

# Comparison of Payne Effect, dispersion mix tests

By John Dick and Edward Norton  
Alpha Technologies

First of two parts

During the mixing process for a rubber compound, the base elastomer is masticated while the other ingredients, such as carbon black, begin to incorporate.

As this process continues, the carbon black agglomerates are deagglomerated and dispersed as primary aggregates while the base raw elastomers are simultaneously masticated and “broken down,” usually through some degree of depolymerization.

We constructed simple model recipes of these selected raw elastomers with N330 carbon black and studied the rheological effects on these experimental

## TECHNICAL NOTEBOOK

Edited by Harold Herzlich

compounds from controlled amounts of applied work history during BR Banbury mixing in the laboratory.

### Experimental

Table 1 shows the 11 different raw elastomers which were selected for this study.

As can be seen, the selected polymers include a very wide selection of both tire and non-tire rubbers that are commonly used. This selection includes NR, SBR, BR, IIR, CR, BIIR, NBR, EPDM, CSM, and HNBR.

These raw elastomers also were mixed with N330 carbon black in a carefully controlled manner with a laboratory BR Banbury, which was stopped periodically during the mixing cycle to take small sample aliquots between 3 and 7.5 min-

Fig. 1: RPA 2000.



Fig. 2: Alpha View Dispergrader.



## Executive summary

Compounds based on different base elastomers will break down in different ways during the mixing process and have different degrees of interaction with carbon black, which affects carbon black dispersion. This affects downstream factory performance in extruding, calendaring and molding.

Last year a new standard method for measuring the Payne Effect was developed as ASTM D8059 using the RPA. Also, in 2011 a standard method was developed using a special reflected light microscope to measure state of mix by percent carbon black dispersion under ASTM D7723.

In this study, an RPA 2000-brand Rubber Process Analyzer with EDR was used to measure the differences in rheological behavior from using different base elastomers with variation in the applied work history during mixing. Model rubber compounds were prepared and tested using several different base elastomers. Processability characteristics as seen in the Payne Effect were measured for these mixed stocks with varying work histories using the RPA 2000 with EDR. Comparisons also were made with the AlphaView Dispergrader-brand reflected light microscope.

utes of mixing time. Because the specific gravity for these elastomers were different, all comparisons were made on an equal volume basis so that each batch would always contain exactly 35 percent by volume carbon black.

These mixed samples were tested for “state of mix” with the Alpha Technologies RPA 2000 Rubber Process Analyzer shown in Fig. 1 as well as with the Alpha Technologies Alpha View Dispergrader special light reflected microscope shown in Fig. 2.

This light reflecting microscope works off the principle of quantitatively mea-

suring the reflecting light from the undispersed carbon black agglomerates (white area) vs. the light which is not reflected into the microscope lens as illustrated in Fig. 3.

### Measuring carbon black

This part of the study involved measuring rheologically the effects of carbon black incorporation and deagglomeration at different states of mix during the Banbury mixing process.

In this design of experiment, each raw elastomer compound was mixed with

See **Comparison**, page 16

Table 1: Shows the 11 different raw elastomers which were selected for this study.

Name of Rubber	ASTM Abbreviation	Trade Name	Specific Gravity
Styrene Butadiene Rubber	SBR	SBR 1500	0.94
Hydrogenated NBR	HNBR	Zetpol 2010	0.95
Polychloroprene	CR	GRT	1.23
Polychloroprene	CR	WRT	1.24
Bromobutyl Rubber	BIIR	Bromobutyl 2244	0.93
Ethylene Propylene Diene Rubber	EPDM	Nordel IP5565	0.87
1,4 cis Polybutadiene Rubber	BR	Budene 220	0.92
Acrylonitrile Butadiene Rubber	NBR	NBR DN 2850	0.97
Butyl Rubber	IIR	Butyl 268	0.92
Natural Rubber	NR	SIR 20	0.92
Chlorosulfonated Polyethylene	CSM	Hypalon 3570	1.2

Fig. 3: Alpha View Dispergrader light reflecting microscope.

## The Basic Measurement

- The image is scanned.
- Flat area (no bumps) is seen as black.
- Surface roughness (bumps) is seen as gray to white.

## The authors



Dick

Norton

John Dick has more than 45 years of experience in the rubber industry.

He was with BF Goodrich and later Uniroyal Goodrich Tire Co. as a section manager and development scientist in research and development until 1991 when he joined Monsanto's Rubber Instruments Group (now Alpha Technologies) as a senior scientist, applications.

Dick has authored more than 80 journal and magazine publications including five books on rubber technology. He consults, gives technical papers and has given seminars in more than 40 countries. Some of his publications have been translated into nine languages. He received the Monsanto Master Technical Service Award, the ACS Rubber Division “Best Paper Award,” and the University of Akron and University of Wisconsin Appreciation Awards for Teaching rubber compounding and testing courses in their continuing education programs.

Dick is a fellow in ASTM International, receiving the Award of Merit in 1990 and Distinguished Service Award in 2005. He also has represented the U.S. as a delegate to the International Standards Organization for the last 35 years.

He was appointed in 1992 to be leader of the U.S. delegation to ISO TC-45 on Rubber. He teaches 10 rubber technology courses at the University of Akron and University of Wisconsin continuing education departments.

Dick is a member of the American Chemical Society, Society of Rheology, and ASQ with a CQE and CQA. He also is a co-recipient of the ACS Rubber Division's 2014 Fernley H. Banbury Award for Rheology.

