

Technical

Shelf age-stiffening in high-diene elastomers

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Shelf age-stiffening refers to the progressive modulus increase that is observed in elastomeric products that have been stored at room temperature or at a slightly elevated temperature.

Heat aging refers to the increase in stiffness observed when elastomeric parts are exposed to temperatures significantly above normal storage temperatures. There is no formal line of demarcation between shelf age-stiffening and stiffening due to heat aging.

TECHNICAL NOTEBOOK

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Both phenomena have been observed in high diene elastomers including natural rubber (NR) and polybutadiene (BR), and heat aging is a well known phenomenon in the rubber industry at large.

The typical formulations used in tires and in many aerospace and industrial bonded elastomeric mounts are susceptible to age-stiffening.

The elastomer formulations that impart the best combination of fatigue resistance, low damping and good low-temperature performance (i.e. unsaturated hydrocarbon polymers with sulfur crosslinking systems) also seem to impart a somewhat greater susceptibility to age-stiffening.

Despite technological advances, little is understood about the mechanisms, and potential solutions have remained elusive.

As bonded rubber-to-metal products become more complex and part performance requirements become more demanding, age-stiffening, during both storage and service, poses an increasing problem. It is perhaps of greatest consequence in aerospace products where tight performance specifications, high scrutiny and fatigue-intensive, flight-critical applications are the norm.

With certain elastomeric compounds in sensitive applications, it may be only

Executive summary

High-diene elastomers such as natural rubber and polybutadiene continue to stiffen over time during storage at ambient conditions. As bonded rubber-to-metal products become more complex and part performance requirements become more demanding, age-stiffening, both during storage and service, poses an increasing problem. Investigations were undertaken to determine the cause of this age-stiffening over time.

The project continued over the span of more than six years and determined that shelf age-stiffening occurs in virtually all natural rubber and polybutadiene compounds. An increase in the elastic modulus G' (± 10 percent shear strain, 10 Hz) of 8 to 12 percent in six months is not out of the ordinary for a typical NR/BR blend. Natural rubber generally shelf age-stiffens less than polybutadiene even though polybutadiene is more resistant to high temperature aging than natural rubber.

The only way to study shelf aging is to age parts at room temperature or slightly elevated temperatures. Using higher temperatures and shorter times appears to change the mechanism. Age-stiffening occurs regardless of the choice of cure system, antidegradant system and filler system. The specific causes and mechanisms involved remain undetermined.

a matter of months in storage from the time of manufacture that a product no longer meets the specified spring rate, damping or isolation characteristics.

It was determined as early as 1861 that deteriorated natural rubber always contains combined oxygen and this oxygen causes deterioration. By 1913, it was demonstrated that natural rubber is autoxidizable and that it oxidizes in an autocatalytic manner.¹

Over time, numerous accelerated aging tests have been used by the rubber industry because the deterioration process at room temperature is considered too slow to be practical. By the 1920s, the standard for natural (i.e. room temperature or non-accelerated) aging generally was accepted to be storage in darkness under average room conditions.²

The question of the correlation of artificial and natural aging was considered at a symposium in 1929 and reported in Rubber Chemistry and Technology in 1930. There was no firm consensus, but the general conclusion was that no positive correlation exists between natural aging and accelerated aging.³

An increase in air temperature does not simply increase the rate of degradation in NR. It also changes the efficiency with which oxygen causes chain scission and the balance between oxidative scission and oxidative crosslinking reactions.⁴

Little recent documentation could be found in literature on the subject of age-stiffening during normal storage conditions, perhaps because it is of little concern to much of the rubber industry. For many applications, age-stiffening has very little impact on the performance of parts, regardless of whether it occurs during storage or after a part has been

installed and put in service.

Accordingly, most aging tests are performed at elevated temperatures. The lowest accelerated heat aging temperature used in the ASTM-D2000 specification is 70°C.

Clues to the fact that age-stiffening is a common occurrence can be found in recent literature. Dr. Oon Hock Yeoh published a paper⁵ in 1987 while he was working for the Rubber Research Institute of Malaysia that showed this characteristic in sulfur-cured natural rubber.

He was using natural rubber specimens to validate a new test machine he had built. In the process of characterizing the sensitivity and stability of his test machine, he tested natural rubber specimens at zero, one, seven and 28 days after molding.

Dr. Yeoh's data (Fig. 1) shows a consistent increase in stiffness of a generic natural rubber formulation amounting to approximately 7 percent over a mere 28 days.

Experimental

All compounds in this study were mixed in a BR1600 lab, and final dispersion was accomplished on a 15 x 30 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; and

Dynamic properties: ASTM D5992: G' and tan 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.

