Macro- and micro-dispersion characterization of hose compounds

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Executive summary

Effective dispersion of fillers and additives can have a significant impact on the performance of elastomeric materials. Tensile strength distribution testing can be used to analyze macro-scale dispersion. The method can be sensitive to changes in mixing procedure and detect crack precursors such as undispersed filler agglomerates. Additional analysis can be performed on filler micro-dispersion via the Payne Effect from a strain sweep on the rubber process analyzer (RPA).

The impact of process changes such as mix time, material addition steps, milling procedure and number of passes is investigated for three different rubber compounds for hose applications that are based on chloroprene rubber (CR; neoprene), nitrile butadiene rubber (NBR; nitrile rubber), and ethylene propylene diene rubber (EPDM). The effects of adding micrometer-sized dispersion aids on the dispersion for a chlorinated polyethylene (CPE) compound are also investigated.

The results show that changes in dispersion can be effectively detected via the tensile and RPA testing methodologies. The macro- and micro-dispersion trends in some materials do not always correlate, which reinforces the need for separate characterization of these two distinct types of dispersion.

Introduction

Rubber formulations contain multiple ingredients, including gum polymers, reinforcing and non-reinforcing fillers, oils/plasticizers, crosslinking additives (curatives), stabilizers and other materials that are compounded together in quick mixing processes with total mixing time <10 minutes. Testing approaches are accordingly needed in the rubber lab for evaluating the mixing quality, especially regarding the dispersion of particulate fillers.

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There are two types of dispersion to characterize, macro-dispersion and micro-dispersion, which require distinct testing approaches as will be discussed. In product development these lab measurement tools are needed to evaluate new rubber formulations and alternative raw materials, and in manufacturing they can be applied in efficient ways for monitoring compound quality control and guiding process improvements.

Macro-dispersion relates to the presence of undispersed agglomerates of filler particles or additives in a rubber compound that range in size from about 5 micrometers up to several hundred micrometers. These agglomerates act as crack precursors (flaws, defects) in rubber and accordingly are detrimental to fatigue endurance, abrasion resistance, and other durability-related properties. Various microscopy techniques on a cut surface of the rubber material can be used to quantify the state of macro-dispersion.[1,2] However, the percentage of material investigated with the two-dimensional area probed by microscopy is quite small, and identifying something that looks like an agglomerate does not mean that it will act as a crack precursor. Characterizing tensile strength distribution is a straightforward way to detect micrometer-scale crack precursors in rubber caused by agglomeration of filler or curatives (incomplete dispersion) as well as hard contaminants present in raw materials or introduced in rubber processing.[3,4]

The tensile stress-strain testing of multiple specimens in this method samples a much larger fraction of the compound compared to microscopy. The tensile strength distribution approach is fracture-based, so it identifies the presence of large filler agglomerates and other defects that will actually impact rubber durability, as opposed to viewing filler agglomerates or other inclusions in the microscope and wondering if they will affect fatigue lifetime, abrasion resistance and the like. A shift of the entire strength distribution in the direction of lower strength indicates a reduction in the average state of macro-dispersion. A substantial broadening of the distribution toward the low strength side signifies a minor concentration of very large crack precursors.

Micro-dispersion concerns the tendency of filler particles to interact with each other to form filler networks within the rubber compound, which can be mediated by developing more polymer-filler interactions versus filler-filler interactions. The Payne Effect—which is the well-known hysteretic softening at small dynamic strain amplitudes revealed in a strain sweep—is commonly used as an indicator of micro-dispersion and is measured using dynamic rheometers such as the rubber process analyzer (RPA). The difference, ΔG', between the dynamic storage modulus (G') at low strain amplitude (0.1 percent) and G' at higher strain amplitude (in this study: 100 percent for uncured rubber, 25 percent for cured rubber) is used as a measure of the Payne Effect magnitude. A smaller Payne Effect (lower ΔG') reflects a less extensive filler network, so a reduction in ΔG' is an indicator of improved micro-dispersion.

Because increased mixing intensity can positively affect both macro-dispersion and micro-dispersion, they can often track together[5] despite their distinct nature and origins. This is not always the case, as reported for silica-filled tire tread compounds.[6] An extreme example where the two types of dispersion go in opposite directions can be noted when macro-dispersion is so poor that the filler loading (volume fraction) of filler effectively mixed into the rubber is significantly reduced due to a substantial

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Table 1: Chloroprene mixing modifications.

Compound	Mix Modification
CR1	2 pass, cooling water, 72% fill factor, extra milling
CR2	1 pass, 82% fill factor, <4min mix time, minimal milling
CR3	1 pass, 82% fill factor, <4min mix time, 5% filler added with cure, minimal milling

Table 2: NBR rubber formulary pg. 352- fuel hose inner layer – recipe 3.