He received his bachelor's degree from Virginia Polytechnic Institute and a master's from the University of Akron.

Ed Norton graduated from Rose-Hulman Institute of Technology in 2011 with a bachelor's degree in chemical engineering.

He has been working at Alpha Technologies since 2010 as an applications specialist. His primary job functions include customer training and demonstrations, research and development, and aftermarket support.

He works to help customers in the rubber industry evaluate their formulations, processes and products using viscometers, rheometers, and other instruments. He has participated in many rubber groups and conferences in the U.S.

Norton currently is working on his master's degree at the University of Akron's polymer engineering graduate program.

# Technical

## Comparison

Continued from page 15

exactly 35 percent by volume of N330 carbon black.

During the BR Banbury mixing process, 20 grams aliquot samples were taken from the mixer after 3, 3.5, 4.5, 5.5, 6.5 and 7.5 minutes, as sampling intervals. Each of these samples were tested on the RPA by the new ASTM D8059 Standard for the Payne Effect.

For this study, a time test was applied at ± 0.07 percent strain, 1 Hz and 100°C for 2 minutes before the Payne Effect Strain Sweep was applied. This strain

sweep was applied at 1 Hz and 100°C, starting with ±0.07 percent strain, followed by ±0.1, 0.14, 0.2, 0.28, 0.35, 0.5, 0.7, 1.0, 1.4, 2.0, 2.8, 3.5, 5.0, 7.0, 10.0, 14, 20, 28, 35, 50, 70, 100, and 140 percent.

Also, respectively, samples from these mixing processes were run in duplicate on the Alpha View Dispergrader by the new ASTM D7723 procedure for measuring percent carbon black dispersion. The test conditions for running these tests were as follows:

- White area threshold: 23 μm
- Exposure time: 40 ms
- Position of illumination: Top
- Color channel for analysis: Blue

The following equation was used to calculate percent Z Dispersion:

$$\% Z = 100 - 100 \text{ URF}\%/35$$

Where:

- URF % = % of total scan from undispersed filler measured in reflection
- % Z = Weighted percent dispersion or “Z Value,” which assumes maximum of 35 percent white area.

### Discussion

#### Incorporation and deagglomeration of carbon black

The Payne effect is an effective way of studying deagglomeration of fully reinforcing carbon black during the rubber compound mixing process. It should be an effective way of relating to carbon black aggregate—aggregate attraction vs. the carbon black aggregate attraction to the specific rubber hydrocarbon medium.

Different rubber hydrocarbon mediums have different affinities for the carbon black filler. For example, it is well known that in various blends of different types of rubber polymers, one domain of rubber (at the microscopic level), will have a greater attraction (or affinity) for the available carbon black than the other rubber present in the blend.

Usually different rubbers in a compound blend are not perfectly soluble with each other so they will commonly establish continuous and discontinuous phases. Therefore, typically the available carbon black is attracted more to either the continuous or the discontinuous rubber phase.

The typical carbon black affinity for different elastomers is:

See Comparison, page 18

Fig. 4: Effects of increasing mixing time on measured Payne effect curves for Banbury mixing of SBR 1500 and N330 carbon black.

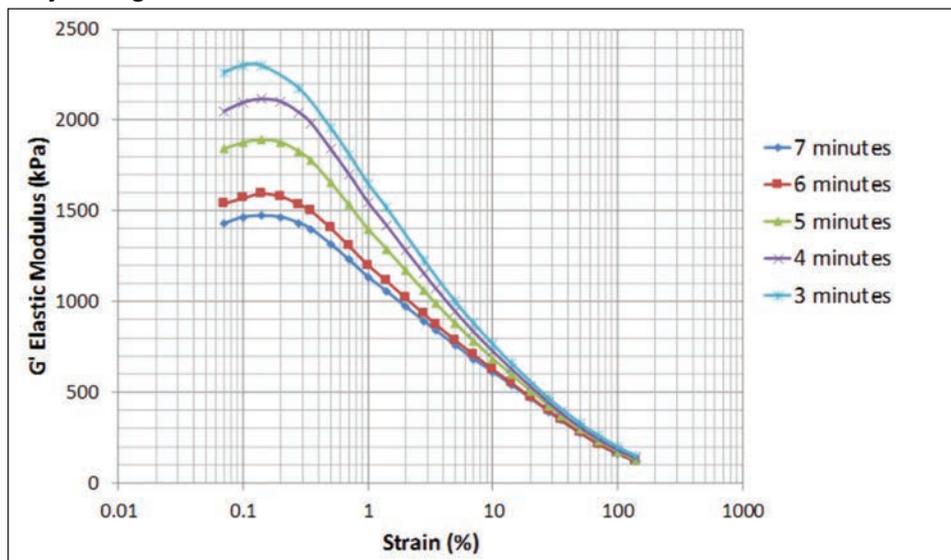


Fig. 5: G' Payne effect at 0.07 percent strain vs. work history for mixing of SBR 1500 and N330.