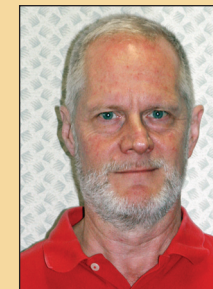
Two double-lap-shear specimens (Fig. 2) were tested for each compound and the results were averaged. The same two specimens were aged in the dark

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Halladay

and then retested after each aging period. The dimensions of the two rubber sections are 5.1 mm thick x 15.9 mm wide x 40.6 mm long.

Discussion The cure system

The cure system is perhaps the most likely part of the formulation to be suspected of being responsible for shelf age-stiffening. Low sulfur cure systems are known to be more resistant to heat aging than normal and high sulfur cures.

Vulcanizates with normal levels of sulfur show increased crosslinking during the early stages of accelerated aging, quite possibly because the polysulfidic sulfur is released to form additional

Fig. 1. Previously published data⁵ showing stiffening of natural rubber.

Moulding ^a	Compression modulus (MPa) as observed on			
	Day 0	Day 1	Day 7	Day 28
1	4.59	4.65	4.85	4.99
2	4.59	4.82	4.87	4.83
3	4.66	4.65	4.97	4.97
4	4.62	4.77	4.77	5.00
5	4.65	4.69	4.75	4.83
Mean	4.60	4.72	4.84	4.92

^a Formulation (phr): 100 NR; 50 SRF black; 5 zinc oxide; 2 stearic acid; 1 IPPD; 1.5 sulphur; 1.5 CBS; cured 40 min at 140°C.

Fig. 2. Double lap shear specimen used for dynamic testing.

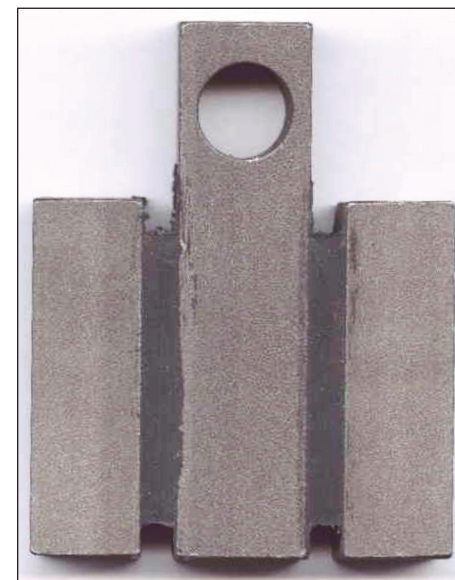
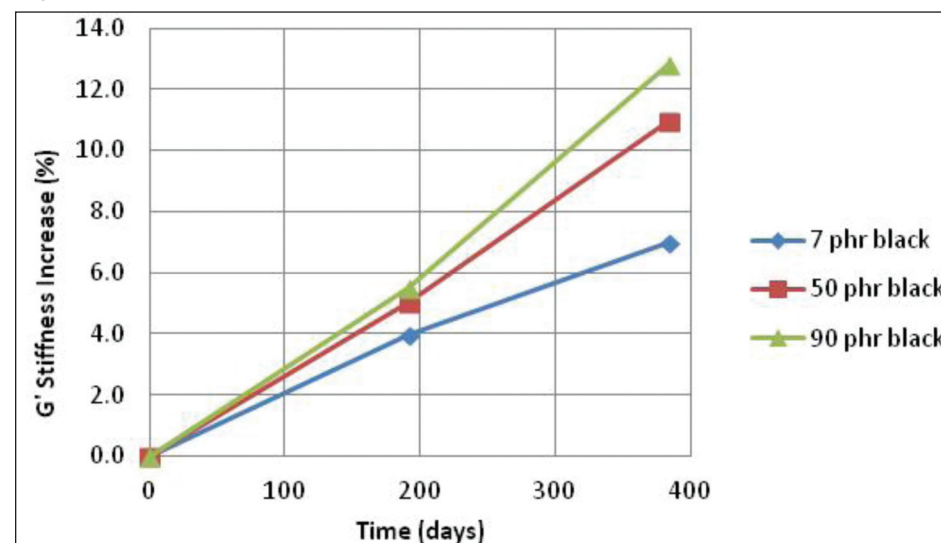

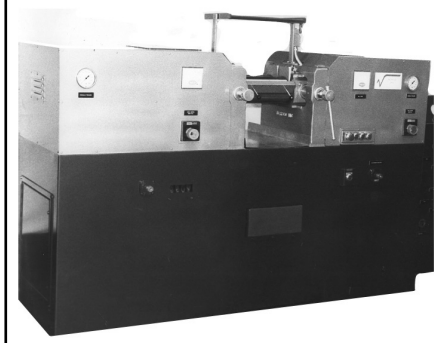


Fig. 3. Effect of carbon black level.





