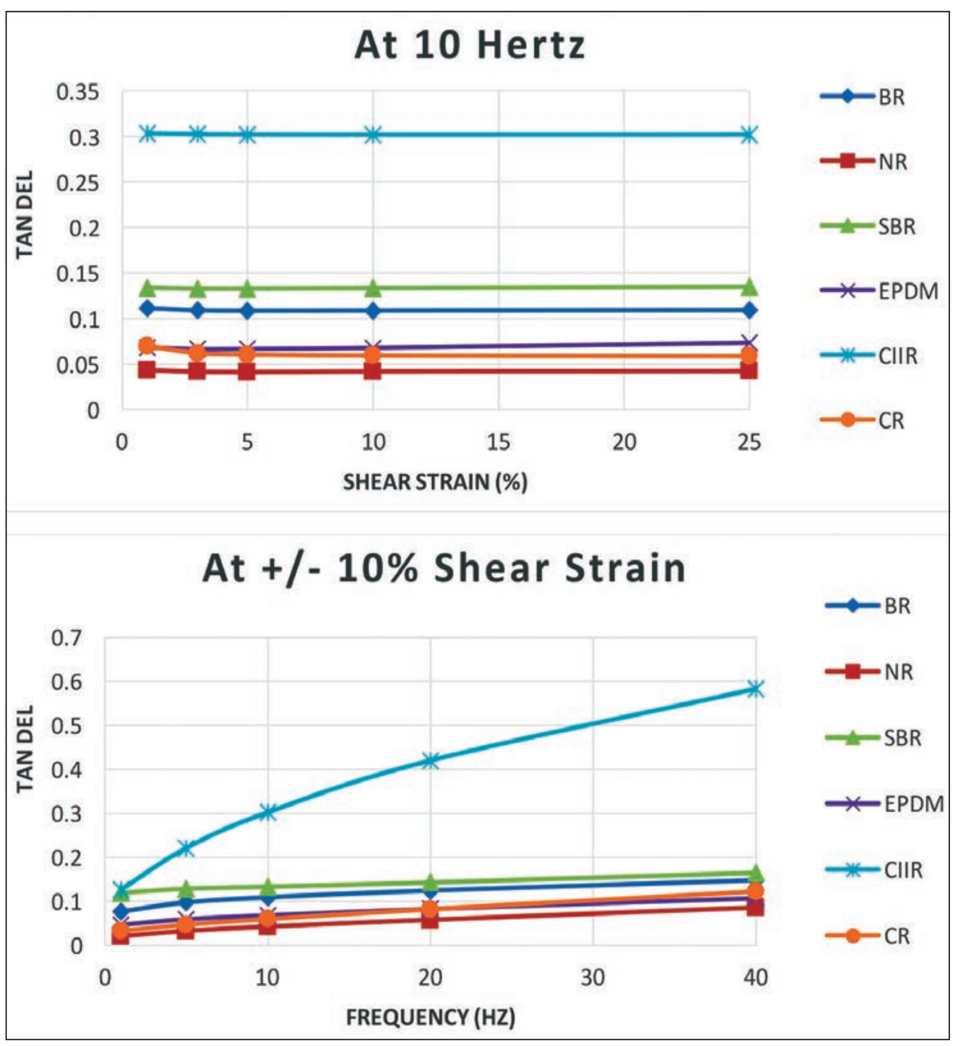
It is convenient to model rubber's behavior using an elastic spring and a viscous damper in parallel. The storage component is characterized by G'—known as the shear storage modulus and the viscous element is characterized by the shear loss modulus G." Rubber has a complex dynamic shear modulus designated as G* (**Fig. 1**).[2,3]

Tangent delta, or the loss factor, is simply the ratio of the loss modulus to the storage modulus. Tangent delta is also referred to as tan delta or tan del.

Hysteretic energy dissipated during the dynamic oscillatory straining of rubber manifests itself in heat build-up. Hysteresis is a measure of the amount of energy lost per cycle of a deformation. Resilience is a measure of the energy returned upon recovery from a deformation compared to the energy required to produce the deformation, so it is the inverse of hysteresis. Damping occurs as a result of hysteresis. High resilience implies low hysteresis while high damping implies high hysteresis.

A dynamic hysteresis loop can be formed by plotting the response force versus the imposed motion. The area within the loop is the energy loss per cycle.[4,5]

Fig. 4: Tangent delta as a function for frequency and strain for general purpose elastomers.



Tangent delta is used to characterize the resilience or, conversely, the damping of an elastomer compound. Higher tangent delta equates to higher damping while lower tangent delta means the elastomer is more resilient.

The characteristics of resilience/damping, glass transition temperature, tensile/elongation and hardness of materials vary greatly with the specific components that make up the compound. The aim of this study was to determine which of the components has the greatest effect on the hysteretic behavior of elastomer compounds.

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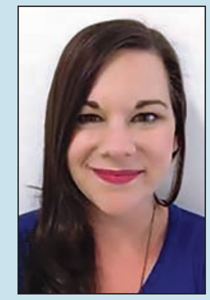
Gates


Halladay

James Halladay has more than 40 years of experience in the rubber industry, focusing on elastomer formulation development. Halladay joined Lord Corp. in 1981 and is currently a senior fellow specializing in compound development for the aerospace industry using both organic and silicone elastomers.

Halladay has authored or co-authored chapters in three books, written more than 30 technical papers, and he holds 18 U.S. patents relating to coatings, adhesives, mechanical designs and elastomer formulations.

Kathryn Gates (Jaglowski) joined Lord in 2013 with a focus on elastomer formulation development. While training under her mentor, Halladay, Gates has gained experience in both organic and silicone elastomer development.

In addition, Gates is skilled in rubber-to-metal bonding applications and processes, and mechanical design.

She graduated from the University of Pittsburgh with a bachelor's in chemical engineering.