Nipol DN 4050	100
ZnO	5
Stearic Acid	1
Mistron Vapor	80
N550	60
N990	50
TP-95	15
Tegmer 812	15
Antioxidant	3
ProAid AC-100	2
TMTD	3
MBTS	1
Sulphur	0.5
	335.5

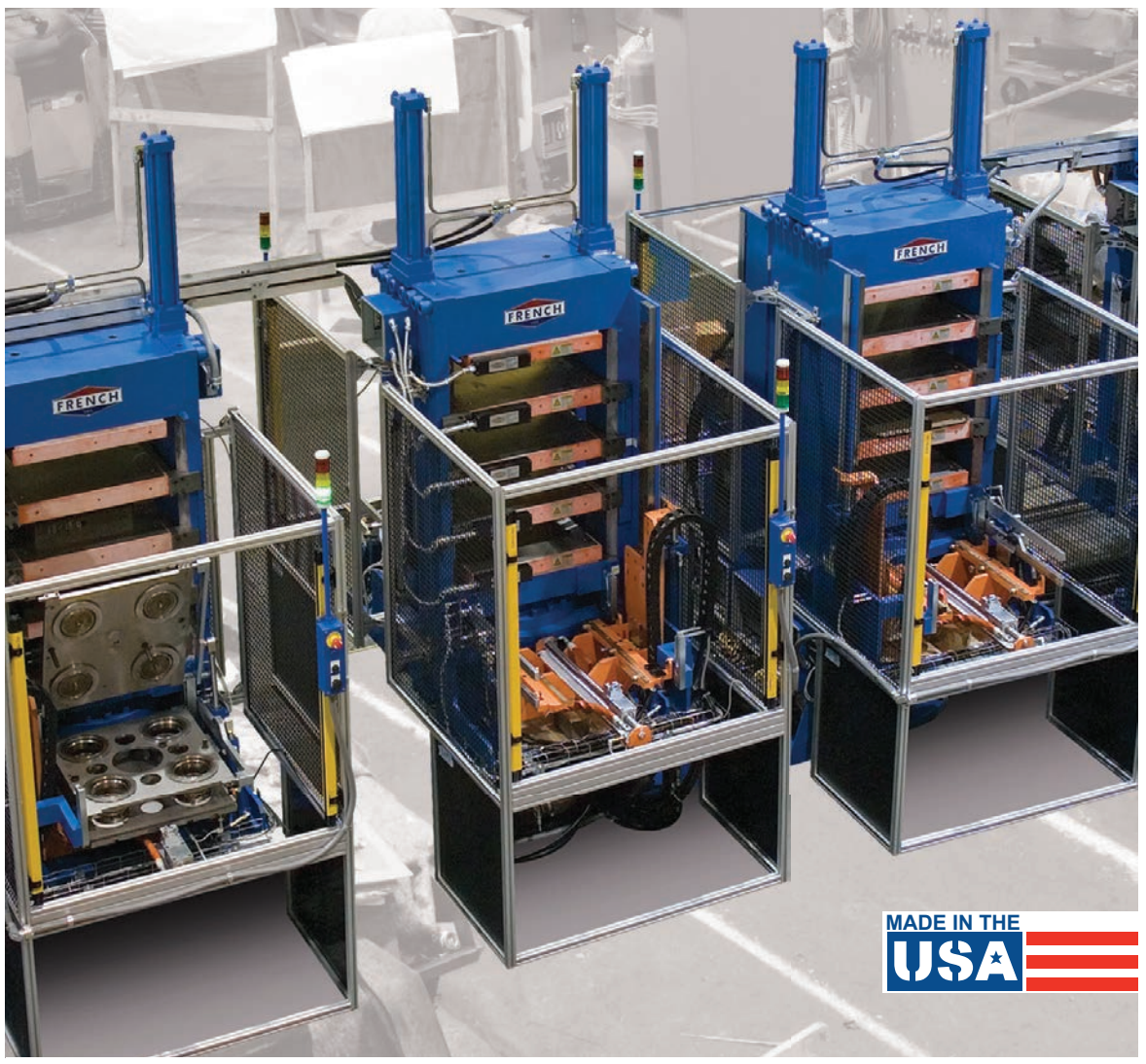


Table 3: NBR mix procedure.

NBR – 72% Fill		
Step 1	Add Polymer	
Step 2	Mix 15 sec.	60 RPM
Step 3	Add Filler & Oil	
Step 4	Mix to 180F	60 RPM
Step 5	Sweep Ram	
Step 6	Mix to 210F	60 RPM
Step 7	Add Cure	
Step 8	Mix to 250F	60 RPM
Step 9	Drop	

Table 4: NBR mixing modifications.