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crosslinks.⁶ There is little reason to doubt that this type of crosslinking could continue at room temperature long after technical cure is complete.

Low, high and very high sulfur cure systems were tested along with an alternative cure system containing low sulfur and a sulfur donor. A soluble cure system (compound 2) was also included in the study.

The soluble cure system is a very low sulfur cure system containing soluble levels of sulfur and accelerator. In the soluble cure system, the primary accelerator is sulfenamide and the secondary accelerator is thiuram. **Table I** shows the results of this experiment.

There is little difference in the amount of stiffening observed with the exception of the soluble cure system, which stiffens about half that of the other systems.

Heat aging is known to be significantly poorer in natural rubber compounds containing high sulfur cure systems. However, compounds 1, 3 and 5 show no difference in shelf age-stiffening despite the significant difference in sulfur content. This suggests that the mechanism in shelf age-stiffening is different than that observed during higher temperature aging, making it difficult to accelerate the aging process.

In order to confirm these results and to determine if sulfur in any form is responsible for age-stiffening, similar testing was run using the low sulfur cure, the soluble cure and a peroxide cure (**Table II**). Small changes were made to the initial formulation in that the soluble soap zinc ethylhexanoate was used in place of the insoluble stearic acid in all formulations, and the level of anti-degradant was increased slightly.

This time, testing was extended to one year to differentiate the results further. **Table III** shows the dynamic property data and the aging data. It is interesting to note that the modulus of the peroxide cure system also age-stiffened similarly to that of the sulfur cure systems.

Antidegradants

Since both the peroxide cure system and all variations of the sulfur cure system show stiffening over time at room temperature, attention was turned to the antidegradant system. Substances that generally reduce or inhibit thermal oxidation are termed antioxidants.

Diene rubber vulcanizates take up oxygen from the air during storage, some of which is chemically bound to the vulcanizate.⁷ The presence of atmos-

pheric oxygen influences thermal degradation of organic materials significantly. It is therefore necessary to recognize that ground state molecular oxygen ³O₂ is capable of interacting with sensitive organic materials, even under very mild conditions.⁸

The following experiment was aimed at determining whether antidegradants affect room temperature age-stiffening, either positively or negatively. TMQ (2,2,4-Trimethyl-1,2-dihydroquinoline polymer) is commonly used in the rubber industry to protect against atmospheric oxygen O₂ while 6PPD (N-1,3-Dimethylbutyl-N'-

phenyl-p-phenylene diamine) is commonly used to protect against ozone O₃. Antiozonant wax (microcrystalline) is generally added to NR and BR formulations to form a physical barrier and impart static ozone protection when it blooms to the surface.

Compound 9 is the same as the low sulfur cure system in compound 6 from **Table II** except that all the antidegradants including the antiozonant wax were removed, and the N326 black was replaced by an even higher level of N330 black. Likewise, compound 10 is the same as compound 9 except that it

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Table I. Effect of different sulfur cure systems on age-stiffening.

Compound	Low Sulfur Cure	Soluble Cure	High Sulfur Cure	Alternative Sulfur Cure	Very High Sulfur Cure
Compound	1	2	3	4	5
Sulfur	1.10	0.70	3.00	1.10	3.75
CBS	1.30	1.40	1.00	-----	0.90
TBTD	-----	0.70	-----	-----	0.20
Post Vulcanization Inhibitor	-----	-----	-----	0.20	0.60
TBSI	-----	-----	-----	1.00	-----
Rhenocure SDT/S	-----	-----	-----	1.00	-----
Physical Properties					
Hardness (Shore A)	68	68	72	67	75
Tensile (MPa)	22.2	21.5	21.5	21.6	17.5
Elongation (%)	453	402	346	432	236
Dynamic Properties at 21 °C					
G'10/10 (MPa)	2.80	2.93	3.49	2.80	3.89
Tan delta 10/10	0.278	0.279	0.252	0.266	0.266
25% static G (MPa)	1.78	1.92	2.38	1.81	2.68
After Aging 6 Months @ 21 °C					
G'10/10 (% change)	12.1	6.9	12.5	10.0	12.3
25% static mod. (% change)	13.3	7.7	13.1	11.6	12.1

Formulation: 50 NR; 50 BR; 5 zinc oxide; 1 stearic acid, 1 TMQ; 1 6PPD; 2 antiozonant wax; 70 N326 black; (soluble cure system contains 1.5 phr zinc ethylhexanoate in place of 1 phr stearic acid)

Post Vulcanization Inhibitor: N-(cyclohexylthio) phthalimide
 Rhenocure SDT/S: 70% active Dialkyldithiophosphate polysulfide
 TBSI: N-t-butyl-2-benzothiazole sulfenamide
 TBTD: Tetrabutylthiuram disulfide
 CBS: N-cyclohexyl-2-benzothiazole sulfenamide

Fig. 4. Shelf age-stiffening of an NR/BR blend at 21°C.

