Dynamic mechanical techniques for compound performance

By Edward Terrill, Barry Palmer and Jonathan Martens
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This paper will review techniques useful to better understand (and predict) compound performance.

The experimental techniques will include a Dynamic Mechanical Analysis (multi test deformation), utilizing a Metravib DMA150. The techniques which will be presented in this paper are:

- Strain sweep (Payne Effect/Lissajou analysis);
- Temperature sweep/tire performance predictors;
- WLF superposition/friction prediction;
- Crystallization;
- Vibration Isolator;
- Tack;
- Flocculation resistance;
- Modeling (Prony series evaluation and deformation index); and
- Strain sweep experiment (simple shear deformation to perform a double strain sweep experiment, as described below).

Table 1: List of compounds.

<table>
<thead>
<tr>
<th>ARDL NB #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEMNB1-1-1</td>
<td>Control (extended mix time)</td>
</tr>
<tr>
<td>JEMNB1-1-2</td>
<td>Functionalized (extended mix time)</td>
</tr>
<tr>
<td>JEMNB1-1-3</td>
<td>Control (no hold time/standard mix)</td>
</tr>
<tr>
<td>JEMNB1-1-4</td>
<td>Functionalized (no hold time/standard mix)</td>
</tr>
</tbody>
</table>

Fig. 1: Explanation of Payne Effect (Shingo Futamura—private conversation).

Fig. 2: Explanation of Payne Effect.

Fig. 3: Dual lap shear test specimen.

Fig. 4: Sample holder.

Fig. 5: Comparison of carbon black type.

Fig. 6: Performance of two compounds using the WLF superposition method.

Fig. 7: Performance of two compounds using the TTS superposition method.

The scope of the paper will include: tire performance prediction; Lissajou analysis; WLF superposition; TTS superposition; friction prediction; damping and vibration isolation; and Prony series evaluation.

Fig. 8: Lissajou loop showing the stress-strain relationship.

Fig. 9: Storage modulus as a function of dynamic strain

Where possible, examples are shared to illustrate the utility of the technique.

Strain sweeps

Strain sweeps are useful to understand filler to polymer interaction. This is commonly called the Payne Effect. The basic description and meaning of the strain sweep is shown in Figs. 1 and 2. The change in modulus as a function of strain was described by Payne. Understanding of the Payne Effect was aided by conversations with Shingo Futamura (retired Goodyear research scientist). The experimental technique used is described below:

Dynamic Mechanical Analysis (Strain Sweeps): A Metravib DMA150 Dynamic Mechanical Analyzer was used in strain deformation to perform a double strain sweep experiment (simple shear 10mmX2mm geometry, called dual lap shear geometry). The experimental conditions were 0.001 to 0.5 dynamic strain at 13 points in evenly spaced log steps at 30°C and 10 Hz.

Fig. 2 shows how the filler-filler interactions are reduced. The agglomerates are broken into smaller agglomerates thereby reducing the modulus. The test geometry (dual lap shear) is shown in Fig. 3. The sample holder is shown in Fig. 4. The rubber is sandwiched between the outside lugs and center lug.

In Fig. 4, the top clamp is attached to the shaker (displacement head), which typically cycles back and forth through the zero (neutral) position. The bottom clamp is attached to the force transducer.

An example of the utility of the DMA strain sweep is shown in Fig. 5, which differentiates carbon black types. The more reinforcing filler had a larger Payne Effect (change in modulus with strain).

The effects of mix method and functional polymer on silica dispersion were studied using the strain sweep experiment. The four compounds included in the study are shown in Table 1. The DMA strain sweep experiment has been useful to characterize filler reinforcement effects (Figs. 6 and 7).

Fig. 6 shows the storage modulus as a function of dynamic strain. Both mix method (adding first pass hold time) and functionalized polymer reduced the Payne Effect. Fig. 7 shows the tangent delta as a function of dynamic strain for these four polymers. Mix method (adding first pass hold time) and functionalized polymer reduced tangent delta.

Lissajou analysis

The Lissajou loop (Fig. 8) is the stress as a function of strain and thereby contains all of the raw data necessary for data analysis. In this way the analysis does not assume linearity, for situations where non-linear effects may be significant. The analysis method is shown schematically in Fig. 9. See *Dynamic* page 16

The author

Edward Terrill is an applied research fellow at Akron Rubber Development Laboratory Inc. He received his bachelor's in chemistry from Ur•sinas College and his doctorate in polymer science from the University of Akron.