Compound	Mix Time	Mix Modification
NBR1	4:30	1st Batch
NBR2	3:30	Control
NBR3	4:30	2 Pass: w/ Cooling Water 2nd pass 1:45 mix w/230F drop
NBR4	4:00	Minimal Milling – 1 pass through mill
NBR5	7:10	"Bad Mixing" - 85RPM, add 10% filler w/ cure, minimal milling
NBR6	4:00	Added NR w/cure (10phr) - simulate cleanout hangup



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Compounds

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portion of the filler being contained within the widespread agglomerates. The extent of filler networking is thus reduced (lower Payne Effect; better micro-dispersion) as a consequence of the lower filler loading within the rubber. The study presented here for a variety of rubber formulations will show that macro- and micro-dispersion trends do not always correlate.

The investigation described here involves the characterization of macro-dispersion and micro-dispersion, using tensile strength distribution and Payne Effect from RPA strain sweep, respectively, for four different hose compounds based on chloroprene rubber (CR; neoprene), nitrile butadiene rubber (NBR; nitrile rubber), ethylene propylene diene rubber (EPDM), and chlorinated polyethylene (CPE). Mixing conditions were varied and dispersion aids were introduced to evaluate the influences on the two types of dispersion.

Experimental details

As mentioned in the introduction, macro-dispersion was evaluated using the tensile strength distribution methodology. Tensile testing was conducted per ASTM D412. For each compound evaluated, four cured slabs were used to generate 24 specimens of Type C that were cut from the slabs in the direction parallel with the milling grain direction. Testing was conducted on an Instron T2020 tensometer at 500 mm/min at room temperature. The ultimate tensile strength (stress at break) values from all 24 specimens were sorted from smallest to largest against the fraction of samples plotted to generate a distribution curve for tensile strength. Weibull statistics were used to fit the tensile strength failures and calculate probability distribution functions as detailed in prior research.[3]

Micro-dispersion was investigated via strain sweeps on an Alpha Technologies Premier RPA. The uncured strain sweep was conducted at 121.1°C (250°F) after a one-minute dwell for the material to equilibrate. The sweep was performed in reverse from 100 percent strain amplitude to 0.1 percent over 7 logarithmically-spaced points, at a frequency of 0.25 Hz. The cured strain sweep begins with a 5 min cure step at 193.3°C (380°F) at 7 percent strain and 1.67 Hz. The sample is rapidly cooled to 100°C (212°F) and thermally equilibrated for one minute before the strain sweep begins in reverse from 25 percent, to 1 percent to 0.1 percent at 0.25 Hz. The maximum strain at 25 percent is necessary to allow all compounds to be tested under the same conditions, as the RPA is unable to provide enough torque to reach 100 percent strain for some cured rubber compounds.

Additionally, this cured test procedure was developed to run as quickly as possible (<10 minutes) to allow incorporation into production mixing schedules. The difference, ΔG', between the dynamic storage modulus (G') at low strain amplitude (0.1 percent) and G' at the highest strain amplitude (100 percent for uncured rubber; 25 percent for cured rubber) was used as a measure of the magnitude of the well-known Payne Effect. Smaller ΔG' reflects better filler micro-dispersion. For characterizing the nature of the filler network (micro-dispersion state) that manifests as the Payne Effect, the reverse strain sweep approach detailed above was selected because this method has been shown to eliminate rubber storage effects from slow networking/flocculation,[7] thus giving more reproducible data. There also is a fundamental physical basis for breaking up the filler network at higher strain and then reducing the strain as the material transitions into the jammed/networked state.[8]

Compounds were mixed using a 1L Moriyama tilt body lab mixer model DS-1-5 with tangential 2-wing rotors. Some mixing was two-pass (two-stage) while others were one-pass. Key changes in mixing conditions related to dispersion will be mentioned later. All rubber compound formulations detailed in the text and tables that follow are expressed in terms of parts-per-hundred-rubber (phr), where 100 phr is the loading of total raw elastomer(s) in the dry state (not including any extender oil) in the formulation.

Mixing conditions were investigated in three distinct rubber formulations to demonstrate utility of lab tests for micro- and macro-dispersion. One material was a chloroprene rubber (CR; neoprene) compound used as a cover compound for industrial hoses. This CR compound was sulfur cured and filled with a total of 107 phr of non-reinforcing and reinforcing fillers, with mixing variations detailed in **Table 1**. A second formulation was based on a published nitrile rubber (NBR) compound described as a fuel hose inner layer (tube) in The Rubber Formulary, Sec-

Table 5: EPDM rubber formulary pg. 264- garden hose tube compound.