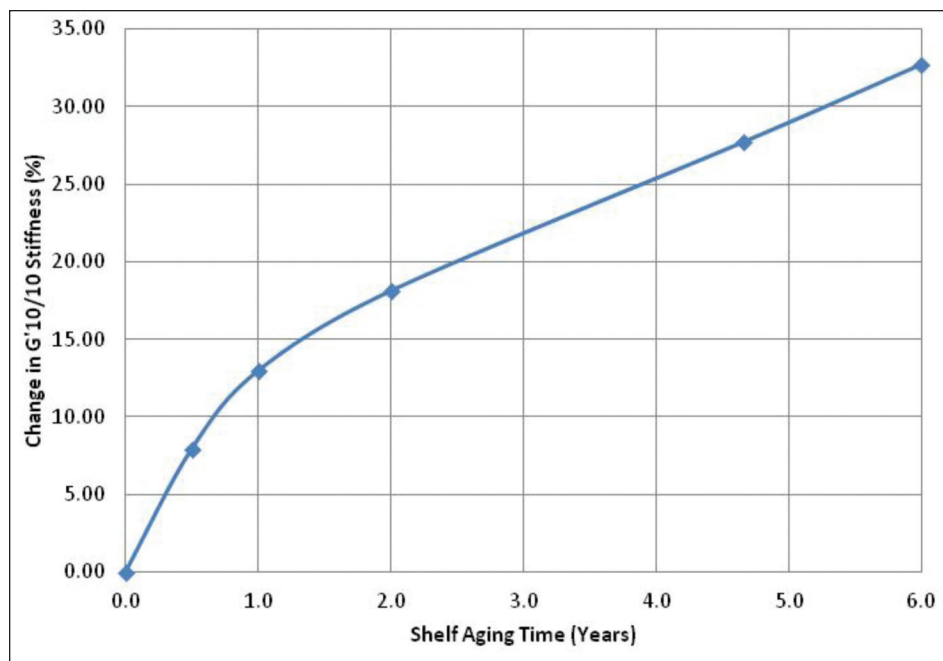


Table II. Formulations.

	Compound		
	6 Low sulfur	7 Soluble	8 Peroxide
Natural Rubber	50.00	50.00	50.00
Polybutadiene Rubber	50.00	50.00	50.00
Zinc oxide	5.00	5.00	5.00
Zinc ethylhexanoate	1.50	1.50	1.50
TMQ antioxidant	2.00	2.00	2.00
6PPD antiozonant	2.00	2.00	2.00
Antiozonant Wax	1.00	1.00	1.00
N326 Black	70.00	70.00	70.00
Sulfur	1.10	0.70	-----
CBS	1.30	-----	-----
OBS	-----	1.40	-----
TBTD	-----	0.70	-----
Dicumyl peroxide (40% active)	-----	-----	6.00

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Elastomers

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uses the soluble cure system from **Table II**. The change in black was to ensure that the N326 black was not part of the problem. Subsequent iterations (Compounds 11 through 13) use the soluble EV cure system, and antidegradants were added in one at a time starting with the antioxidant TMQ, followed by the antiozonant wax and ending with the PPD antiozonant (**Table IV**).

As the previous experiment showed, there is a significant reduction in stiffening when a soluble cure system is used in the NR/BR blend. Although the differences observed with the progressive addition of antidegradants are small, there is still a pattern of increasing the stiffening slightly. The addition of antioxidant or antiozonant is well known to retard stiffening at elevated temperatures (classic heat aging), but it has either no effect or may slightly increase stiffening at room temperature.

A key implication is that there may be different aging mechanisms involved. Studies of shelf age-stiffening must be conducted at relatively ambient temperatures in real time rather than being accelerated by significantly increasing temperatures and shortening time as is commonly done in the rubber industry.

The term "antioxidant" covers a number of classes of chemical compounds including hindered phenols, secondary aromatic amines and other miscellaneous chemicals.

It is well known that synergistic effects are often observed in antidegradant systems where blends can be more effective than single ingredients. Starting with an antidegradant system similar to that used in compound 13 and the low sulfur cure system from Compound 6, different antioxidants or antiozonants were added in combination (**Table V**).