He has more than 30 years of experience in the rubber industry, including working at Goodyear in the Polyester, Tire Physics and Compound Science departments. He also spent time at DuPont in the Textile Fibers Pioneering Research Laboratory. Terrill joined ARDL in March 2003. His research interests include structure property relationships, rubber compounding and testing. His work has included dynamic mechanical analysis for performance prediction.

Executive summary

The purpose of this review is discuss techniques to better understand (and predict) compound performance.

The scope of the paper will include: tire performance prediction; Lissajou analysis; WLF superposition; TTS superposition; friction prediction; damping and vibration isolation; and Prony series evaluation.

An example of the effective use of the techniques will be illustrated. The effect of polymer type on the compound prediction will be discussed for various techniques.
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The analysis of the Lissajou curve has been used to determine the viscoelastic parameters (E', E", and tangent delta). The analysis is based on either the area of the ellipse or the axis lengths of the ellipse.

Temperature sweep

The DMA temperature sweep is useful for characterization. The transition temperatures may be determined. Also, the tread performance predictors can be obtained.

Work done at ARDL studied the effect of silane loading in silica-filled tread compounds. The silane loading was varied from 0 to 10.6 percent based on silica loading. The ice traction was predicted with tangent delta at -10°C. The wet traction was predicted with tangent delta at 0°C. The effects of silane loading on ice traction and wet traction are shown in Fig. 10.

The temperature sweep data is shown in Fig. 11 in which the effect of silane loading was observed. Hysteresis (tangent delta) at 10°C and 0°C went through a maximum as a function of coupling agent level (~8 percent).

Tire performance predictors are summarized below.

- Winter traction: Complex modulus at -20°C
- Ice traction: Tan delta at -10°C
- Wet traction: Tan delta at 0°C
- Rolling resistance: Tan delta at 30°C
- Dry handling: Storage modulus at 30°C
- Dry traction: Loss compliance at 30°C

WLF Experiment

The WLF experiment is useful to understand dynamic mechanical properties as a function of frequency; in particular, when evaluating properties at high frequencies. This experiment is useful for damping properties, friction properties and vibration isolators.

The WLF experiment consists of a series of frequency sweep at various temperatures (Fig. 12), which through superposition yield a mastercurve (Fig. 13).

Fig. 13 shows the result of shifting the storage modulus results from various temperatures onto a single reduced frequency curve.

The WLF experiments are particularly useful for predicting friction because it is a high frequency phenomenon. The dynamic loss modulus master curve results (Fig. 14) correlated with the experiment friction result (Fig. 15). Fig. 15 shows the peak and slide coefficient for a wide range of polymers types on 150 grit alumina. The results, in general, correlate with their loss modulus results in Fig. 14.

Creep experiment

The creep experiment is a very useful test method to understand dimensional stability. ARDL found that it was helpful to understand (predict) crystallization (strain induced crystallization).

Two compounds shown in Table 2 were compared. The sulfur vulcanized natural rubber compound had higher tensile strength than the peroxide cured natural rubber compound (Fig. 16). Furthermore, the sulfur vulcanized natural rubber compound had faster crystallization kinetics than the peroxide cured natural rubber compound (Fig. 17).

The sulfur cured compound had a higher melting point than the peroxide cured compound, which suggests it had larger (more perfected) crystals (Table 3). The distribution of molecular weight between crosslinks has been determined independently by Professor Juan Valentin using Time Domain NMR with the double quantum experiment.

He found sulfur cured natural rubber to have a narrower distribution of molecular weight between crosslinks than the peroxide cured natural rubber (Fig. 18). Subsequently, a creep experiment was performed on these materials (Fig. 19).

The sulfur cure compound was more resistant to deformation upon rapid Fig. 10: Predicted ice traction and wet traction vs. silane loading.

The overall conclusion is that the sulfur cure is more resistant to deformation than the peroxide cure. Additionally, the sulfur vulcanized natural rubber had better cold flow resistance than the peroxide cure. The sulfur vulcanized compound had a higher melting point than the peroxide cure, which suggests it had larger (more perfected) crystals (Table 3). The distribution of molecular weight between crosslinks has been determined independently by Professor Juan Valentin using Time Domain NMR with the double quantum experiment.

Under the assumption that the sulfur vulcanized compound has a more perfect structure, the sulfur vulcanized compound is expected to have higher tensile strength and lower elongation at break than the peroxide cure.
The Future Tire Conference 2018, organised by the European Rubber Journal, will be held within The Tire Cologne expo at Koelmesse on 30-31 May, 2018. The conference will bring together top-level industry leaders and decision-makers to discuss the technology and market developments that are shaping the future of the tire industry. Register today - Your 2018 Future Tire Conference registration includes a FREE visitor ticket to The Tire Cologne expo!

