

Paper # 84

Modulus-Fatigue Resistance of Silica-filled Tire Tread Formulations

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Abstract

A modulus fatigue test method was found to be useful for ranking fatigue resistance (damage resistance) of tread compounds. This test method has been reported by Beijing University of Chemical Technology.² The method utilized the Metravib DMA + 150 instrument with multi test software. Tension test specimens were cycled in sinusoidal deformation under load-load control. Four silica tread compounds were compared for modulus fatigue resistance. The same silica tread compounds had been reported earlier.¹ That paper examined the effect of mix time and functionalized S-SBR on key properties. It was shown that extra mix time increased tensile strength and tangent delta at 30°C and functionalized styrene butadiene rubber (F-S-SBR) polymer increased tensile and reduced tangent delta at 30°C. In this work, it was found that extra mix time and F-S-SBR polymer, in general, improved fatigue resistance. The test appeared to be able to rank fatigue resistance of tire tread compounds; particularly, by modulus retention and tangent delta change (around 2×10^5 to 5×10^5 cycles). There appeared to be change in damage mechanics around 3×10^5 cycles. Compounds with extra mix time and functionalized polymer exhibit better retention of properties (resistance to damage).

Experimental Techniques

Compound Formulations: Four SBR compounds were prepared as shown in Tables 1 and 2. Compounds 1 and 3 are both S-SBR compounds while compounds 2 and 4 are both F-S-SBR compounds.

| Table 1: General Description of Compounds | |
|---|--------------------------------------|
| <i>ARDL NB#</i> | <i>Description</i> |
| JEMNB1-1-1 | Control (with extra mix time) |
| JEMNB1-1-2 | Functionalized (with extra mix time) |
| JEMNB1-1-3 | Control |
| JEMNB1-1-4 | Functionalized |

Silica tread performance was studied in a two variable/ two level designed experiment. The two variables were polymer functionality and mix method. The first polymer was a functionalized solution styrene butadiene rubber (F-S-SBR). The second polymer was a non-functionalized solution styrene butadiene rubber (S-SBR). In this experiment, the Sprintan[®] SLR 4602 – Schkopau (F-S-SBR) was compared to the Lanxess Buna[®] VSL 5025-0-HM (S-SBR). Secondly, two mix methods were compared. These methods were with and without extended mixing time in the first and second passes.

The compounds were mixed in a Farrel BR lab Banbury. All four compounds were mixed in a three pass process. For the first pass, the rotor speed was 65 rpm, the starting temperature was 65°C, and the ram pressure was 50 psi. The rotor speed was increased to ramp the temperature to 160°C by the 4.5' mark. For the first two compounds, there was a two minute extra hold time at 160°C before dropping. For the third and fourth compounds, there was no extra mixing time once 160°C was reached. The mixed rubber was sheeted out on a two roll mill. For the second pass, the rotor speed, starting temperature, and ram pressure were the same as for the first pass. The rotor speed was increased to ramp the temperature to 140°C by the 3.5' mark. For the first two compounds, there was a four minute extra mix time at 140°C before dropping. Again there was extra mixing time for the third and fourth compounds. The mixed rubber was again sheeted out on the two roll mill. For the final pass, the rotor speed was 60 rpm, the starting temperature was 50°C, and the ram pressure remained at 50 psi. Here, there was no hold for any of the compounds. They were all dropped when the temperature was 110°C, which was near the 2.5' mark. The rubbers were then sheeted out on the mill again.