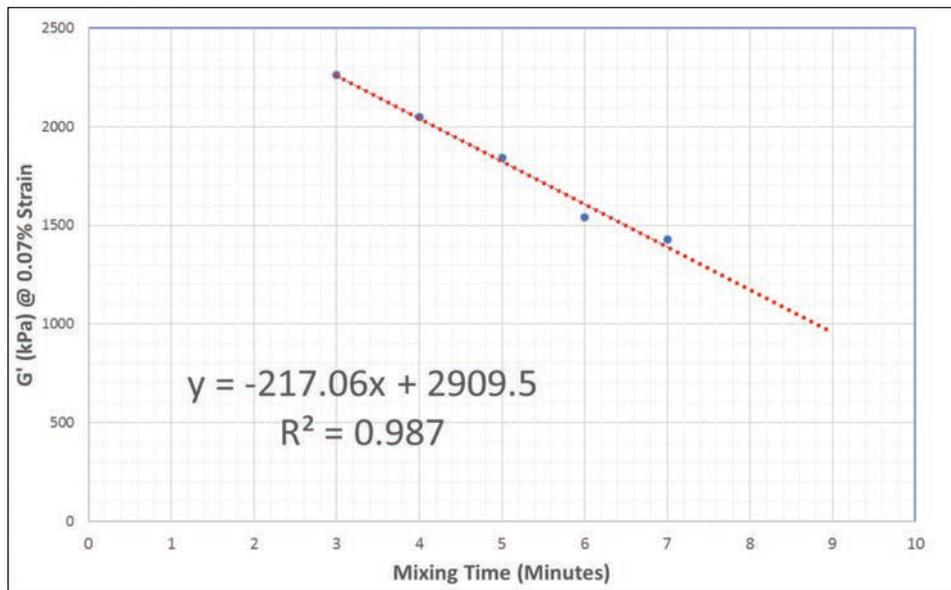


Fig. 6: ASTM D7723 percent Z dispersion vs. work history of mixing SBR 1500 vs. N330.

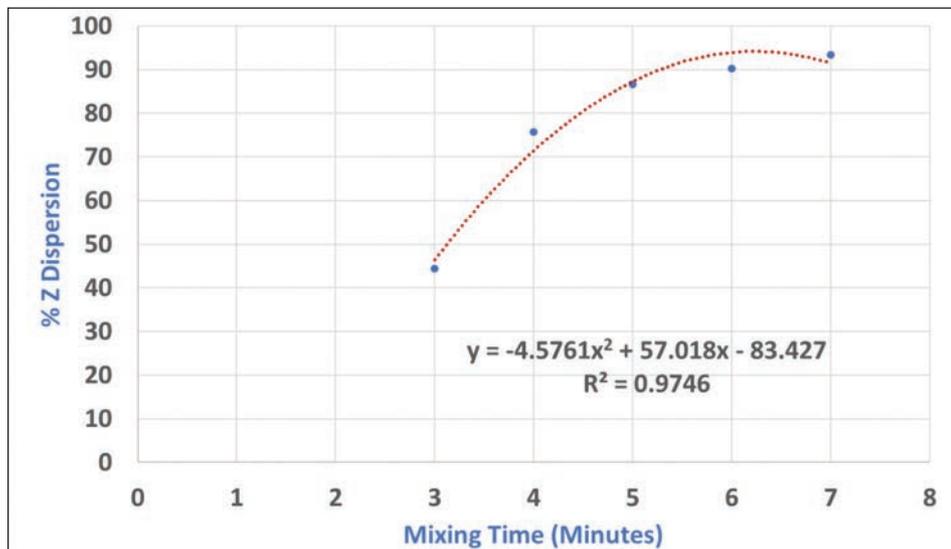


Fig. 7: Effects of increasing mixing time on measured Payne effect curves for Banbury mixing of natural rubber TSR 20 and N330 carbon black.

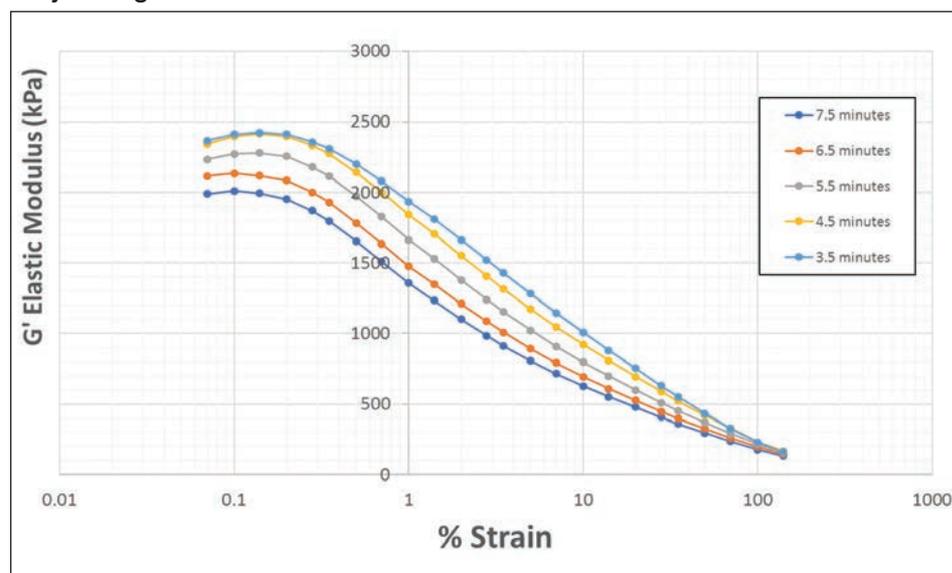


Fig. 8: G' Payne effect at 0.07 percent strain vs. work history for mixing of TSR 20 natural rubber.