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Experimental

All compounds in this study were mixed in a BR1600 lab Banbury and final dispersion was accomplished on a 15x30 cm. two-roll mill. Testing was performed per the following specifications:

Hardness:	ASTM D 2240 Shore A
Tensile, Elongation and Modulus:	ASTM D 412 method A
Dynamic Properties:	ASTM D5992: G' and tangent delta were tested at ±10 percent shear strain, 10 Hz, 21°C. Static modulus G is a 25 percent secant modulus, also tested at 21°C.
Glass Transition Temperature:	Differential Scanning Calorimetry (DSC) on TA Q2000 Model

Double lap shear specimens (**Fig. 3**) were tested for each compound to obtain the dynamic property characterization. The dimensions of the two rubber sections are 5.1 mm thick by 15.9 mm wide by 40.6 mm long.

Glass transition temperatures for the compounds were tested on a TA Q2000 Calorimeter using differential scanning calorimetry (DSC).

Discussion

Polymer

Experiments were run to determine how the choice of polymer affects the damping in an elastomer. A number of general purpose elastomers were compared in simplified formulations, so as to limit the hysteretic influence from other additives. Polybutadiene, natural rubber, styrene butadiene, EPDM, chlorobutyl (CIIR) and polychloroprene formulations were compared to investigate the effect of polymer choice on damping (**Table 1**).

Choice of polymer had a large effect in the amount of hysteresis observed in compounds. By varying the polymer choice from BR, NR, SBR, EPDM, CIIR and CR, tangent delta tested at 10 Hertz and +/-10 percent shear strain ranged from 0.042 for natural rubber to 0.302 for chlorobutyl. Natural rubber was the most resilient material (corresponding to a low tangent delta), followed by CR, EPDM, BR, SBR and CIIR. Tangent delta was plotted as a function of frequency and as a function of strain (**Fig. 4**).

As a function of shear strain, tangent delta was relatively constant for all polymers. As a function of frequency, all polymers except for chlorobutyl showed relatively little change in tangent delta.

Fig. 5: Tangent delta as a function for frequency and strain for oil resistant elastomers.

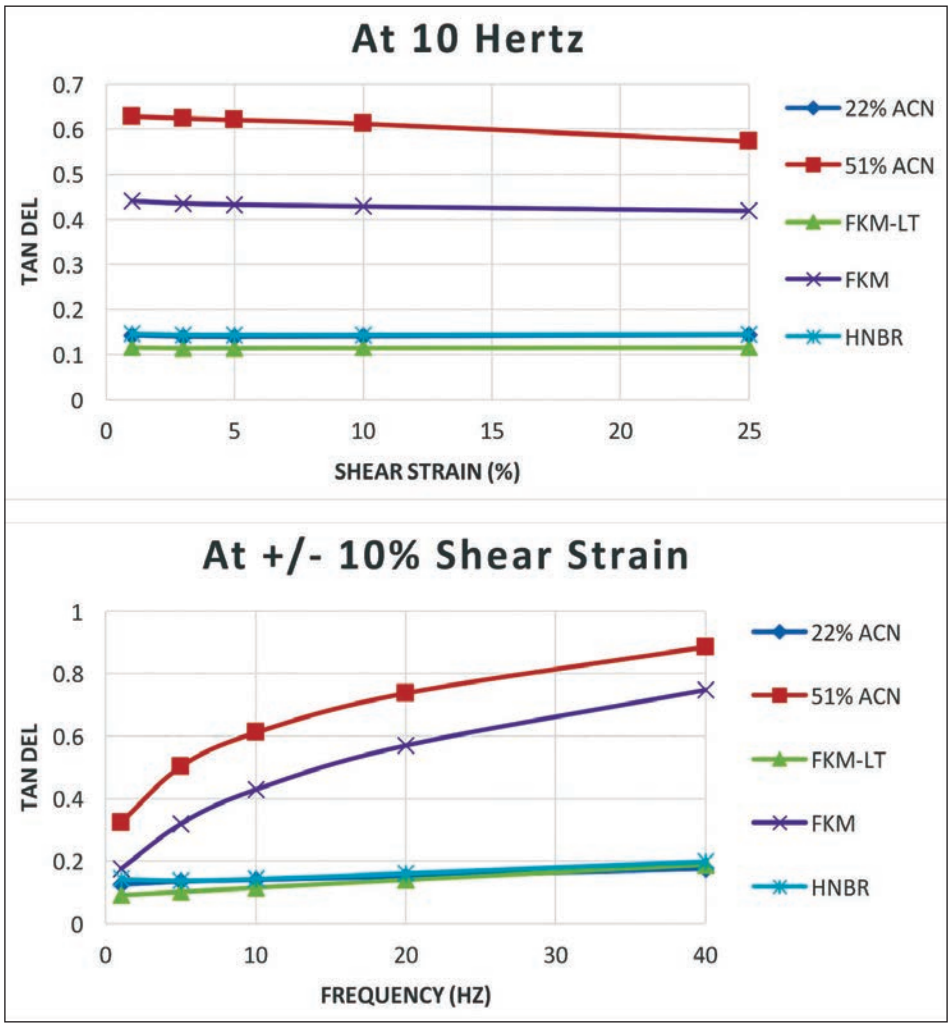

Fig. 6: Effect of carbon black loading on tangent delta.