In addition to hindered phenols and aromatic amines, a metal thiolate, e.g. the zinc salt of mercaptobenzimidazole, was included in the investigation. The aging was conducted for six months, but the temperature was increased to 40°C to attempt to slightly accelerate the aging effect. This temperature is well within the range that is considered reasonable for storage prior to use.

In no case did adding more antidegradant reduce the shelf age-stiffening, and in most cases, there was a slight increase in stiffening.

This again suggests that shelf age-stiffening does not correlate with high temperature heat aging. It also shows that storage at even the modest temperature of 40°C significantly can impact the stiffness of parts made with blends of natural rubber and polybutadiene.

Carbon black reinforcement

Having eliminated the cure system and the antioxidant system as being the primary cause of shelf age-stiffening, the carbon black reinforcement was the next area of focus. While there is some controversy as to whether fillers such as carbon black show pro- or antioxidant activity, it is plausible that the stiffening might be a function of polymer-filler interaction.

It is well known that there is a slow interaction between uncured silicone polymer and silica filler. It seems reasonable to suspect that something similar might be happening between the hydrocarbon polymer and the carbon black filler, manifesting itself after molding but over such a long period of time as to generally escape notice.

Carbon black has many functional groups on the surface that can react with hydrocarbon polymers. These functional groups can be eliminated through a process called graphitization.

In that process, the carbon black is exposed to temperatures of 2,700°C for 48 hours in a nitrogen atmosphere. Graphitized black is generally unavailable to industry because of the difficult and expensive process by which it is made.

An experimental quantity of graphitized N330 black and some non-graphitized black from the same lot were obtained from Cabot Corp. These were mixed into a 100 percent NR compound containing the soluble cure system of compound 2.

In addition to the regular and graphitized N330 blacks, formulations were made using a large particle-size, low structure N762 black along with a gum stock containing no black.

The specimens were aged for one year in order to get reasonable differentiation between them. Duplicate samples were stored at 21°C both in air and in nitrogen. **Table VI** shows the differences observed for both storage conditions with the different blacks.

The gum stock and the compound with graphitized black show slightly less stiffening in room temperature air, but the amount of stiffening is still significant. Storage in nitrogen appeared to reduce the storage stiffening slightly as well.

The effect of the amount of carbon black in a formulation was investigated using a 50:50 NR/BR blend with a medium sulfur cure system. N326 black was used at three levels ranging from 7 phr to 90 phr. Stiffening was somewhat greater in compounds containing more carbon black (**Fig. 3**).

Polymer

Experiments were run to determine if the choice of polymer had a measurable impact on the amount of stiffening observed. Compounds made with 100 percent polybutadiene are difficult to process, so the comparison was made between 100 percent natural rubber compounds and 50:50 blends of NR and BR. Two different molecular weights of butyl lithium catalyst polybutadiene (35 percent cis content) were compared against a neodymium catalyst polybutadiene (97 percent cis content).

This latter variable was designed to determine if residual catalyst left over from the polymerization process might be contributing to the stiffening or if the stiffening was affected by the molecular weight or cis content of the polybutadiene rubber.

Three different natural rubber polymers were also used in this experiment. CV stands for constant viscosity, and CV-60 is a 60 Mooney viscosity-stabilized natural rubber. Viscosity stabilization is accomplished by the addition of hydroxylamine to the latex before coagulation.

Natural rubber is derived from latex harvested from rubber trees (*Hevea brasiliensis*), and it contains residual plant proteins. Deproteinized natural rubber (DPNR) is produced by treating the natural rubber latex with an enzyme that breaks down the naturally occurring protein into water-soluble residues that are substantially eliminated during coagulation and washing. One DPNR is viscosity stabilized and the other DPNR is not viscosity stabilized.

With the exception of the polymer variations, the rest of the formulation is the same as was used in low sulfur compound 6 from **Table II**.

Table VII shows the effect of these compounding variations. A blend of natural rubber and polybutadiene consis-

tently stiffens more than natural rubber by itself. This is interesting because it is well known that polybutadiene is more resistant than natural rubber to heat aging. It is also known that NR is susceptible to chain scission, which may mitigate the amount of stiffening observed. There is little difference in the shelf age-stiffening between the different grades of polybutadiene or between the different grades of natural rubber.

Acid acceptors and anti-reversion additives

It was also speculated that the shelf age-stiffening phenomenon might be attributable to the formation of acids. Kirchhof showed that when vulcanized rubber oxidizes, a portion of the sulfur forms an acid, which combines with and hardens the rubber,⁹ so the deterioration of physical properties may be largely due to isomerization catalyzed by acid formed in the rubber.

If the stiffening observed at room temperature is caused by acid formation, acid acceptors such as magnesium oxide or calcium hydroxide might reduce or eliminate it. Magnesium oxide and calcium hydroxide were used separately and in combination with each other (**Table VIII**).