**PROGRAMME - DAY ONE - MORNING**
**TIRE MARKET TRENDS**
Chairman: Peter Taylor, OBE, Secretary General, TRA
- Dr. Philipp Struck, Continental AG
- Dr. Bernd Lowenhaupt, Sumitomo Rubber Europe: Smart Tyre Concept: Sumitomo's Future Tyre Technologies
- Stephan Rau, WDK: Update on Regulatory Developments Likely to Impact the Tire Industry
- Jacob Peled, Pelmar Engineering Ltd: Update on the Latest M&A Activity Among Tire Manufacturers and its Continuing Role in Accelerating Technology-Transfer Across the Sector
- Paul Settles, LMC International: Global Market Overview & Implications of Changes in Vehicle Technology for the Tire Industry
- Panel Discussion: Which Companies are Playing the Biggest Role in Defining How the Tire Industry Adapts to the New Digital Era?

**PROGRAMME - DAY ONE - AFTERNOON**
**SUPPLY CHAIN, BRANDING, CONSUMER TRENDS**
Chairman: Bruce Davis, Special Projects Editor, Tire Business
- Stephan Helm, BRV: In-Depth Analysis of the German Tire Market in 2017
- Speaker TBC: New Performance Requirements for Tires in the Era of Connected Mobility, Electric Vehicles and Autonomous Driving
- Dennis Melka, MisterTyre Malaysia: The Impact of Internet-Buying on the Tire Market of the Future
- Panel Discussion: How Emerging Automotive Industry & Market Trends Will Impact the Tire Market and Tire Brands

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loading. Subsequently it slowly increased in deformation, presumably from crystallization. The sulfur compound had lower permanent set. The differences were attributed to a greater propensity to crystallize on stretching in the sulfur cure compound.

Fig. 16 compares the tensile stress strain properties of sulfur cured natural rubber compound to a peroxide cured natural rubber compound. The sulfur cured compound had higher ultimate tensile properties than the peroxide cured compound.

The crystallization kinetics were performed at -25°C under 75 percent elongation. It measures the compound's ability to crystallize on stretching. Crystallization kinetics were measured using the technique published by Gent.1

The melting point was obtained by slowly warming the stretched and crystallized sample at the conclusion of the crystallization kinetic experiment. Fig. 17 compares the crystallization kinetics of the sulfur cured compound to the peroxide cured compound. The sulfur cured compound crystallized faster and had a higher melting point than the peroxide cured compound. Fig. 18 shows the work of Professor Valentin using time domain NMR double quantum technique. He found that the sulfur cured natural rubber had narrower distribution of molecular weight between crosslinks than the peroxide cured natural rubber.

Fig. 19 is an example of a creep and relaxation experiment. Fig. 20 shows DMA creep and recovery of the sulfur and peroxide cured compounds. The sulfur cured compound had better resistance to deformation and better recovery than the peroxide cured compound, presumably because it has a greater propensity to crystallize on stretching.

Green compound properties

Flocculation resistance

Briefly, one DMA technique for measuring flocculation involves the following:

1: Mill the compound to eliminate flocculation;

2: Strain sweep at 160°C (to further eliminate flocculation); and

3: Perform a “time” experiment at 160°C in which dynamic modulus was measured as a function of time. The resistance to modulus build-up was a measure of flocculation resistance (lower modulus increase is better).

Tack

In this method, two green compounds brought into contact for controlled time and load followed by static lift-off.

Modeling and FEA

Two DMA tests which have found particular utility for modeling are (1) Prony Series and (2) Deformation Index. In any given experiment, the energy dissipated will depend on the deformation (whether it is strain controlled, energy controlled, or stress controlled). Futamura2 performed rebound experiments and plotted the results as a function of DMA variables (the DMA variable shown in Equations 1 and 2: loss modulus, tangent delta, and loss compliance).

The correlation between rebound and DMA variables for five compounds was determined (Fig. 21). In this case a high correlation with energy was obtained. The technique has been used to determine the deformation mode present in particular regions of a rubber article such as a tire.

Equation 2 shows how Futamura constructed the equations for deformation index. Herein he defined N=0 for strain controlled deformation, N=1 for energy deformation, and N=2 for stress controlled deformation.

The rebound results correlated best with tangent delta, signifying energy controlled deformation.

Vibration isolator

The important property for a vibration isolator is usually low transmissibility at high frequency. Usually dynamic modulus is measured as a function of frequency (in Hz).

Table 2: Material in crystallization study.