Royalene 539	100
N650	150
N762	150
Whiting-$CaCO_3$	200
Naphthenic Oil	160
ZnO	5
Stearic Acid	2
Paraffin Wax	2
MBTS	3
DTDM	0.8
TETD	0.8
ZDBC	2.5
Sulphur	0.8
	776.9

Table 6: EPDM mix procedure.

EPDM – 75% Fill		
Step 1	Add Polymer	
Step 2	Mix 15 sec.	60 RPM
Step 3	Add Filler & Oil	
Step 4	Mix to 170F	60 RPM
Step 5	Sweep Ram	
Step 6	Mix to 200F	60 RPM
Step 7	Add Cure	
Step 8	Mix to 230F	60 RPM
Step 9	Drop	

tion VI,[9] which is detailed in **Table 2**. The NBR control mix cycle is listed in **Table 3**, with variations listed in **Table 4**. Finally, an EPDM based on a published garden hose tube compound in The Rubber Formulary, Section V,[10] was also considered, with formulation reported in **Table 5**, mix procedure in **Table 6** and mixing variation in **Table 7**.

Dispersion aids were studied in a hydraulic hose tube compound that was based on chlorinated polyethylene as the elastomer type, with peroxide cure system, and reinforced with 65 phr filler. The addition of Fortimix NC3 and Spherix 20M (supplied by Spherix Products) are detailed in **Table 8**.

Results and discussion

To study macro- and micro-dispersion effects, lab-scale rubber batches were mixed with conditions that were considered near optimal, and with adjusted conditions intended to give poorer mixing quality. The mixing variations for the chloroprene rubber formulation are summarized in **Table 1**. Shown in **Fig. 1**, the near optimal mixing of CR1 with a two-pass procedure resulted in a narrow unimodal distribution of tensile failures with an average strength 2 MPa greater on average than both CR2 and CR3, which had one-pass mixing. It was unexpected that the late addition of 5 percent of the filler in CR3 resulted in a narrower distribution than CR2 although it resulted in lower maximum tensile strength.

The micro-dispersion results for the uncured chloroprene rubber compounds follow the same trend as the macro-dispersion. Shown in **Fig. 2**, the CR1 reference compound has a smaller Payne Effect than CR2 and CR3. However, in the cured state CR1 has a greater Payne Effect, apparently reflecting more filler network build-up/flocculation at the early part of the curing process.

There was minimal impact on macro-dispersion between the first batch NBR1 and control NBR2 despite a one-minute shorter mixing time. Both compounds possess a unimodal distribution, which are offset from each other less than 0.2 MPa.

Going to a two-pass mix, NBR3, showed a significant jump in tensile strength by over 1 MPa, while the distribution did not change significantly. There is little overlap in performance between the distribution of NBR3 and NBR1 tensile strength. By reducing the milling procedure to the bare minimum in NBR4 with a single roll through, the average ultimate tensile strength stayed the same as NBR2, however a tail of low strength failures appears likely due to undispersed filler causing stress concentrations (i.e. acting as large crack precursors). This tail is visible in **Fig. 3** with tensile failures as low as 7.67 MPa along with the related broadening of the probability distribution toward the low-strength side.

NBR5 displayed the same tail as well as a lower average strength, likely due to undispersed filler from both the reduced milling as well as the late addition of filler. NBR6 included 10 phr of natural rubber added at the same time as the cure ingredients were added. This was intended to simulate potential hang-up from cleanout batches. The additional polymer added late in the mixing process gave a surprising improvement in the average tensile strength with no noticeable impact on the distribution of values. There was no visible undispersed polymer when dropping batch NBR6 nor at any point during milling.

The micro-dispersion of the NBR batches shows opposite trends based on uncured Payne Effect shown in **Fig. 4** as compared with the macro-dispersion. NBR3, the two-pa0 ss mix, had the greatest Payne Effect (highest ΔG'; worst micro-dispersion) in the uncured state of 1.3 MPa. Whereas the poorly mixed and reduced milling compounds NBR4 and NBR5 had uncured Payne Effects much closer to the control batch. NBR6 had the lowest uncured Payne Effect of 0.57 MPa, likely because the additional polymer (10 phr natural rubber) increased the polymer/filler ratio resulting in less filler-filler interaction.