Various anti-reversion compounds find use in NR and BR. The anti-reversion agent 1,3-bis(citraconimidomethyl) benzene (BCI-MX) often has been used in natural rubber formulations to minimize reversion and stabilize the compounds against heat.

This was added to compound 30 to see if it had either a positive or negative effect. The formulation is the same as was used in the low sulfur compound 6 from **Table II**. Neither the addition of acid acceptors nor the BCI-MX made a measurable difference in the shelf age-stiffening characteristics (**Table VIII**).

Extended aging tests

Further work was done to see if the age-stiffening continues indefinitely or whether it levels off and approaches an asymptote. Samples stored at 21°C were tested over the course of six years (**Fig. 4**). The increase continues through the entire period with no appreciable change in rate from the end of the first year onward.

Conclusions

Shelf age-stiffening occurs in all conventionally-formulated natural rubber and polybutadiene compounds. The only

Table III. Dynamic properties, initial and aged.

Compound	6 Low Sulfur	7 Soluble	8 Peroxide
Dynamic Properties at 21 °C			
G'10/10 (MPa)	2.60	2.76	2.70
Tan delta 10/10	0.284	0.275	0.248
25% static G (MPa)	1.58	1.80	1.86
After Aging 6 Months @ 21 °C			
G'10/10 (% change)	9.8	5.9	9.9
25% static mod. (% change)	12.5	5.4	8.1
After Aging 12 Months @ 21 °C			
G'10/10 (% change)	13.2	8.0	11.3
25% static mod. (% change)	15.7	7.0	9.9

Table IV. Effect of antidegradants on age-stiffening behavior.

Compound	Low Sulfur 9	Soluble 10	Soluble 11	Soluble 12	Soluble 13
N330 black	85.00	85.00	85.00	85.00	85.00
TMQ antioxidant	----	----	2.0	2.0	2.0
6PPD antiozonant	----	----	----	----	2.0
Antiozonant wax	----	----	----	2.0	2.0
Dynamic Properties at 21 °C					
G'10/10 (MPa)	4.71	5.09	4.74	4.42	4.18
Tan delta 10/10	0.228	0.232	0.246	0.250	0.261
25% static G (MPa)	3.04	3.40	3.17	2.95	2.77
After Aging 6 Months @ 21 °C					
G'10/10 (% change)	7.7	5.1	5.7	6.4	7.5
25% static mod. (% change)	8.8	4.0	4.9	5.1	5.5

Table V: Effect of additional antidegradant on age-stiffening behavior.

Compound	14	15	16	17	18	19
TMQ antioxidant	1.00	1.00	1.00	1.00	1.00	1.00
6PPD antiozonant	1.00	1.00	1.00	1.00	1.00	1.00
Antiozonant wax	2.00	2.00	2.00	2.00	2.00	2.00
Flexamine G	----	1.00	----	----	----	1.00
Flexamine 4L	----	----	1.00	----	----	----
Wingstay L	----	----	----	1.00	----	----
Wingstay S	----	----	----	----	1.00	----
Vulkanox ZMB2/C5	----	----	----	----	----	0.50
Dynamic Properties at 21 °C						
G'10/10 (MPa)	2.64	2.63	2.65	2.61	2.60	2.65
Tan delta 10/10	0.259	0.268	0.263	0.264	0.263	0.276
25% static G (MPa)	1.71	1.76	1.69	1.70	1.70	1.69
After Aging 6 Months @ 40 °C						
G'10/10 (% change)	32.1	38.2	33.5	39.3	34.9	38.3
25% static mod. (% change)	34.7	37.6	38.2	41.3	35.2	41.5
Flexzone 4L:	N, N'-bis-(1,4-dimethylpentyl)-p-phenylenediamine					
Wingstay L:	p-Cresol/dicyclopentadiene butylated reaction product					
Wingstay S:	Styrenated Phenol					
Vulkanox ZMB2/C5:	Zinc-4- and -5-methyl-2-mercaptobenzimidazole					
Flexamine G:	Mixture of N,N'-diphenyl-para-phenylenediamine and complex diarylamine-ketone reaction product					

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way to study shelf aging is to age parts at room temperature or slightly elevated temperatures. Using higher temperatures and shorter times appear to change the mechanism of the aging. An increase in G'10/10 (± 10 percent shear strain, 10 Hz) of 8 to 12 percent in six months at room temperature is not out of the ordinary for a typical NR/BR blend.

Natural rubber shelf age-stiffens less than polybutadiene, even though polybutadiene is more resistant to high temperature aging than natural rubber. There are no observable differences in the age-stiffening characteristics between different grades of polybutadiene or between different grades of natural rubber.