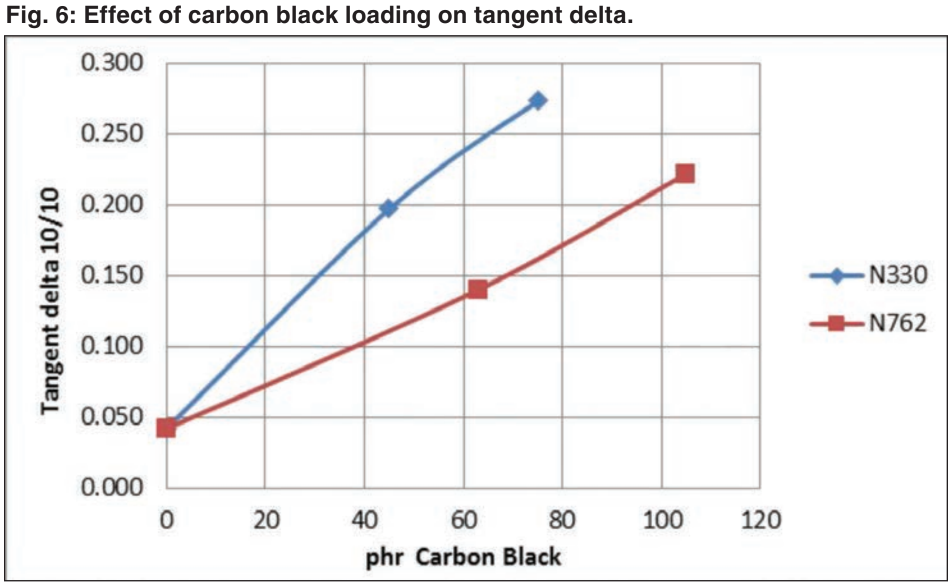

Fig. 7: Effect of type and amount of black on G' and tangent Delta.

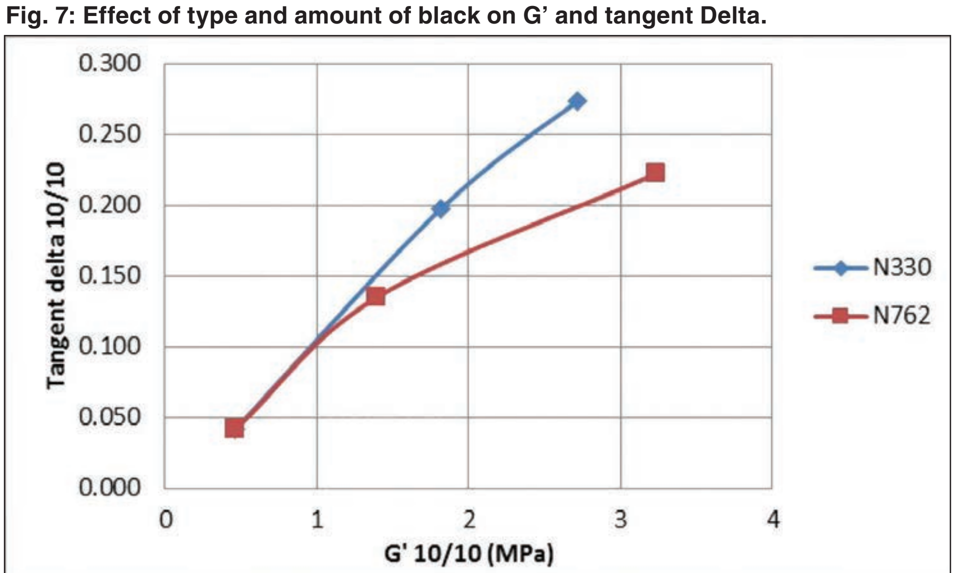

Table 1: General purpose elastomers.

Ingredient	BR	NR	SBR	EPDM	CIIR	CR
Diene 40NF BR	100.0	-----	-----	-----	-----	-----
SCV-60 NR	-----	100.0	-----	-----	-----	-----
Plioflex 1500 SBR	-----	-----	100.0	-----	-----	-----
Vistalon 6505 EPDM	-----	-----	-----	100.0	-----	-----
Chlorobutyl 1066 CIIR	-----	-----	-----	-----	100.0	-----
Neoprene GNA CR	-----	-----	-----	-----	-----	100.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0
Magnesium oxide	-----	-----	-----	-----	0.25	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	0.5
TMQ	1.0	1.0	1.0	1.0	1.0	-----
CBS	1.0	1.0	1.0	-----	-----	-----
Sulfur	2.0	2.0	2.0	1.5	-----	-----
MBT	-----	-----	-----	0.5	-----	-----
TMTD	-----	-----	-----	1.5	1.0	-----
ETU	-----	-----	-----	-----	-----	0.5
PROPERTIES						
Hardness (Shore A)	40	35	39	43	18	44
Tensile (MPa)	0.9	21.1	2.1	1.82	2.4	19.6
Elongation (%)	192	833	482	176	485	940
100% modulus (MPa)	1.1	0.9	0.8	1.30	0.5	1.2
Dynamic properties at 21°C						
G'10/10 (MPa)	0.74	0.47	0.71	0.89	0.39	0.91
Tangent delta 10/10	0.109	0.042	0.133	0.068	0.302	0.059
25% static G (MPa)	0.58	0.44	0.48	0.76	0.27	0.82
Dynamic/static ratio	1.28	1.07	1.47	1.17	1.45	1.10
Glass Transition Temperature (°C)	-85.7	-59.6	-45.8	-45.5	-61.1	-42.0

Table 2: Oil resistant elastomers.

Ingredient	22% ACN	51% ACN	FKM-LT	FKM	HNBR
Nipol 1094-M80 22% ACN	100.0	-----	-----	-----	-----
Nipol 1000X132 51% ACN	-----	100.0	-----	-----	-----
Dyneon LTFE 6400Z FKM-LT	-----	-----	100.0	-----	-----
Viton A401C FKM	-----	-----	-----	100.0	-----
Zetpol 2020EP HNBR, 36% ACN	-----	-----	-----	-----	100.0
Zinc Oxide	5.0	5.0	5.0	-----	5.0
Magnesium oxide	-----	-----	-----	3.0	-----
Stearic acid	1.0	1.0	-----	-----	1.0
TMQ antioxidant	1.0	1.0	-----	-----	1.0
Calcium Hydroxide	-----	-----	-----	6.0	-----
CBS	1.0	1.0	-----	-----	1.0
Sulfur	2.0	2.0	-----	-----	2.0
Peroxide DBPH-50%	-----	-----	2.5	-----	-----
TAIC	-----	-----	1.8	-----	-----
PROPERTIES					
Hardness (Shore A)	41	61	43	50	45
Tensile (MPa)	3.2	14.1	5.9	5.6	22.7
Elongation (%)	367	466	252	308	854
100% modulus (MPa)	1.2	3.1	1.6	1.4	0.9
Dynamic properties at 21°C					
G'10/10 (MPa)	0.89	2.89	0.76	1.45	1.15
Tangent delta 10/10	0.140	0.612	0.115	0.429	0.144
25% static G (MPa)	0.60	1.29	0.56	0.89	0.71
Dynamic/static ratio	1.49	2.24	1.35	1.64	1.62
Glass Transition Temperature (°C)	-44.5	-3.3	-40.5	-15.9	-22.3

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Chlorobutyl, however, showed a significant increase in tangent delta as the frequency was varied from 1 to 40 Hertz.