| NB # | | jembn1-1-1 | jembn1-1-2 | jembn1-1-3 | jembn1-1-4 |
|--------------------|--|------------|----------------|------------------------|-------------------------------|
| Description | | Control | Functionalized | Control (no hold time) | Functionalized (no hold time) |
| ingredient | Description | phr | phr | phr | phr |
| First Pass | | | | | |
| Buna VSL 5025-0 HM | S-SBR, 37.5phr TDAE, high vinyl (67% of BD), 25% S | 75 | | 75 | |
| SLR-4602 | tin coupled F-S-SBR | | 75 | | 75 |
| Budene 1207 | PBD rubber | 25 | 25 | 25 | 25 |
| N234 | Carbon Black | 15 | 15 | 15 | 15 |
| Ultrasil 7000 GR | Silica | 65 | 65 | 65 | 65 |
| Si266 | Coupling agent | 5.2 | 5.2 | 5.2 | 5.2 |
| Aromatic Oil | Sundex 790 | 24 | 24 | 24 | 24 |
| stearic acid | | 1.5 | 1.5 | 1.5 | 1.5 |
| Second Pass | | | | | |
| master batch 1 | MB1 | 210.70 | 210.70 | 210.70 | 210.70 |
| zinc oxide | Cure activator | 1.9 | 1.9 | 1.9 | 1.9 |
| Okerin wax 7240 | microcrystalline wax | 2 | 2 | 2 | 2 |
| Santoflex 6PPD | 6PPD | 2 | 2 | 2 | 2 |
| Wingstay 100 | diphenyl p-phenylene diamine | 0.5 | 0.5 | 0.5 | 0.5 |
| Third Pass | | | | | |
| master batch 2 | MB2 | 217.10 | 217.10 | 217.10 | 217.10 |
| sulfur | Cross-linker | 1.05 | 1.05 | 1.05 | 1.05 |
| Santocure CBS | Accelerator | 0.91 | 0.91 | 0.91 | 0.91 |
| Perkacit DPG-grs | Accelerator | 1.05 | 1.05 | 1.05 | 1.05 |

Banbury Mixing: A Farrel BR mixer with steam heating/water cooling which is instrumented with computer monitors for temperature, rpm, power, and integrated power.

Curing: The compounds were cured $T_{90} + 5$ minutes at 320°F (160°C).

Dynamic Mechanical Analysis (Multi Test Deformation): Metravib DMA150 Dynamic Mechanical Analyzer was used for Multi Test Deformation for the four compounds. The experimental conditions were tension load-load control approximately 0.05 N/m² to 0.15 N/m² dynamic strains at 50°C and 10 Hz under sinusoidal deformation for 15 hours.

Results

The dynamic mechanical properties were measured as a function of the number of cycles for four compounds. Storage modulus, tangent delta, and loss compliance were plotted and compared to determine the effect of mix method and polymer type on fatigue resistance. These particular properties are important for tire performance. Storage modulus is a predictor for dry handling. Tangent delta is a predictor for rolling resistance. Loss compliance is a predictor for dry traction.

All the compounds exhibited loss of modulus as a function of the number of cycles. The compounds with extra mix time had better modulus retention during the later stage (2×10^5 to 6×10^5 cycles). The compounds with extra mix time had lower modulus than compounds without extra mix time. The compounds with functionality (F-S-SBR) had higher modulus than compounds without functionality (S-SBR).

Figure 2 depicts the percent-retained storage modulus for the four compounds. The normalized modulus (normalized by its original storage modulus) was comparable; however, the compounds without extra mix time appear to be decaying faster during the later stage (2×10^5 to 6×10^5 cycles).