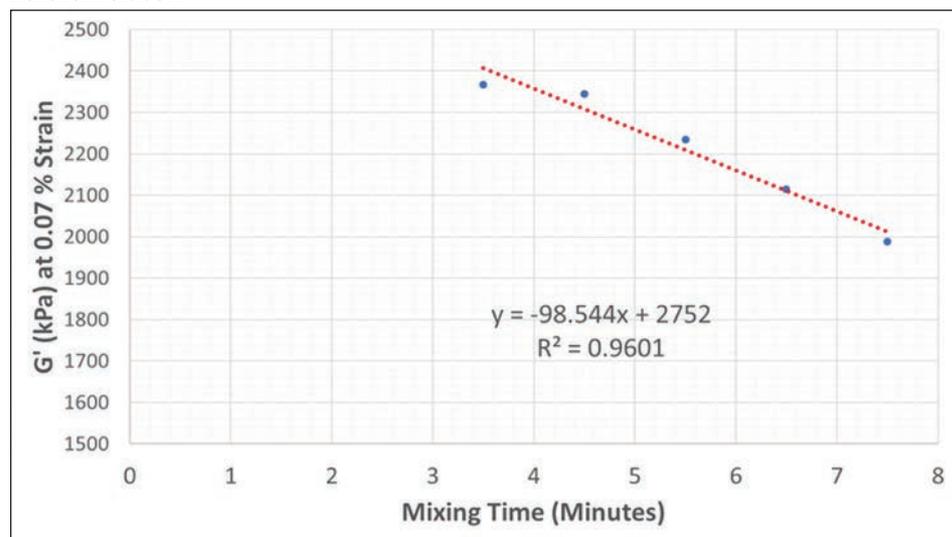
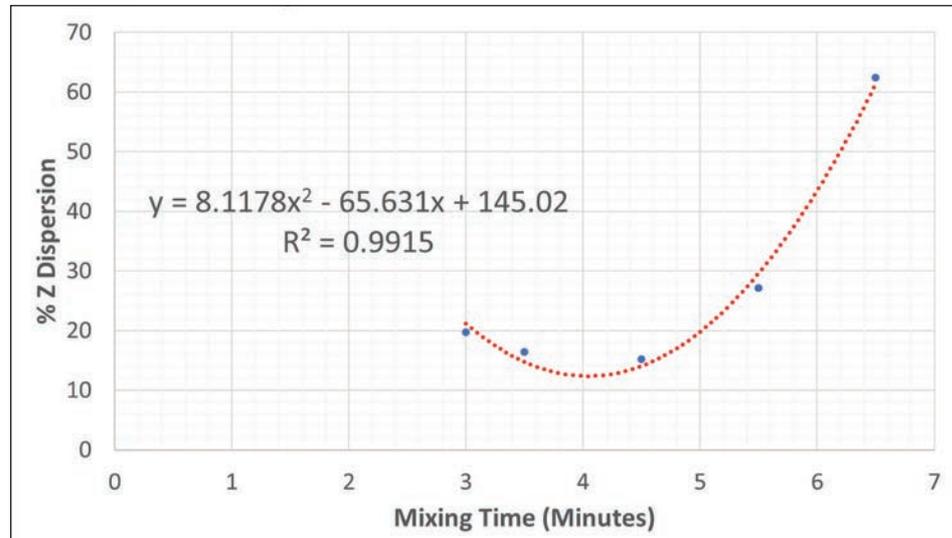


Fig. 9: ASTM D7723 dispersion vs. work history of mixing TSR 20 natural rubber with N330.



# Technical

## Comparison

Continued from page 16

BR > SBR > CR > NBR > NR > EPDM > IIR

So carbon black is much more attracted to the BR phase (polybutadiene rubber) than the IIR (butyl rubber) phase.

### SBR

From the Payne Effect RPA measurements, the SBR test results show a great distinction in the Payne Effect curves based on the time intervals being applied during the mixing of SBR 1500 and N330 carbon black shown in Fig. 4.

The affinity of carbon black to SBR 1500 is high. During the mixing process,

the carbon black readily deagglomerates in the SBR medium because of this attraction between SBR and carbon black.

As can be seen, with only the limited work history applied from 3 minutes of mixing time, the filler agglomeration network is rather high as shown from the G' elastic modulus value measured at the low initial applied strain of only 0.07 percent. However, as the mixing time and resulting work history increase, the measured G' value decreases from the destruction of the agglomerate-agglomerate filler network and the corresponding increase in the macro-dispersion of the N330 carbon black.

Fig. 5 shows how well the G' Elastic Modulus for the Payne Effect at 0.07 percent strain predicts the state of mix and degree of deagglomeration for the

Fig. 10: Effects of increasing mixing time on measured Payne effect curves for Banbury mixing of Budene 220 (BR) and N330 carbon black.