<table>
<thead>
<tr>
<th>ARID. N#</th>
<th>Description</th>
<th>ERN83-108-1</th>
<th>ERN83-108-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural rubber, unfilled, soft cure</td>
<td>Natural rubber, unfilled, peroxide cured</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 13: WLF master curve.

Fig. 14: Dynamic loss modulus as a function of frequency.

Fig. 15: Peak and slide COF for six compounds on 150 grit alumina (medium).

Fig. 16: Room temperature tensile properties.

Fig. 17: Crystallization kinetics at -25°C.

Fig. 18: Crosslink distribution using double quantum experiment.
Cooper reintroduces truck and bus tire line

By Bruce Davis

ATLANTA—Cooper Tire & Rubber Co. is reintroducing a Cooper-brand truck and bus tire line to its portfolio 11 years after phasing it out and making the Roadmaster brand its sole truck/bus product line.

The SmartWay-verified Cooper truck/bus radial line debuted at the Technology & Maintenance Council’s Annual Meeting and Transportation Technology Exhibition in Atlanta the first week of March.

The tires, produced at the Cooper Qingdao Tire Co. Ltd. venture in Qingdao, China, will go on sale May 1 in the U.S. in application-specific series—Pro Series for long haul; Work Series for regional haul, pick-up and delivery; and Severe Series for mixed service.

The Cooper and Roadmaster brands will co-exist in the marketplace. Cooper said, with the Cooper line targeted for fleets, OE accounts and commercial servicing dealers, while the Roadmaster brand serves the replacement channel and the owner-operator primarily through wholesale as well as standard fitment to trailer OEMs.

The Cooper line will be available in Canada and Mexico this summer.

Commercial truck tires was a positive business segment for Cooper last year. The company reported its truck tire shipments increased 14.7 percent in the U.S. in 2017 over 2016, outperforming the industry as a whole and its fellow domestic producers represented by the U.S. Tire Manufacturers Association, according to the firm’s 10-K filing.

The Cooper TBR tires feature a full width, four steel-belt package for casing integrity and are backed by a seven-year, two-replacement warranty with full replacement value on the first 50 percent of tread life on all Pro and Work Series tires, Cooper said.

“Fleets are continually faced with the pressure of lowering their operating costs, and tires are an area that can have a big impact on meeting those targets,” said Gary Schroeder, director of Cooper’s global truck and bus tire business.

“Our North American team of engineers developed the Cooper-brand truck tires with a focus on lowering the total cost of ownership for fleets, making these tires an attractive choice.”

Cooper did not disclose pricing information nor say how much of a price difference will exist between the brands.

Cooper said the Pro Series tires are designed to offer balance of fuel efficiency and original tread life, while the Work Series balances fuel efficiency and tread life with scrub-resistant properties. The Severe Series is engineered to withstand heavy scrub and cut/chip environments.

Cooper’s decision a decade ago to suspend the use of the Cooper brand for truck tires coincided with the phase-out of domestic truck tire production and a move to source commercial vehicle tires from China.

The relaunch comes just a few weeks after Cooper disclosed a series of moves to shore up its commercial tire business, starting with the signing of an off-take production deal with Sailun Vietnam Co. Ltd. for radial truck and bus tires.

That deal gives Cooper a third source for truck tires it sells under the Roadmaster, Dean and Starfire brands and one it can count on after its off-take agreement with Prinx Chengshan (Shandong) Tire Co. expires in mid-2019.

Cooper also plans to open a 400,000-sq.-ft. warehouse in San Bernardino, Calif., this spring dedicated to distributing commercial tires to its customers in North America.

Cooper is the majority owner of Cooper Qingdao Tire Co. Ltd., having acquired a 65 percent interest in the former Qingdao Ge Rui Da Rubber Co. Ltd. in late 2016 for about $83 million.

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a frequency sweep experiment). Subsequently, transmissibility is determined as a function of frequency using the equations in Equation 3. There is another important factor and that is static to dynamic modulus ratio.

An example of work performed at ARDI, is shown in Fig. 22. Fig. 22 compared degree of transmissibility for 10 compounds. Low transmission is desirable in the isolation region (for vibration isolators). Ranking the compounds from best (lowest transmission) to worst was silicone rubber, natural rubber, solution SBR/polybutadiene, hydrogenated nitrile rubber, butyl rubber, and fluoroelastomer FKM.

Fig. 21: An example of the use of deformation index concept.

Equation 2: Energy loss of deformation process = DE”/(E”) m + F.

Equation 3: Determination of transmissibility.

Fig. 22: Comparison of 10 compounds (degree of transmission as a function of frequency ratio).