Age-stiffening is affected by both the antioxidant system and the cure system. The addition of antioxidant or antioxidant retards stiffening at elevated temperatures (heat aging) but promotes stiffening at room temperature, which again suggests a change in mechanism of aging. Compounds containing a soluble cure system stiffen less than those with low, normal or high sulfur cure systems. Peroxide cure systems age-stiffen similarly to standard sulfur cure systems.

The choice of the grade of carbon black makes only a minor difference in

the shelf age-stiffening characteristics.

Increasing the amount of carbon black increases the amount of stiffening. Neither acid acceptors (magnesium oxide and calcium hydroxide) nor the reversion inhibitor BCI-MX had a significant effect at reducing the shelf age-stiffening. The specific causes and mechanisms involved remain undetermined.

References

1. Carroll C. Davis and John T. Blake, "The Chemistry and Technology of Rubber," p. 416-417, Reinhold Publishing Corp., New York, 1937.
2. Carroll C. Davis and John T. Blake, "The Chemistry and Technology of Rubber," p. 423, Reinhold Publishing Corp., New York, 1937.
3. Symposium on Aging, Ind. Eng. Chem., vol. 21, p. 1,008-1,020 (1929); Rubber Chemistry and Technology, vol. 3, p. 144-177 (1930).
4. A. D. Roberts, "Natural Rubber Science and Technology," p. 671, Oxford University Press, New York, 1988.
5. O. H. Yeoh, (1987). A Method for the Routine Determination of Compression Modulus of Rubber Vulcanizates, Polymer Testing, 7, 121-136.
6. G. Alliger and I.J. Sjöthun "Vulcanization of Elastomers," p. 139, Reinhold Publishing Co., New York, 1964.
7. Werner Hofmann, "Rubber Technology Handbook," p. 265, Hanser Publishers, New York, 1989.
8. Jan Pospíšil and Peter P. Klemchuk, "Oxidation Inhibition in Organic Materials, Volume 1," p. 4, CRC Press, Inc, Boca Raton, FL, 1990.
9. Carroll C. Davis and John T. Blake, "The Chemistry and Technology of Rubber," p. 420, Reinhold Publishing Corp., New York, 1937.

Table VI. Effect of carbon black type and storage conditions.

	N330 Black	N330 Graphitized	N762 Black	Gum Stock
Natural Rubber	100.0	100.0	100.0	100.0
Zinc Oxide	5.0	5.0	5.0	5.0
Zinc Ethylhexanoate	1.5	1.5	1.5	1.5
TMQ	2.0	2.0	2.0	2.0
6PPD	2.0	2.0	2.0	2.0
N330 Black	50.0	0.0	0.0	0.0
Graphitized N330 Black	0.0	50.0	0.0	0.0
N762 Black	0.0	0.0	75.0	0.0
Sulfur	0.7	0.7	0.7	0.7
OBS	1.5	1.5	1.5	1.5
TBTD	0.7	0.7	0.7	0.7
Dynamic Properties at 21 °C				
G'10/10 (MPa)	1.68	1.72	1.66	0.41
After Aging 1 Year @ 21 °C				
In Air (G' % change)	8.0	6.8	8.8	5.0
In Nitrogen (G' % change)	5.5	5.2	5.8	4.3

Table VII. Effect of polymer on shelf age-stiffening behavior.

Compound	20	21	22	23	24	25
BuLi catalyst (low cis, low MW)	50.00	-----	-----	-----	-----	-----
BuLi catalyst (low cis, high MW)	-----	50.00	-----	-----	-----	-----
Nd catalyst (high cis)	-----	-----	50.00	-----	-----	-----
CV-60 NR	50.00	50.00	50.00	100.00	-----	-----
DPNR (non-CV)	-----	-----	-----	-----	100.00	-----
CV-60 DPNR	-----	-----	-----	-----	-----	100.00
Dynamic Properties at 21 °C						
G'10/10 (MPa)	2.71	2.80	2.83	2.63	2.27	2.38
Tan delta 10/10	0.285	0.278	0.262	0.320	0.280	0.354
25% static G (MPa)	1.68	1.78	1.90	1.74	1.56	1.53
After Aging 6 Months @ 21 °C						
G'10/10 (% change)	11.7	12.1	13.3	7.8	9.1	9.3
25% static mod. (% change)	13.6	13.3	13.2	9.3	9.7	11.7

Table VIII. Effect of additives on age-stiffening behavior.