In the cured state, NBR6 still has the lowest Payne Effect, followed by NBR4 and NBR5. The cured Payne Effect was slightly lower for two-pass mix NBR3 compared to the control NBR2, which was opposite the ranking of these two batches in the uncured state. The Payne Effect increases upon high-temperature annealing due to filler networking/flocculation,[11] so cured Payne Effect is typically significantly higher than uncured Payne Effect due to filler network build-up during the early stages of curing before significant cross-

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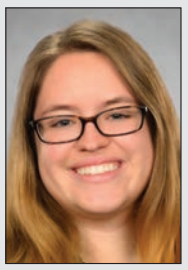
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Table 7: EPDM mixing modifications.

Compound	Mix Time	Mix Modification
EPDM1	5:00	1st Batch
EPDM2	3:30	Control
EPDM3	3:45	80% Fill Factor
EPDM4	4:15	72% Fill Factor
EPDM5	4:15	Drop at 240F
EPDM6	3:15	Drop at 220F
EPDM7	3:40	Upside Down Mix – Filler and Oil 30 sec before polymer
EPDM8	4:45	2 Pass: 2nd pass 3:30 mix w/220F drop
EPDM9	4:00	Minimal Milling – 1 pass through

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linking occurs.

This was the case throughout the present study, but the magnitude of the increase in ΔG' for cured vs. uncured compounds was not systematic. The results shown here indicate quite different compound rankings of micro-dispersion depending on whether uncured or cured strain sweep data are used, which motivates future research to develop a better understanding of the behavior.

The tensile macro-dispersion test showed limited changes for the EPDM compounds (**Fig. 5**) caused by mixing variation, with less than 1 MPa tensile strength separating most of the samples. Except for EPDM5, all other batches possess unimodal distribution in tensile failures with similar distributions shown. The primary variation between batches appears in the horizontal shift of average tensile strength. EPDM8, the two-pass mix, has the greatest tensile strength. EPDM6, with a lowered drop temperature and commensurately lessened mix time has the lowest tensile strength. The strength distributions spanned a tensile strength (x-axis) range from 7 to 12 MPa for the NBR compound mixing effects discussed earlier (**Fig. 3**), in contrast to the mixing-induced changes for the EPDM system that occurred over a much smaller strength window from 4.5 to 6.1 MPa (**Fig. 5**).

The micro-dispersion results for uncured and cured EPDM compounds are plotted in **Fig. 6**. Batches with better macro-dispersion tend to also have better micro-dispersion evidenced by lower Payne Effect, for both cured and uncured states, excepting EPDM6, which has the lowest uncured Payne Effect (best micro-dispersion) while having the worst macro-dispersion by tensile strength distribution. The control batches and two-pass mix have better micro-dispersion while upside down mixing (EPDM7) and reduced milling (EPDM9) gave reduced micro-dispersion (higher ΔG').

Two micron-sized dispersion agents were evaluated in a hydraulic hose CPE tube compound (see **Table 8**). The macro-dispersion via tensile strength distribution is shown in **Fig. 7**. The control compound has a very broad range of tensile failures in addition to a low strength tail, requiring a bimodal Weibull distribution fit, likely due to undispersed carbon black. CPE2 did not show any improvement in this compound, but CPE3 and CPE4 show improvements in both average dispersion (shift of distribution to higher strengths) and reduction/elimination of low-strength tail. Slightly better macro-dispersion was seen with the lesser addition of additive in CPE3 (5 phr) vs. CPE4 (10 phr). There was minor to no impact of the dispersion agents on RPA strain sweep behavior (micro-dispersion), as demonstrated in **Fig. 8**, which is further evidence that micro- and macro-dispersion can have distinct trends for rubber compounds.

Conclusion

Tensile strength distribution and dynamic strain sweeps can

Table 8: Chlorinated polyethylene formulation modifications.

Compound	Formulation Addition
CPE1	control
CPE2	+ 10 phr Fortimix NC3
CPE3	+ 5 phr Spherix 20M
CPE4	+10 phr Spherix 20M

Fig. 1: Measured tensile strength distributions for the three mix procedures of polychloroprene (symbols) and Weibull cumulative distribution function fits (lines) (a). Associated Weibull probability density functions (b).