The study was further expanded to include some specialty oil resistant elastomers (**Table 2**). These included nitrile elastomers (NBR) with low and high acrylonitrile (ACN) content, a hydrogenated nitrile rubber (HNBR) with medium ACN content, and two fluorocarbon (FKM) polymers. One of the fluorocarbon polymers was a copolymer which used a bisphenol cure system. The other was a low temperature terpolymer requiring a peroxide cure system.

Increasing the ACN content in NBR from 21 percent to 51 percent increased tangent delta from 0.140 to 0.612 and it increased the glass transition temperature from -44.5°C to -3.3°C.

Tangent delta was again plotted as a function of frequency and as a function of strain (**Fig. 5**). As a function of shear strain, tangent delta was relatively constant for all polymers. The 22 percent

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Fig. 8: G' as a function for frequency and strain.

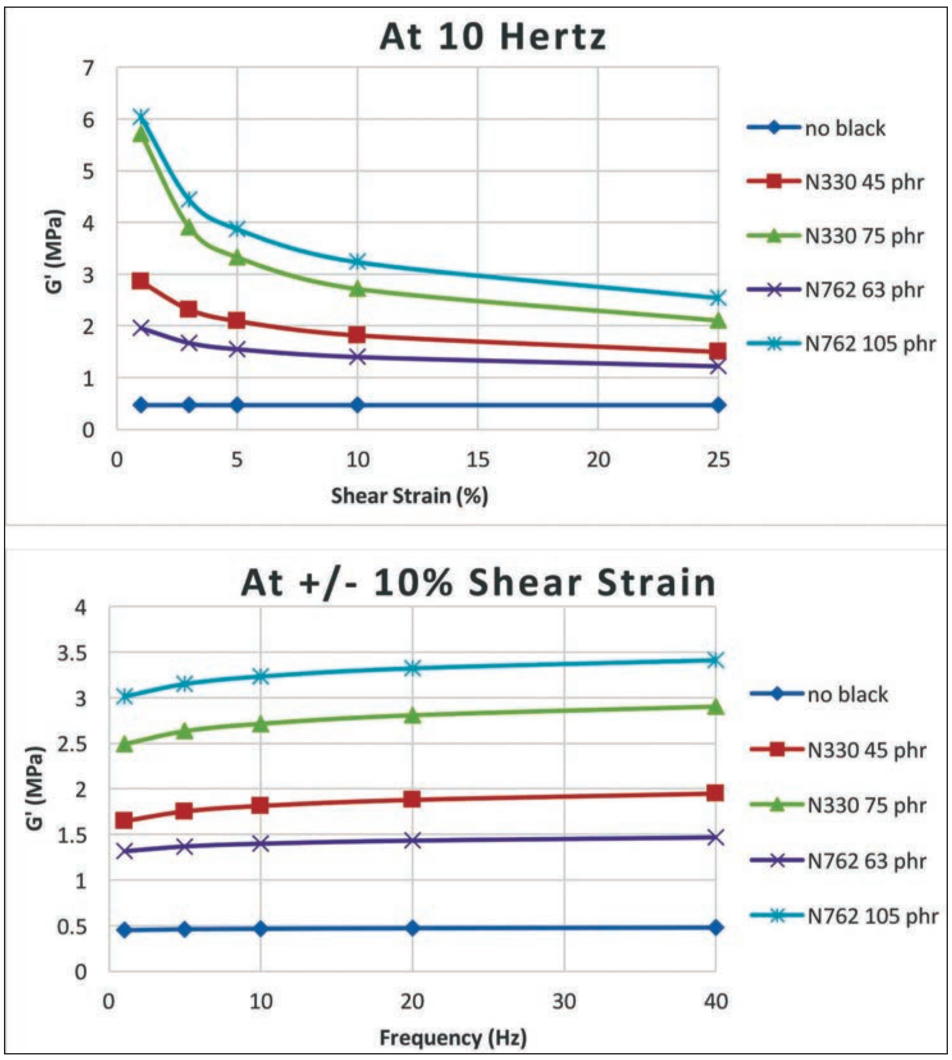


Fig. 9: Tangent delta as a function of frequency and strain.