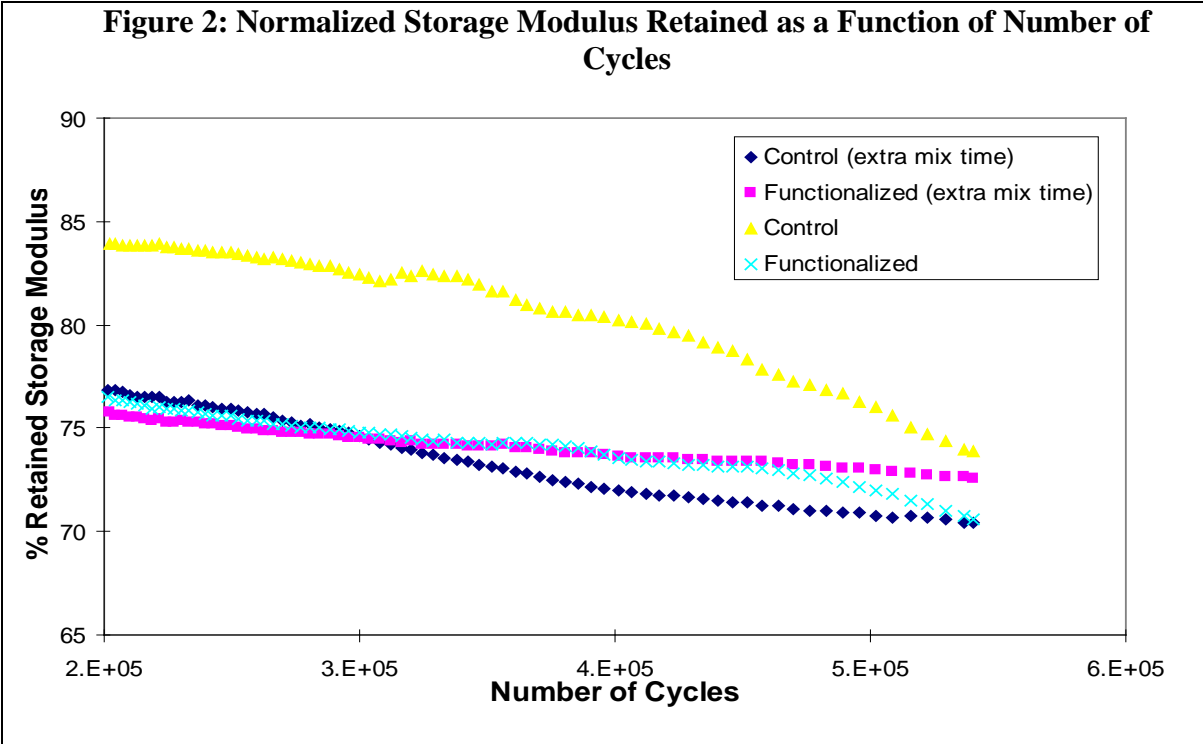
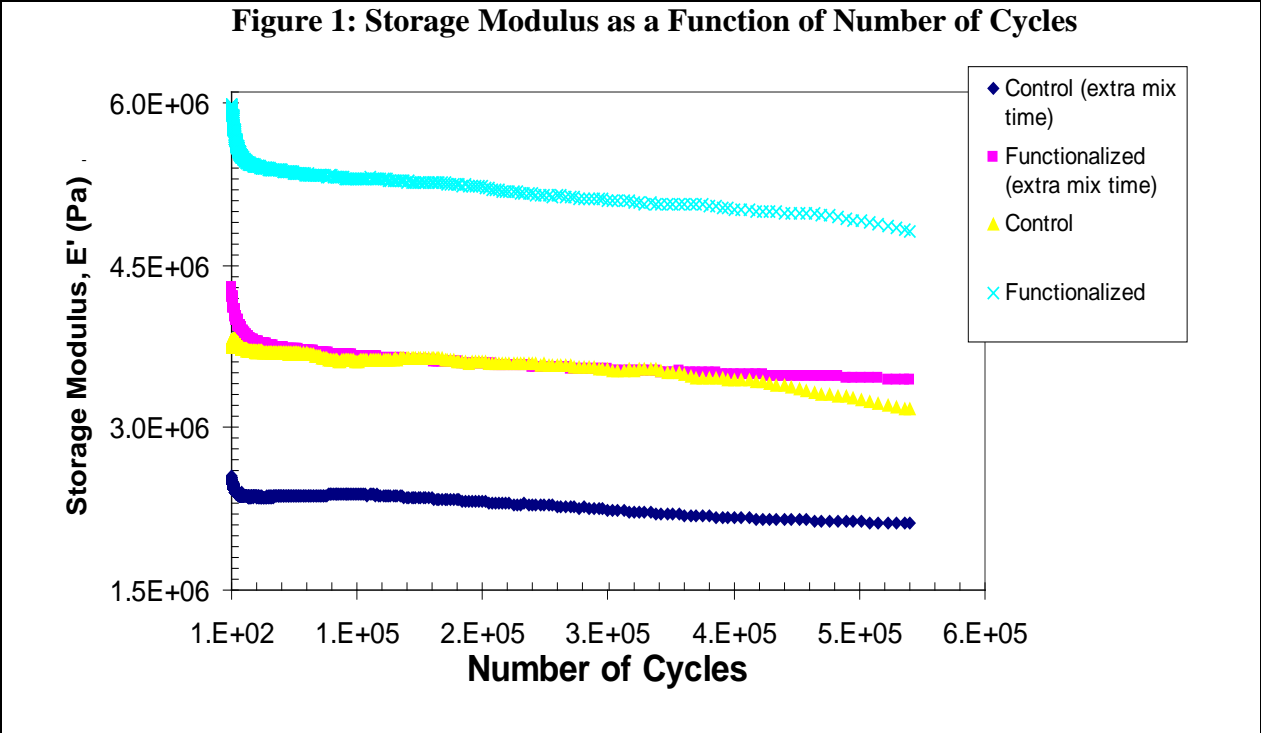