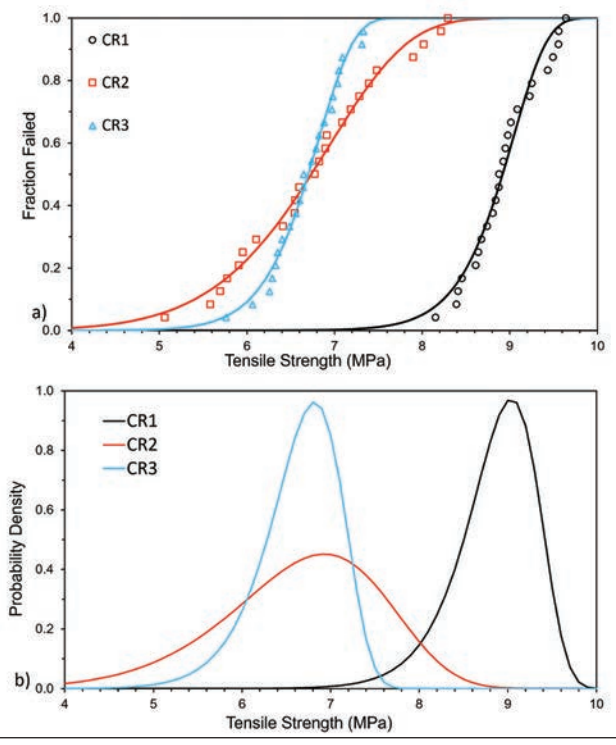


Fig. 2: RPA strain sweep vs. elastic modulus of three polychloroprene mix procedures, cured (solid) and uncured (dash). Calculated Payne Effects for both listed in embedded table.

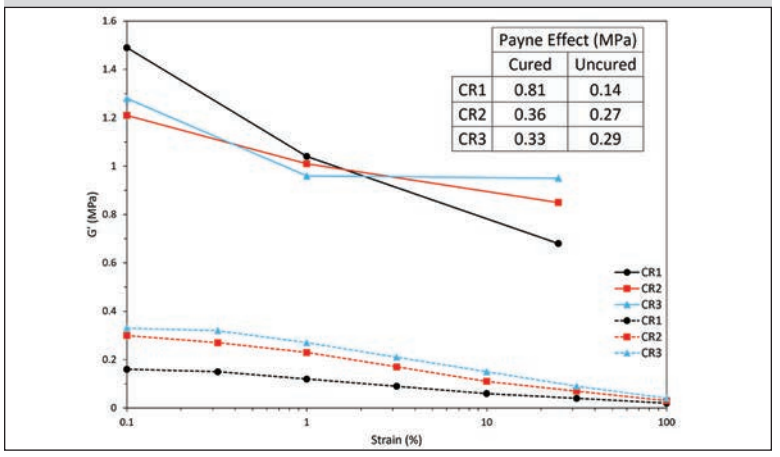


Fig. 3: Measured tensile strength distributions for mix procedures of nitrile-butadiene rubber (symbols) and Weibull cumulative distribution function fits (lines) (a). Associated Weibull probability density functions (b).

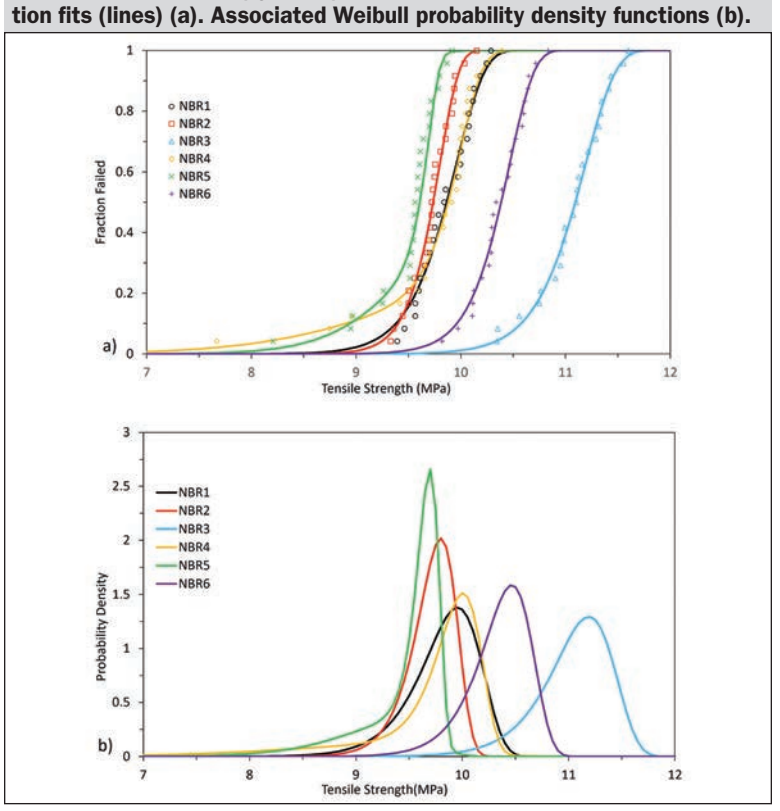
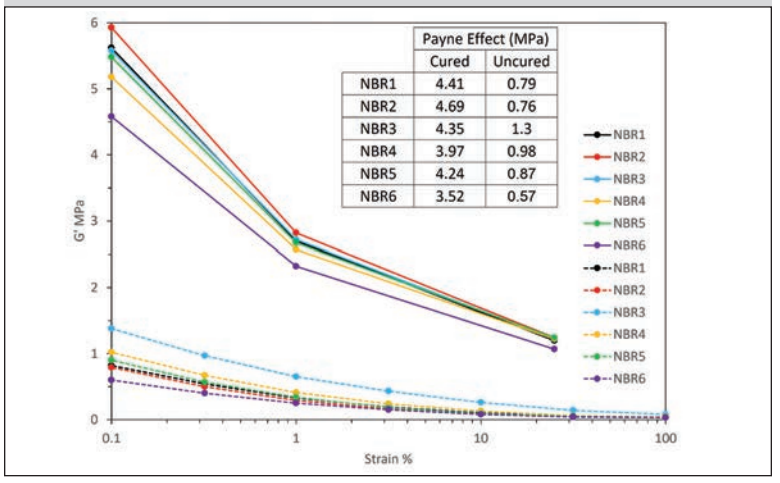