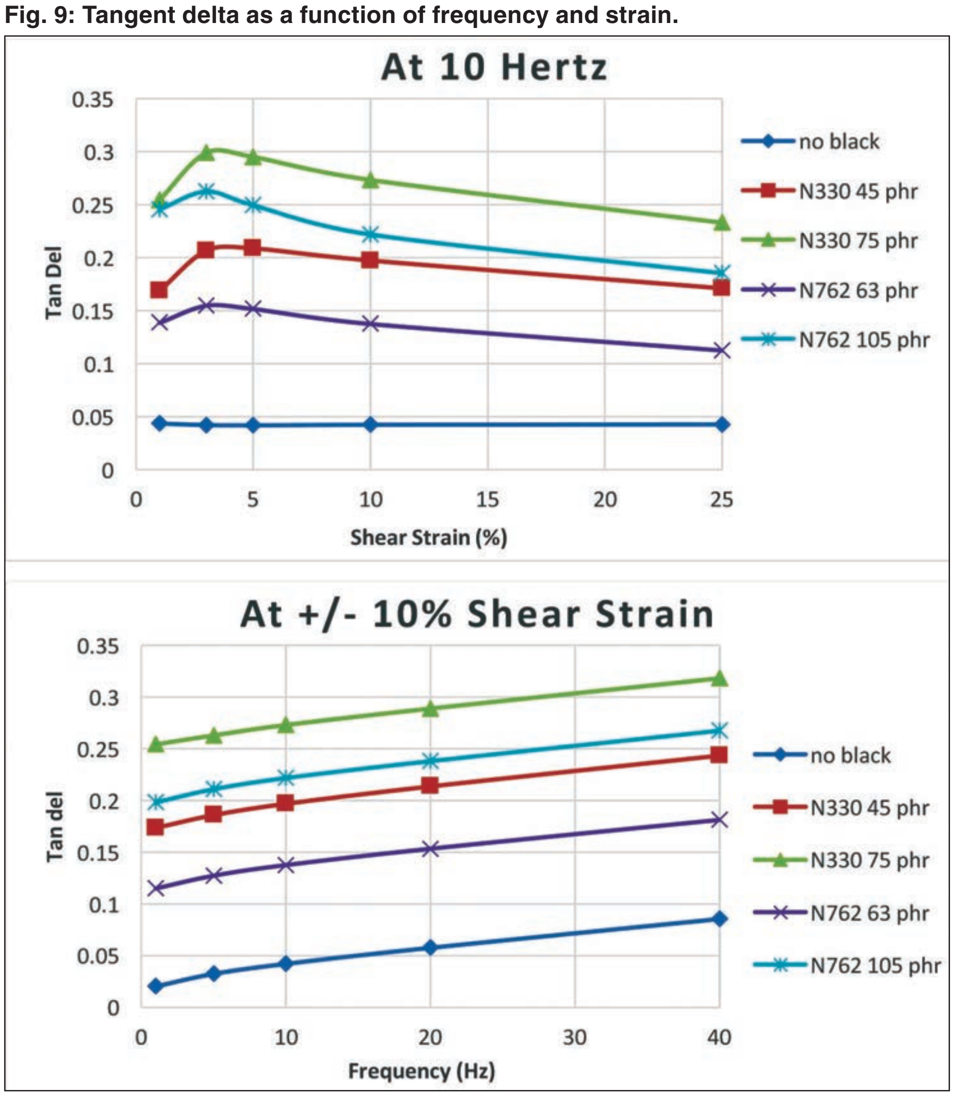


Fig. 10: Tangent delta as a function of frequency and strain.

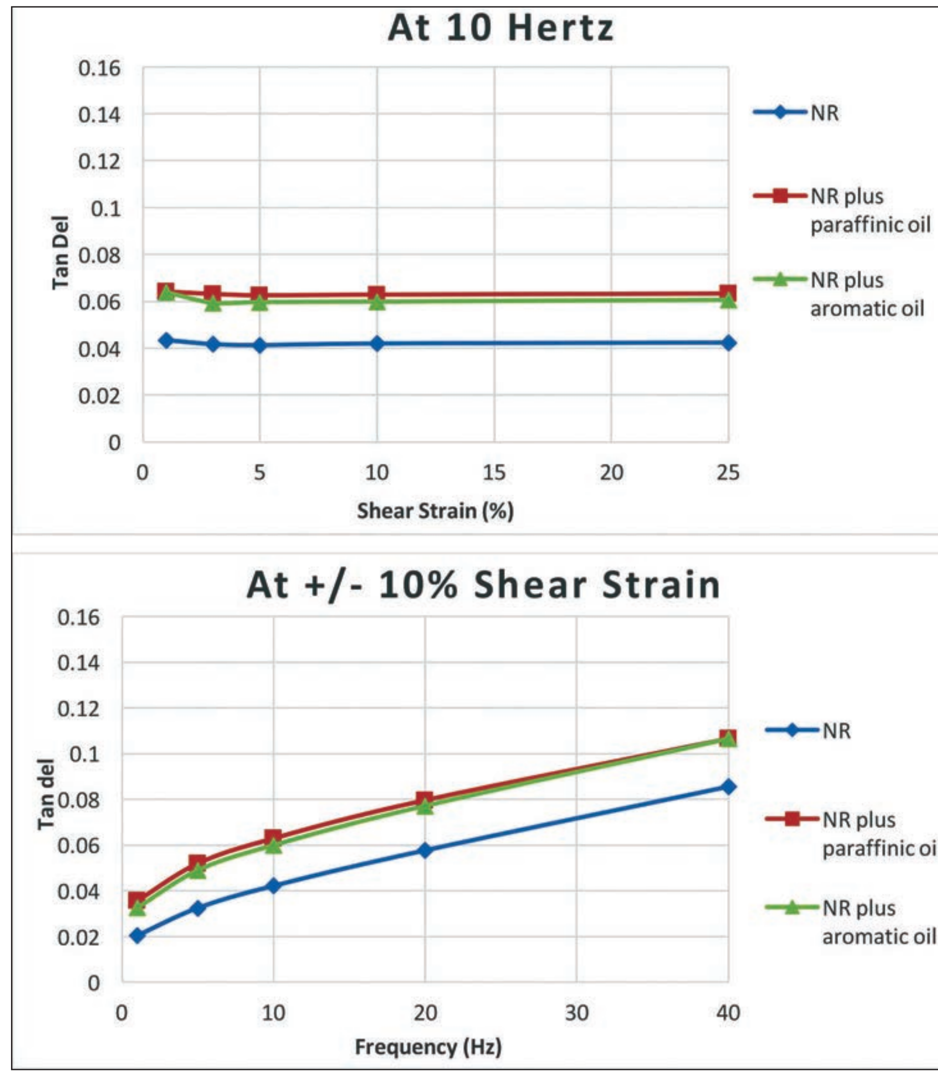
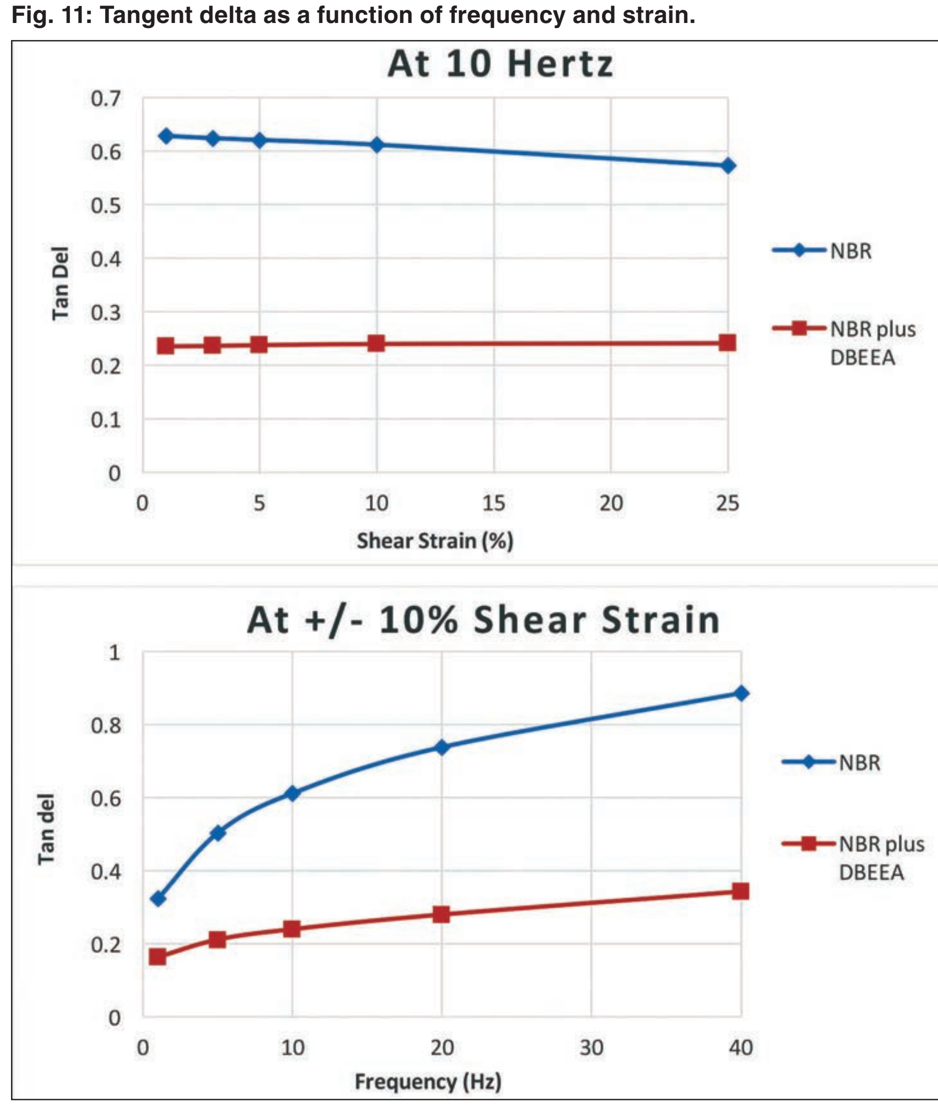