Figure 3 displays the tangent delta results as a function of number of cycles. All compounds decrease in tangent delta with cycles (presumably improved rolling resistance during service). This was the case for the first 3×10^5 cycles; afterward, the tangent delta

increased (between 3×10^5 to 5×10^5 cycles). Presumably the change in slope is associated with a mechanism change. Possibly the changes for the compounds during the first stage (0 to 3×10^5 cycles) was mechanical softening from filler-filler breakdown. Afterward the mechanism involves a more permanent, non-recoverable, damage associated with tangent delta increase and modulus decrease. The compound with functionalized polymer had lower tangent delta than the control. The extra mix time compound had lower tangent delta than the compound with standard mix time, for the compounds with functional polymer.

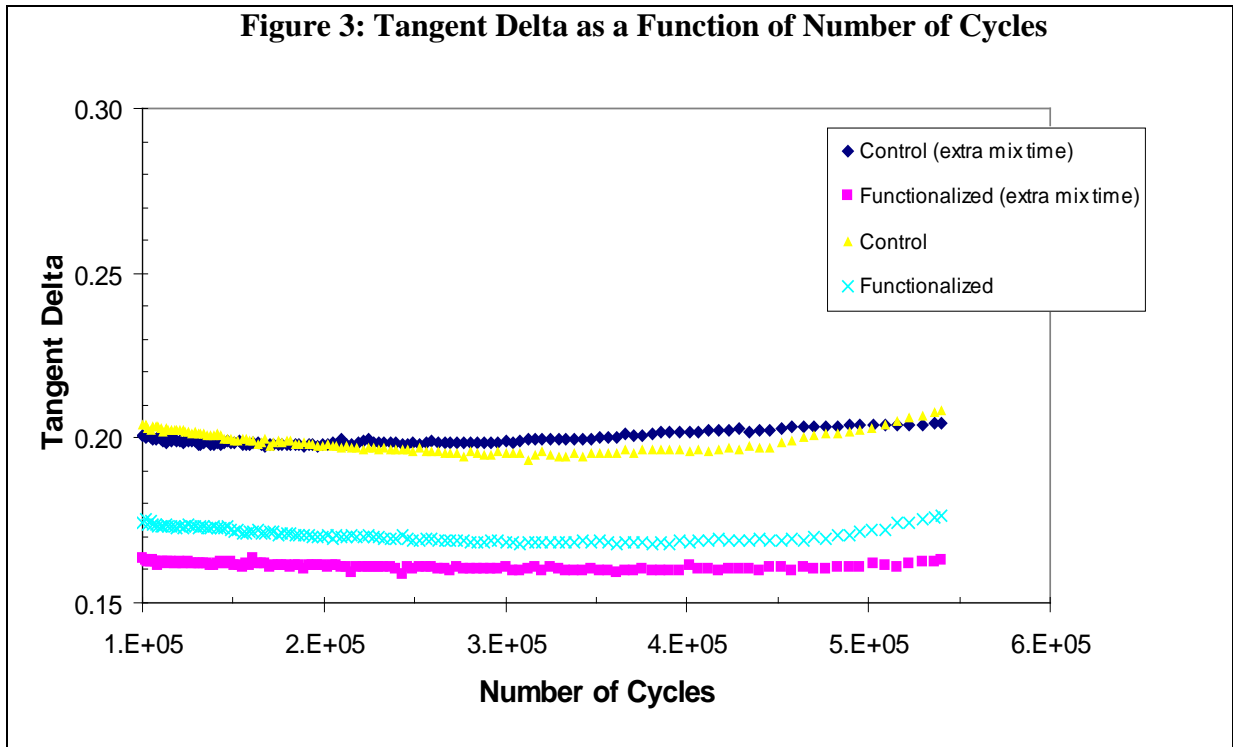
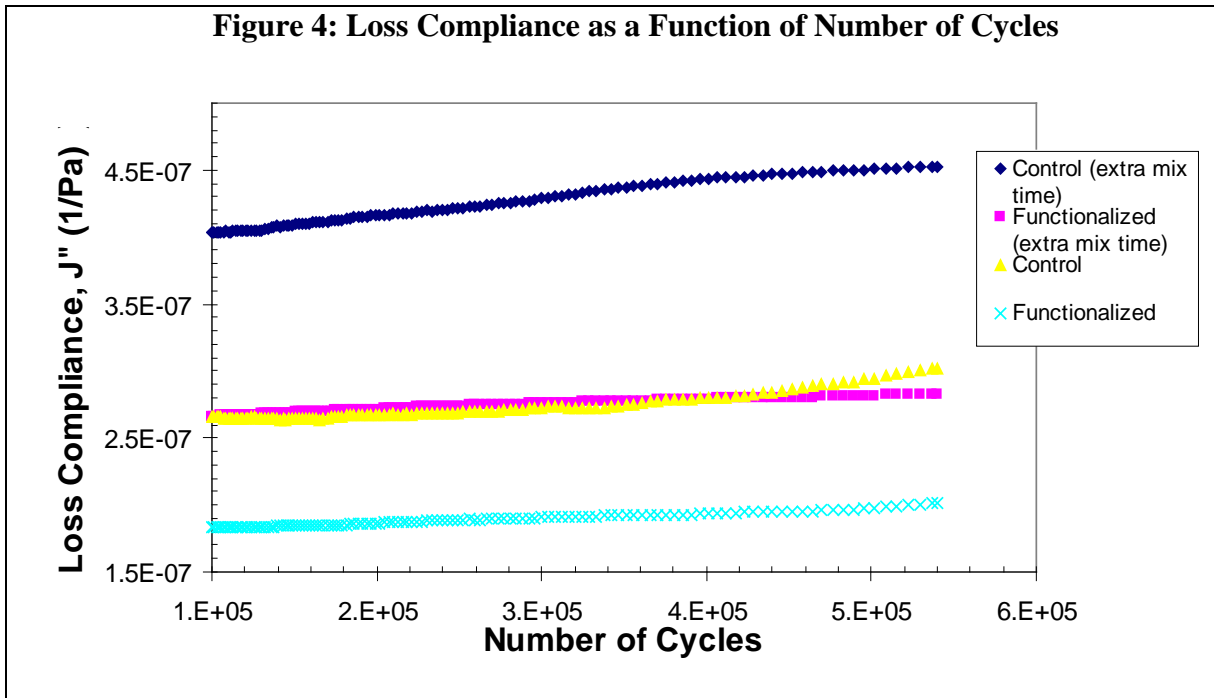