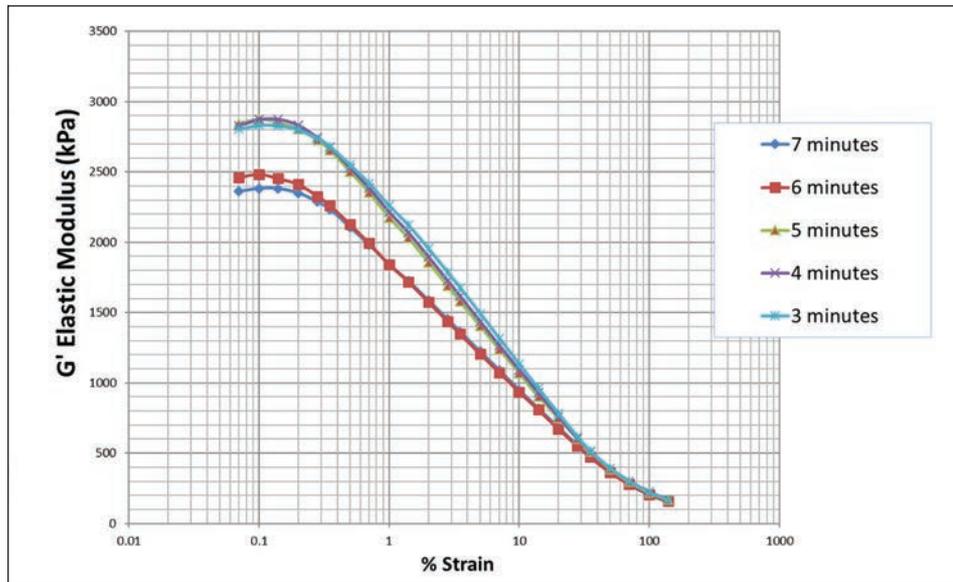


Fig. 11: G' Payne effect at 0.07 percent strain vs. work history for mixing polybutadiene rubber (BR).

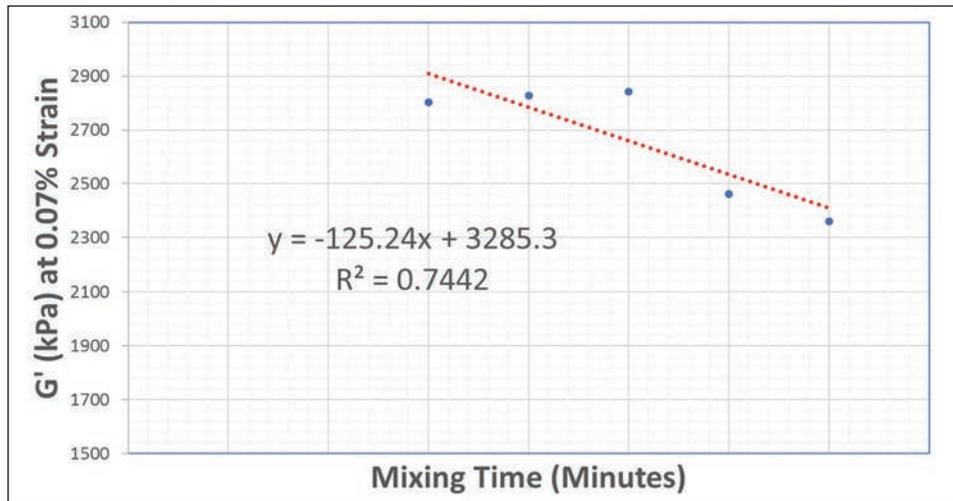


Fig. 12: ASTM D7723 dispersion vs. work history of mixing BR (Budene 220) with N330.

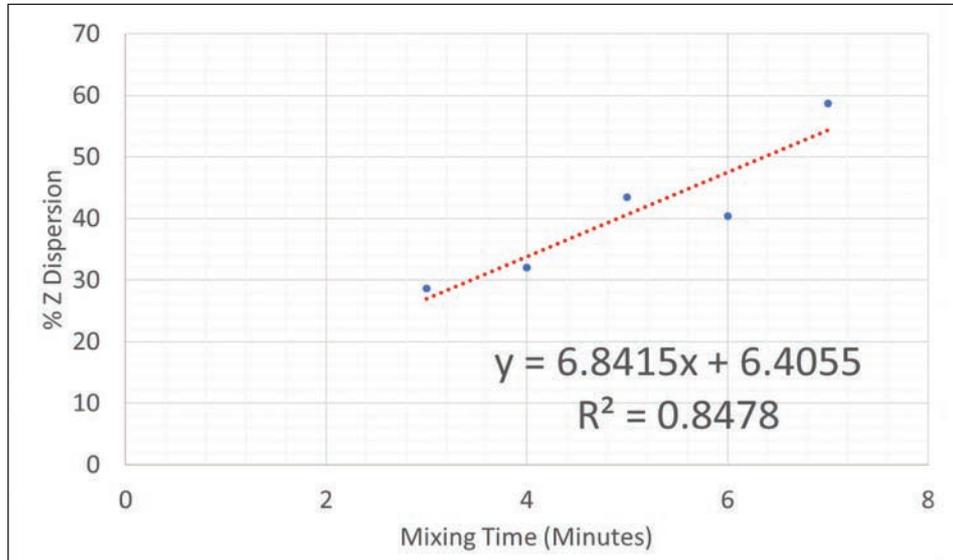


Fig. 13: Effects of increased mixing time on measured Payne effect curves for Banbury mixing of bromobutyl 2244 rubber (BIIR) and N330 carbon black.