Compound	26	27	28	29	30
Calcium Hydroxide	-----	2.00	-----	2.00	-----
Magnesium Oxide	-----	-----	4.00	5.00	-----
BCI-MX	-----	-----	-----	-----	1.00
Dynamic Properties at 21 °C					
G'10/10 (MPa)	370.0	387.0	360.0	368.0	374.0
Tan delta 10/10	0.271	0.279	0.276	0.285	0.295
25% static G (MPa)	237.0	242.0	229.0	225.0	228.0
After Aging 6 Months @ 21 °C					
G'10/10 (% change)	16.2	13.3	14.2	14.1	15.8
25% static mod. (% change)	15.2	12.4	11.9	12.9	16.4

Dow Corning Corp. has released its 1299 Silicone Seam Sealer that it said outperforms traditional acrylic sealants in narrow seam applications.

Dow Corning said this helps manufacturers deliver windows and doors that prevent air and water infiltration to reduce energy costs. It also delivers proven silicone performance at the cost of lower-performing organics, Dow said.

The Dow Corning 1299 Silicone Seam Sealer has a 100 percent silicone formulation, the company said, so it will not crack, degrade or discolor. The sealant is not extended with oils or solvents, ensuring there is little to no shrinkage during cure.

More information is available at www.dowcorning.com/construction.

Cimcorp Automation Ltd. said its enhanced gripping technology used for Cimcorp's layer picking solution has proven its ability to pick and place almost any product in distribution centers worldwide.

With a near 100 percent picking capability, Cimcorp said its system can automate virtually any layer picking process accurately and provide increased efficiency and reduced labor costs, while ensuring complete traceability as products move throughout a facility.

Cimcorp said its layer pick system is made of a heavy-duty clamping and vacuum-based tool and a large, fast gantry robot. In this system, tools can be used together or independently with variable force and vacuum strength based on the SKU to be handled. Cimcorp said the layer pick system is suited for facilities that pick more than 1,000 layers per day from 50-500 SKUs.

Cimcorp said it began using the layer picking technology in the beverage industry and has since enhanced the tooling to handle anything from standard corrugated cases to shrink wrap products, bottles, tubs and open trays. For more info, go to www.cimcorp.com.

Solvay Specialty Polymers said 13 of its advanced polymer grades were included in the latest release of the Digimat platform, a materials database and simulation tool from e-Xstream engineering, an MSC Software Co.

The polymer grades from Solvay allow Digimat to offer expanded capabilities for computer design and simulation of fiber-reinforced composite parts that target automotive, electronics, food-contact and other applications, Solvay claimed.

Solvay said the 13 additions to the simulation platform's Digimat-MX database draw from Solvay's Amodel polyphthalamide (PPA), Ixef polyarylamide, Veradel polyethersulfone product

families and deliver mechanical properties across a range of temperatures to meet customer requirements.

Among the new materials added to Digimat-MX are six automotive grades of Amodel PPA, including Solvay's A-1133, A-6135, AS-1145, AS-1933, AS-1945 and AS-4145 grades. Compared to standard polyamides, Solvay said Amodel PPA grades offer higher strength and stiffness at elevated temperatures, better retention of properties in humid environments and resistance to a broader range of chemicals.

For more information, go to www.solvay.com.

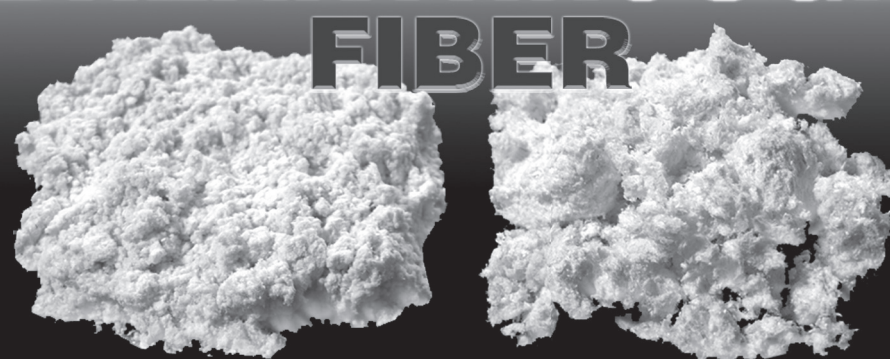
Jet Edge Inc. has introduced its iP60-30 60,000 psi (4,100 bar), 30hp (22 kw) hydraulic waterjet intensifier pump.

Designed for waterjet shops that desire the reliability of a hydraulic intensifier pump but have limited power, Jet Edge said the iP60-30 is capable of producing 0.6 gpm (2.3 l/m) of ultra-high pressure water at a continuous operating pressure of 55,000 psi (3,800 bar), Jet Edge said, and is economically priced and easy to maintain.

For specifications, visit www.jetedge.com, e-mail sales@jetedge.com or call 763-497-8700.

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