Fig. 11: Tangent delta as a function of frequency and strain.



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ACN nitrile, the HNBR, and the low temperature FKM were all fairly resilient and showed relatively little change in tangent delta as a function of frequency. The 51 percent ACN nitrile and the FKM copolymer were significantly higher damped and showed a measurable change in tangent delta as the frequency was varied from 1 to 40 Hertz.

Carbon Black

Most of the previous formulations are relatively useless without a reinforcing filler. Only strain-crystallizing polymers like NR and CR are used without reinforcement and even these elastomers use reinforcing fillers in compounds to modify the hardness or modulus.

Carbon black is the most commonly used reinforcement in organic elastomers. Because natural rubber is commonly used in dynamic applications, it was used as the basis for comparison of the effect of carbon black as a reinforcing agent. Two different particle-size blacks were each used at two different levels in natural rubber: N762 with a mean particle size of 80 nanometers and N330 with a mean particle size of 28 nanometers (**Table 3**).[6]

Table 3: Carbon black reinforcement.

Ingredient	No black	N330-45	N330-75	N762-63	N762-105
N762 Black	-----	-----	-----	63.0	105.0
N330 Black	-----	45.0	75.0	-----	-----
PROPERTIES					
Hardness (Shore A)	35	58	71	56	76
Tensile (MPa)	21.1	25.0	23.0	23.5	15.5
Elongation (%)	833	894	585	588	305
100% modulus (MPa)	0.9	1.8	3.4	2.3	5.1
Dynamic properties at 21°C					
G'10/10 (MPa)	0.47	1.81	2.71	1.38	3.23
Tangent delta 10/10	0.042	0.197	0.273	0.140	0.222
25% static G (MPa)	0.44	1.32	2.16	1.08	2.38
Dynamic/static ratio	1.07	1.37	1.26	1.27	1.36

Base Formulation: NR CV-60: 100, zinc oxide: 5, stearic acid: 1, TMQ: 1, sulfur: 2, CBS: 1.

The addition of carbon black increased tangent delta, but N330 black increased tangent delta much more than N762 black (**Fig. 6**).

It is well known that N330 increases modulus significantly more than N762 on an equal parts (phr) basis. A plot of tangent delta as a function of dynamic modulus G' shows that N330 increases tangent delta more than N762, even at equal moduli, particularly in higher modulus compounds. (**Fig. 7**).

The particle size and quantity of carbon black also has a significant effect on the overall dynamic response. Addition of either grade of black slightly increases the frequency sensitivity of dynamic modulus G', but both grades greatly increase the strain sensitivity of G' (**Fig. 8**). Addition of black has essentially no impact on the frequency sensitivity of tangent delta but black increases the strain sensitivity of tangent delta, which goes through a maximum between 3 percent and 5 percent shear strain (**Fig. 9**).

Plasticizers

As plasticizers are viscous materials, it seems reasonable to assume that introduction of plasticizer into the formulation will increase the viscous characteristic of rubber and thus increase the amount of damping. To investigate the validity of this assumption, two different petroleum plasticizers were added to NR and a single ester plasticizer was added to a nitrile elastomer (**Table 4**).