Fig. 4: RPA strain sweep vs. elastic modulus of NBR mix procedures, cured (solid) and uncured (dash). Calculated Payne Effects for both listed in embedded table.



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respectively pick up differences in macro-dispersion and micro-dispersion caused by variations in mixing conditions and compound formulation. A control compound is required, as the testing methods provide relative rather than absolute measures of dispersion. The specific magnitudes of these macro- and micro-dispersion differences are very dependent on the formulation; an EPDM compound shows relatively limited changes in dispersion with mixing method variations, likely because of its high extendibility, whereas an NBR compound shows significant variation with similar adjustments to mixing conditions.

Tensile strength distribution validated macro-dispersion improvements from adding one type of micron-size dispersion aid to a chlorinated polyethylene formulation, with no measurable benefit on micro-dispersion detected using Payne Effect from RPA strain sweep. The macro-dispersion and micro-dispersion of a formulation do not necessarily correlate with each other, which is not surprising as they have distinct physical origins.

This research therefore emphasized the importance of characterizing both types of dispersion.

Fig. 5: Measured tensile strength distributions for mix procedures of EPDM (symbols) and Weibull cumulative distribution function fits (lines) (a). Associated Weibull probability density functions (b).

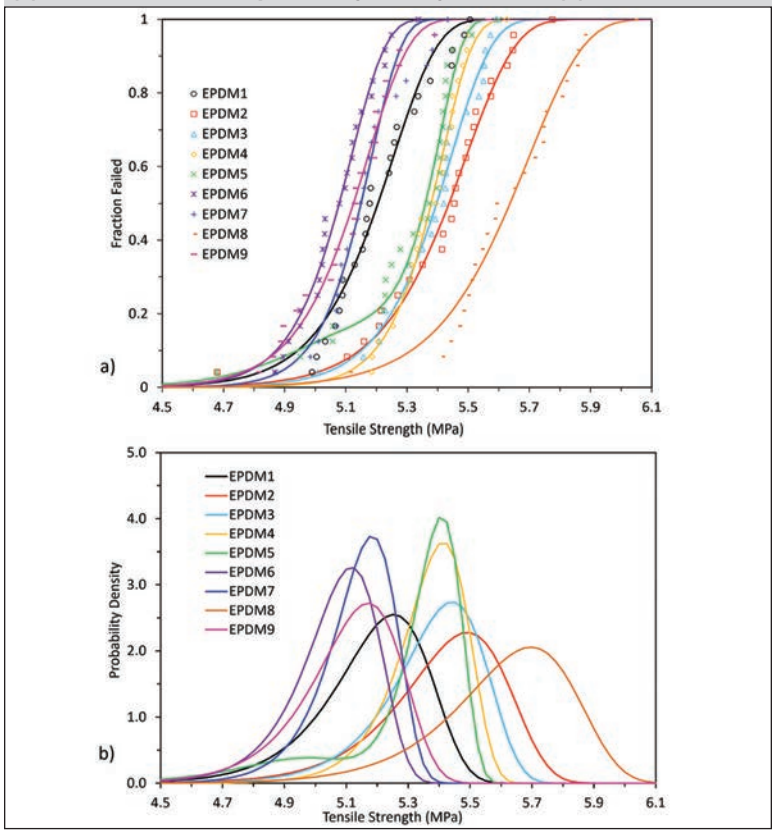


Fig. 6: RPA strain sweep vs elastic modulus of EPDM mix procedures; cured (solid) and uncured (hollow). Calculated Payne Effects for both listed in embedded table.