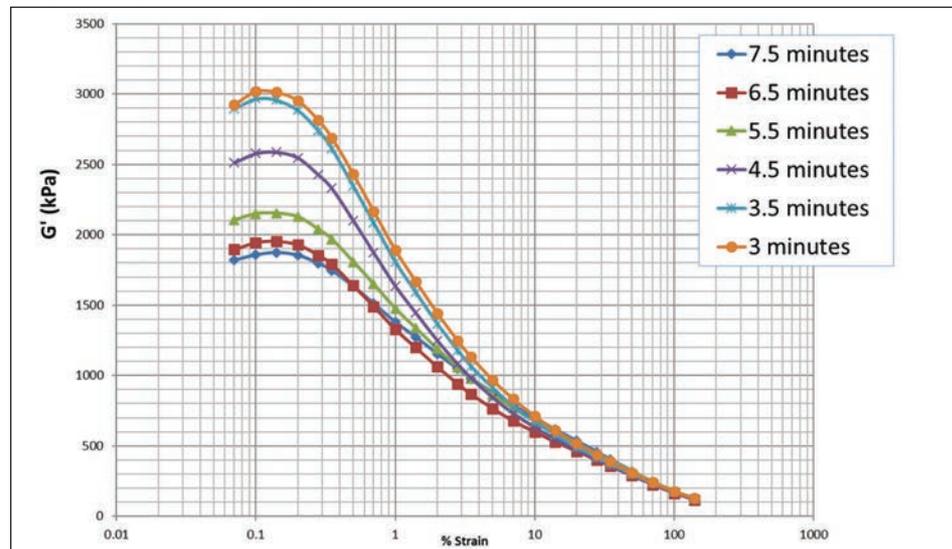


Fig. 14: G' Payne effect at 0.07 percent strain vs. work history for mixing bromobutyl 2244 with N330.

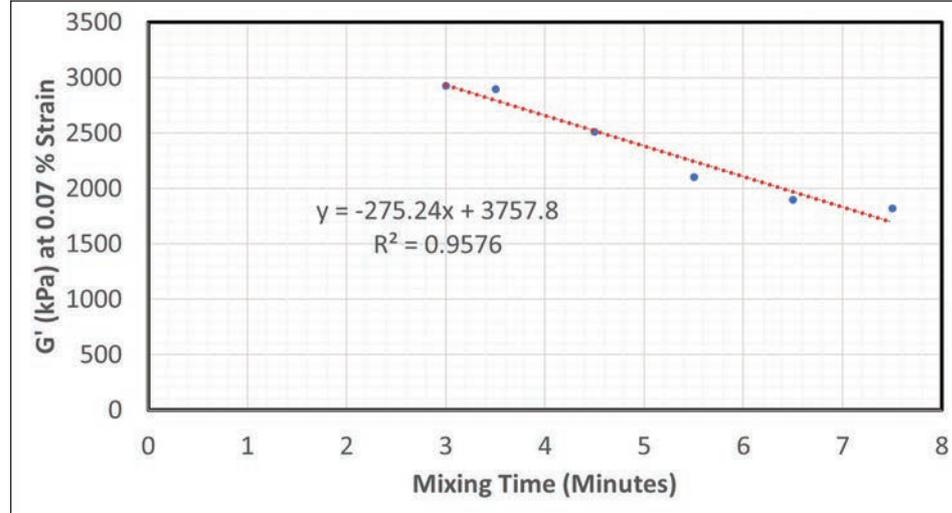


Fig. 15: ASTM D7723 percent Z dispersion vs. work history of mixing BIIR vs. N330.

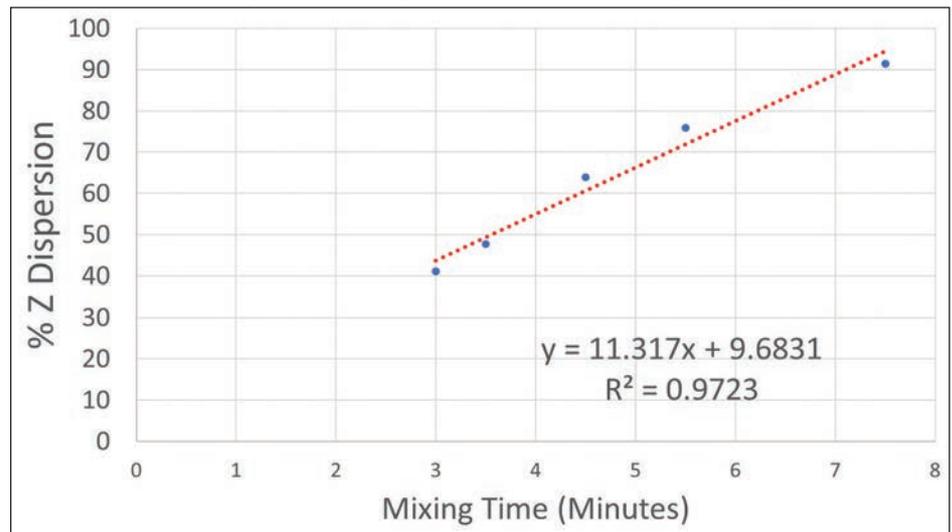
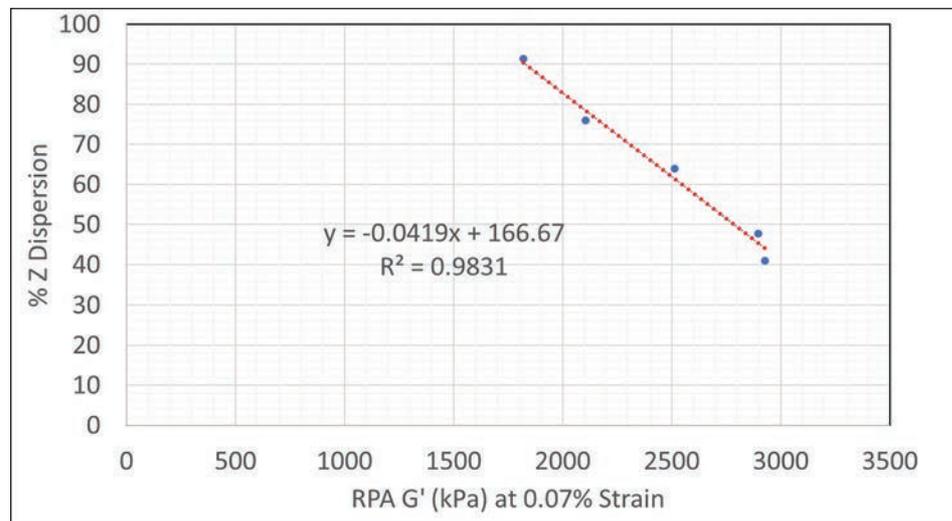


Fig. 16: ASTM D8059 G' at 0.07 percent strain vs. ASTM D7723 percent Z dispersion for BIIR.