Adding 25 phr of either a paraffinic or an aromatic oil to NR significantly decreased the dynamic modulus G' (as expected), but it only increased tangent delta by a nominal amount. Neither plasticizer has much impact on the strain or frequency sensitivity of tangent delta (**Fig. 10**).

Addition of 25 phr of an ester plasticizer to a 51 percent ACN nitrile rubber reduced G' as would be expected, but it significantly lowered both the glass transition temperature (Tg) and tangent delta. The plasticizer had significant impact on the frequency sensitivity of tangent delta and a small but measurable effect on strain sensitivity (**Fig. 11**).

Cure System

The choice of cure system has an impact on heat resistance, fatigue resistance and compression set resistance. Natural rubber finds a lot of use in dynamic applications where it is most commonly sulfur-cured. Sulfur-cure systems generally use elemental sulfur and at least one accelerator.

The common classes of sulfur accelerators include dithiocarbamates, thiurams, thiazoles, sulfenamides, and guanidines. The impact of the accelerator on damping was investigated in NR containing a high sulfur cure system and one accelerator chosen from each of the five main families.

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CBS: N-cyclohexyl-2-benzothiazole sulfenamide
TMTD: Tetramethylthiuram disulfide
ZDMC: Zinc dimethyldithiocarbamate
MBTS: Benzylthiozole disulfide
DOTG: N, N' Di-o-Tolyguanidine

The level of each accelerator was selected in an attempt to obtain a similar hardness (durometer) and 25 percent static modulus (**Table 5**).

Although the accelerator choice had a major impact on cure time, the choice had only a minimal impact on tangent delta in natural rubber (**Fig. 12**).

Robert F. Shaw concluded in a study published in Rubber Chemistry and Technology that the resilience of natural rubber is affected by the sulfur content of the compound.[7] Natural rubber is quite resilient, even in the uncured state. A study was run to determine the effect of sulfur level on the dynamic properties of natural rubber (**Table 6**).

CBS will not cure a natural rubber compound without sulfur so with no sulfur, there is no measurable cure. However, double lap shear specimens were made by transferring rubber into the mold and cooling the mold down before demolding the specimens. The curative in the adhesive was sufficient to bond the uncured rubber to the metal interface so that the specimen could be tested.

Although the dynamic modulus G' dropped off as the sulfur levels were reduced to zero (**Fig. 13**), tangent delta was remarkably constant (**Fig. 14**). This indicated that the loss modulus G" dropped off such that the ratio of G" to G' (tangent delta) is relatively unaffected by the crosslink density.

Other cure systems were investigated in natural rubber. These included high sulfur/low accelerator, low sulfur/high accelerator, a peroxide cure system and a sulfur donor system containing no free sulfur (**Table 7** and **Fig. 15**). Again, there was relatively little difference in tangent delta in natural rubber based on the choice of cure system.

Conclusions

Hysteresis is a measure of the amount of energy lost per cycle during deformation of an elastomer. Tangent delta, or the loss factor, is a measure of hysteresis and is the ratio of the loss modulus to the storage modulus.

- Tangent delta is strongly influenced by the choice of polymer;
- The addition of carbon black increases damping in rubber compounds. N330 black increases damping significantly more than the N762 black at similar moduli;
- Paraffinic or aromatic plasticizers slightly increase damping in natural rubber. Addition of an ester plasticizer to a nitrile rubber reduces damping along with the glass transition temperature;
- In natural rubber compounds, the choice of accelerator in the cure system had a very large effect on the cure times of the compounds; however, it did not

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Table 4: Effect of plasticizers on tangent delta.

Ingredient	NR no oil	NR paraffinic oil	NR aromatic oil	NBR no oil	NBR DBEEA
5CV-60 NR	100.0	100.0	100.0	-----	-----
NBR 51% ACN	-----	-----	-----	100.0	100.0
Sunpar 115 (paraffinic)	-----	25.0	-----	-----	-----
Sundex 790TN (aromatic)	-----	-----	25.0	-----	-----
DBEEA (ester)	-----	-----	-----	-----	25.0
PROPERTIES					
Hardness (Shore A)	35	22	22	61	42
Tensile (MPa)	21.1	14.4	18.5	14.1	5.2
Elongation (%)	833	770	724	466	463
100% modulus (MPa)	0.9	0.6	0.6	3.1	0.9
Dynamic properties at 21°C					
G'10/10 (MPa)	0.47	0.28	0.30	2.89	0.83
Tangent delta 10/10	0.042	0.063	0.060	0.612	0.240
25% static G (MPa)	0.44	0.25	0.27	1.29	0.53
Dynamic/static ratio	1.07	1.12	1.11	2.24	1.57
Tg measured (°C)	-59.6	-64.7		-3.3	-31.8

All Formulations contain: zinc oxide: 5, stearic acid: 1, TMQ: 1, sulfur: 2, CBS: 1.
DBEEA: Dibutoxyethoxyethyl adipate

Table 5: Effect of accelerator choice on tangent delta.

Ingredient	CBS	TMTD	ZDMC	MBTS	DOTG
Sulfur	2.10	2.10	2.10	2.10	2.10
CBS	0.50	-----	-----	-----	-----
TMTD	-----	0.40	-----	-----	-----
ZDMC	-----	-----	0.50	-----	-----
MBTS	-----	-----	-----	1.00	-----
DOTG	-----	-----	-----	-----	1.00
PROPERTIES					
Rheometer @ 153°C (MDR)					
Low torque	1.89	1.89	1.63	1.91	1.83
High torque	10.67	10.86	9.80	9.45	9.70
Tc90 (minutes)	7.90	3.15	3.93	6.69	14.72
Physical Properties					
Hardness (Shore A)	47	50	48	48	48
Tensile (MPa)	25.8	24.2	26.1	25.8	24.1
Elongation (%)	560	515	615	565	530
100% modulus (MPa)	1.9	2.1	1.4	1.8	1.8
Dynamic properties at 21°C					
G'10/10 (MPa)	1.08	1.10	0.94	1.01	1.07
Tangent delta 10/10	0.095	0.093	0.095	0.102	0.105
25% static G (MPa)	0.89	0.91	0.78	0.83	0.88
Dynamic/static ratio	1.21	1.20	1.20	1.23	1.22

Base Formulation: NR CV-60: 100, zinc oxide: 5, stearic acid: 2, TMQ: 1, IPPD: 1, N762 black: 40, naphthenic process oil: 5.