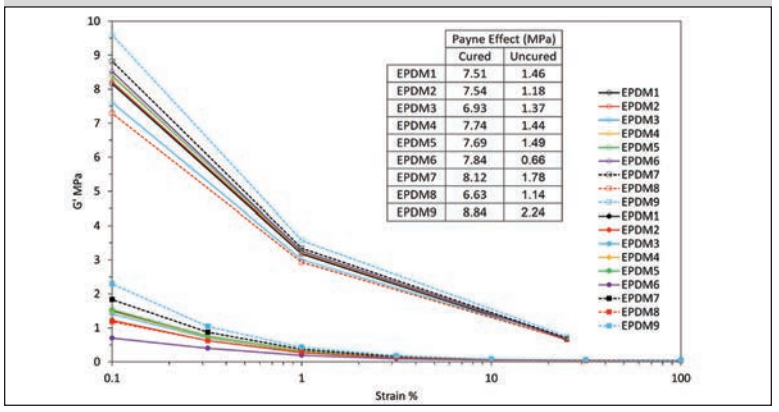


Fig. 7: Measured tensile strength distributions for CPE dispersion agent additions (symbols) and Weibull cumulative distribution function fits (lines) (a). Associated Weibull probability density functions (b).

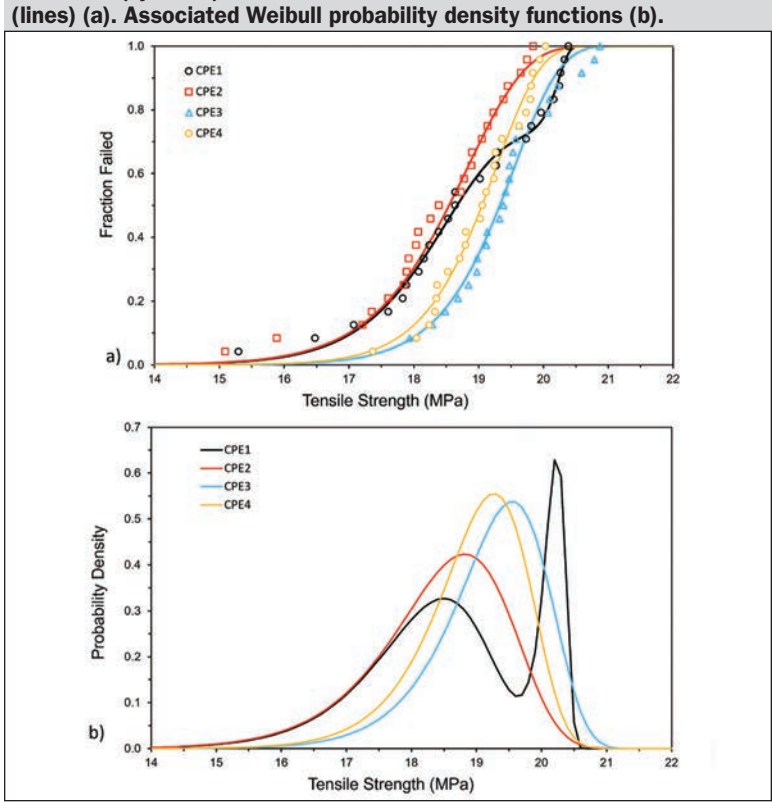
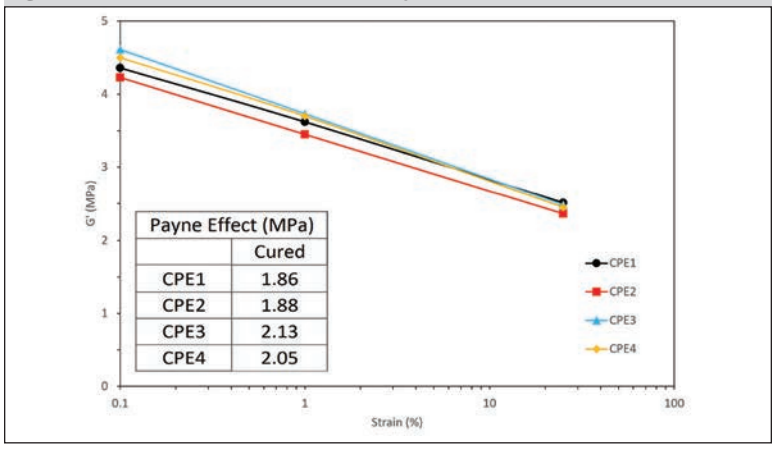


Fig. 8: RPA strain sweep vs. elastic modulus of CPE with added dispersion agents in the cured state. Calculated Payne Effects listed in embedded table.



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