# Technical

dispersing of N330 carbon black in the SBR 1500 rubber.

As can be seen, the Payne Effect  $G'$  correlates very well to the state of mix and inversely to the aggregate-aggregate network density.

**Fig. 6** shows the very good correlation of the percent Z Dispersion as performed by ASTM D7723 with the state of mix.

In a way, the shape of this curve represents the “law of diminishing returns,” which we reported in 1992 using the older, slower, optical microscopy method ASTM D2663, which gave close to the same profile.

For each marginal addition in work history, there was a smaller increase in percent dispersion of carbon black. By using the Alpha View Dispergrader (ASTM D7723), one produces a very

similar curve but much faster and perhaps more accurate. ASTM D7723 also was quite effective at measuring the “state of mix” using SBR as the raw elastomer in this mixing experiment.

## TSR 20 Natural Rubber

Also, TSR 20 natural rubber was studied for its carbon black dispersion characteristics. **Fig. 7** shows the effects of different amounts of work history on the Payne Effect profiles.

Just using the  $G'$  at 0.07 percent applied strain on the RPA can be used to predict state of mix as shown in **Fig. 8**. Also the ASTM D7723 percent Z value for carbon black dispersion is a good predictor of state of mix for a natural rubber base, as shown in **Fig. 9**.

In this experiment, unlike the SBR,

which readily accepted the N330 carbon black during the early stages of mixing, the TSR 20 natural rubber was more resistant in accepting the carbon black initially, but readily accepted the N330 in the later stages of mixing.

Normally the TSR 20 grades of natural rubber can contain as high as 0.20 percent dirt, which usually is defined as impurities which have a particle size greater than 44  $\mu\text{m}$ . This level of contaminant can appear as contributors to the “white area” in the percent Z calculation and actually make the percent Z values lower than they normally would be with SBR, for example.

More work needs to be performed to determine just how much negative effect that a relatively high “dirt” level might have on the percent Z values.

## BR

Comparisons also were made with 1,4 cis-polybutadiene rubber used as the base rubber in this study. In rubber compounding, BR is seldom used as the sole rubber in a formulation because of some processability issues.

Normally BR is used in many applications as a blend with either SBR or natural rubber (already discussed). **Fig. 10** compares the Payne Effect profiles for the test BR compounds being mixed with N330 carbon black with different applied work histories.

This BR compound did not break down in the same manner that the SBR did. In fact, using the  $G'$  at 0.07 percent strain gave only a fair prediction of state of mix, as shown in **Fig. 11**.

However, **Fig. 12** shows that the ASTM D7723 (Dispergrader) did somewhat better in measuring the progression of the state of mix than the  $G'$  Payne Effect. Because of these particular problems with 100 phr BR (which is rarely used by itself), the ASTM D7723 percent Z dispersion was somewhat better.

## BIIR

**Fig. 13** shows the effects of using bromobutyl rubber in these experiments. With the halogenation of butyl into bromobutyl rubber, there is very significant separation of the Payne Effect curves from applying different mixing times.

**Fig. 14** shows the effectiveness of using the Payne Effect  $G'$  at 0.07 percent to predict the state or quality of mix of the subject compound.

As can be seen from the brominated butyl compound, the  $G'$  Payne Effect at 0.07 percent curve is very effective at predicting the state or quality of mix with carbon black. From **Fig. 15**, the ASTM D7723 Dispergrader test was able to also achieve an equally effective prediction of state of mix for the BIIR with the N330 carbon black.

The direct correlation between ASTM D7723 percent Z Dispersion vs. the ASTM D8059  $G'$  Payne Effect at 0.07 percent strain (using the RPA with EDR), all with BIIR, is shown in **Fig. 16**.

The R square shows 98 percent of this correlation. The brominating of butyl rubber has a profound effect on the mixing quality of BIIR and N330 carbon black.

## IIR

Regular butyl rubber behaves and processes very differently from the bromobutyl that we were just discussing earlier. Rheologically and from a processing perspective, regular butyl rubber (IIR) behaves very differently because it is not brominated as seen from its Payne Effect Curves shown in **Fig. 17**.

Unlike the BIIR, which has its Payne Effect curves greatly affected from variations in applied mixing work history, the regular IIR (without the benefit of bro-

mine) shows very little change from variations in mixing work history. **Fig. 18** shows the resulting poor correlation between  $G'$  at 0.07 percent and mixing time.