Fig. 12: Effect of accelerators on tangent delta.

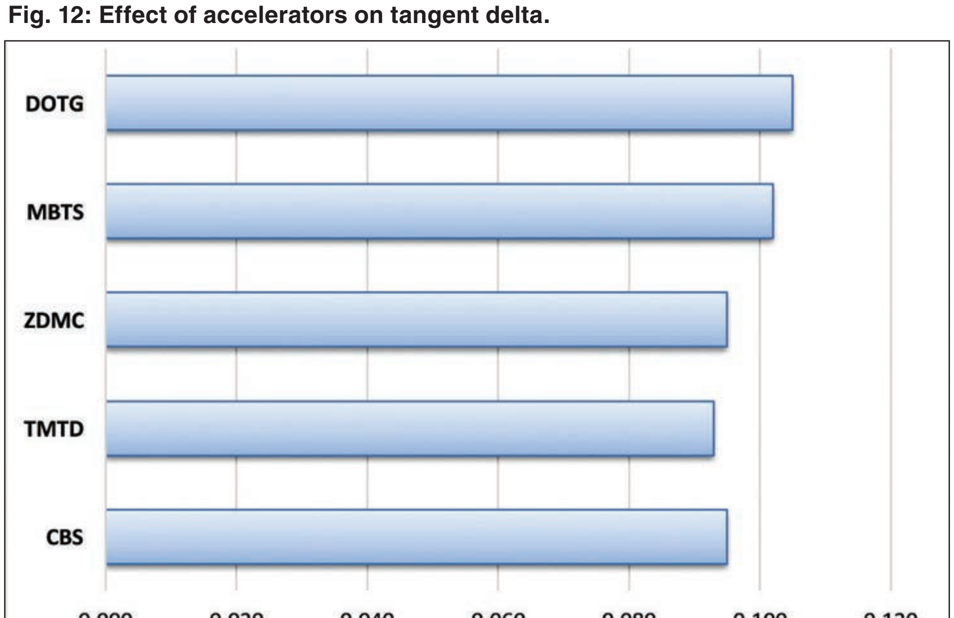

Fig. 13: Effect of crosslink density on dynamic modulus G'.

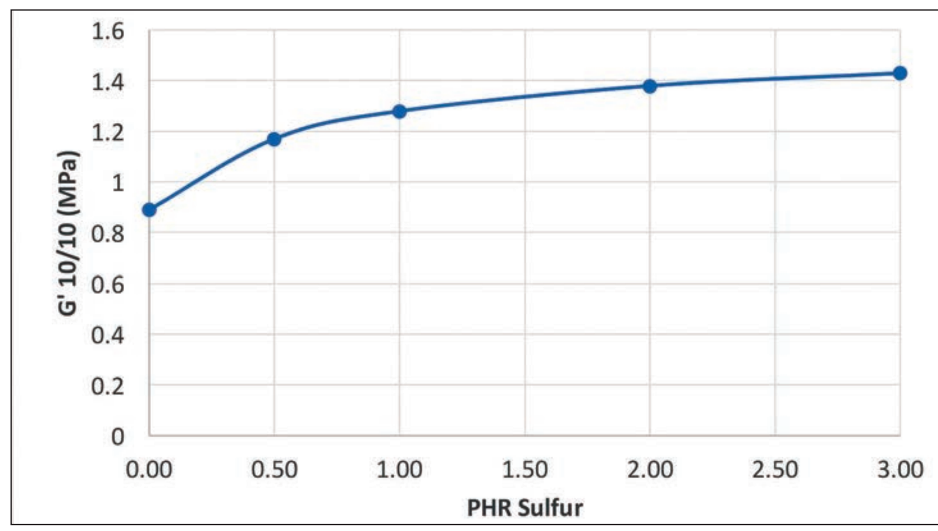

Fig. 14: Effect of crosslink density on tangent delta.

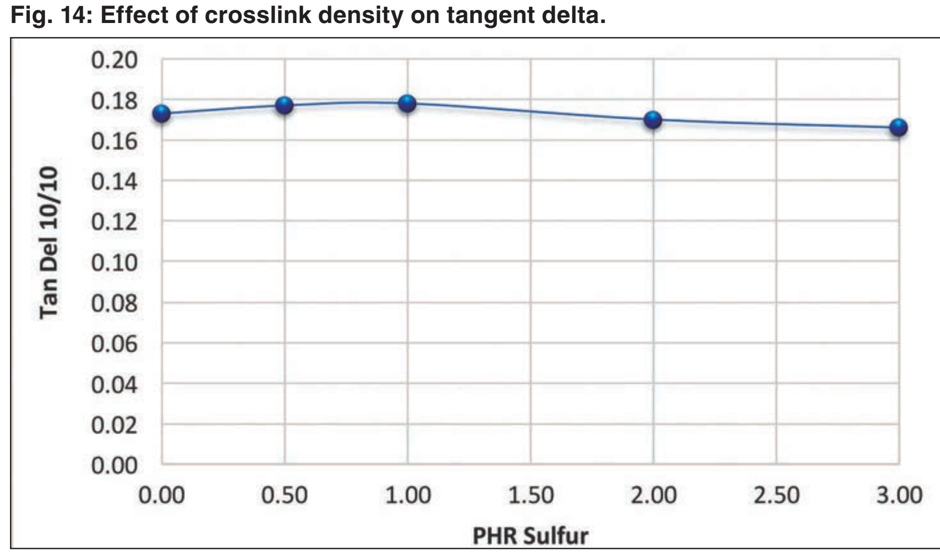

Fig. 15: Effect of cure system on tangent delta.