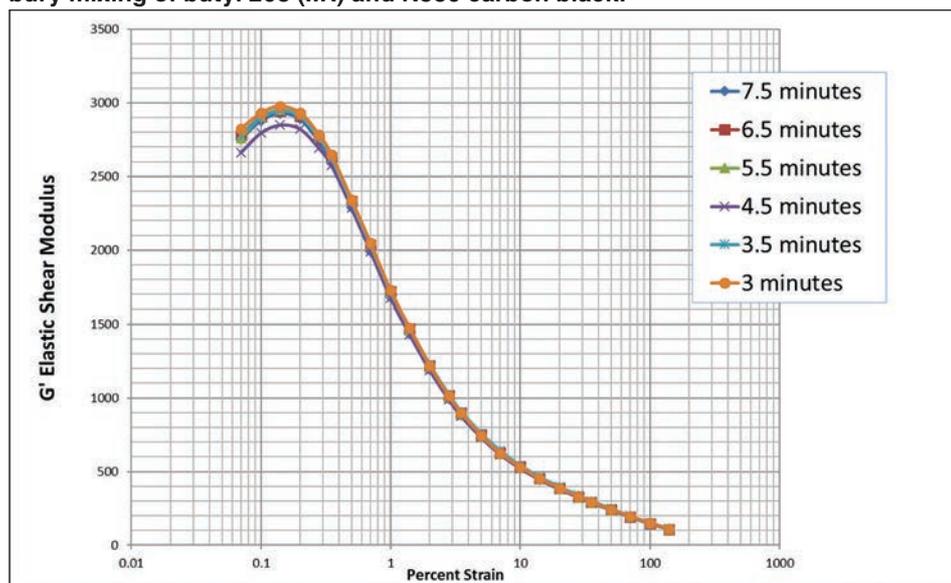
Because of the closeness of the  $G'$  Payne Effect curves for regular butyl rubber, the correlation between  $G'$  at 0.07 percent strain with mixing time is very poor and “noisy.” The butyl rubber is relatively less compatible in the dispersion of the N330 carbon black compared with the BIIR discussed earlier.

On the other hand, **Fig. 19** below shows some correlation of measured percent Z dispersion with mixing time for this regular butyl rubber experiment.

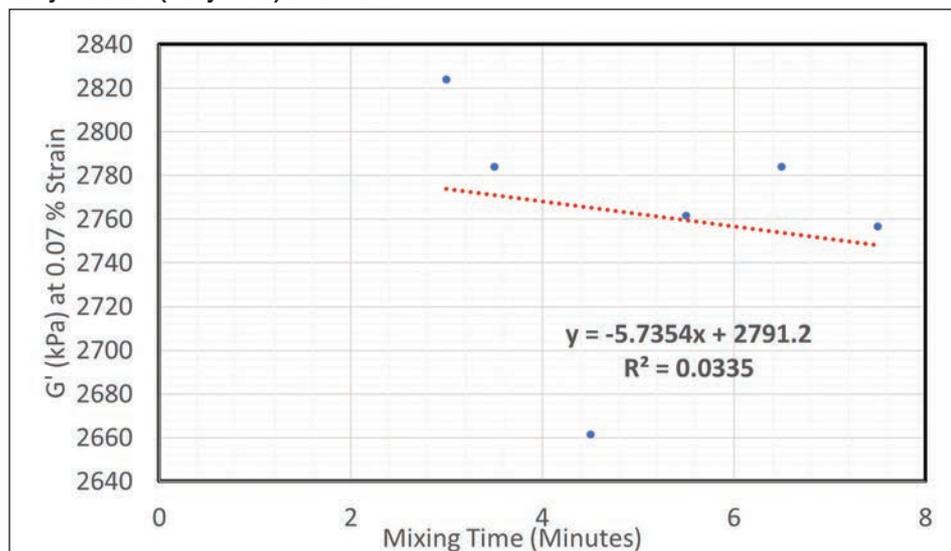
ASTM D7723 may have some advantage here over the ASTM D8059 Payne Effect method for compounds based solely on IIR.

*The conclusion of this technical notebook will appear in the Nov. 27 edition of Rubber & Plastics News.*

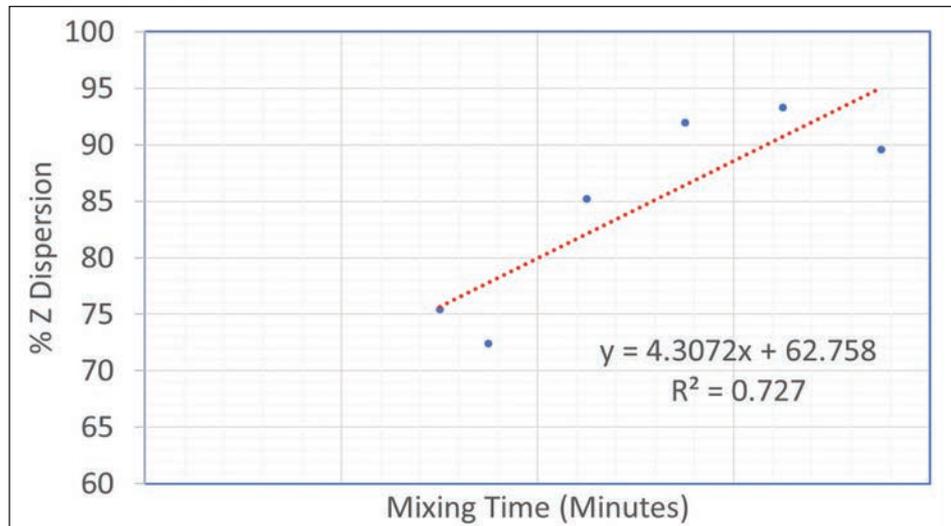
**Fig. 17: Effects of increased mixing time on measured Payne effect curves for Banbury mixing of butyl 268 (IIR) and N330 carbon black.**



**Fig. 18:  $G'$  Payne effect at 0.07 percent strain vs. work history for mixing of regular butyl rubber (butyl 268) and N330.**



**Fig. 19: ASTM D7723 percent Z dispersion vs. work history of mixing butyl 268 rubber with N330.**



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