Figure 4 shows loss compliance as a function of number of cycles for the four tire specimens. This plot may help predict effect of fatigue on dry traction. The functionalized specimen had a steady increase through the whole process while the control greatly increased near the end, around 5×10^5 cycles. Presumably, the results show that the more mixing time improved the dry traction. Also the control compound, specimen had higher results. All the compounds increased in loss compliance during the fatigue process.



Conclusion

Three tire performance predictors (storage modulus, tangent delta, and loss compliance) were studied as a function of fatigue. The polymer type and mix method contributed differently to the factors of dry handling, rolling resistance, and dry traction. Storage modulus was calculated for dry handling. The functionalized Sprintan[®] compound with and without extra mix time gave the best results, but retained the least of its original. Each of the specimens lost modulus during the cycles, showing weakening of the tire and loss of dry handling. The control specimen without extra mix time retained the most storage modulus throughout fatigue. This combination of the control polymer type and less time mixing method proved to resist softening the most throughout the cycling process.

The tangent delta was graphed to give insight on the rolling resistance of the different polymer types and mixing methods. All compounds first decreased in tangent delta, improving the rolling resistance during cycling, until the end of the test. The polymers without extra mix time had a greater increase in tangent delta around 5×10^5 cycles, proving less mix time might help rubber retain rolling resistance during a long fatigue process. Figure 3 showed that the functionalized Sprintan[®] compound with more mixing time was the best specimen when comparing rolling resistance. The amount of mixing time on the Buna[®] mix, the control specimens, did not seem to effect rolling resistance.

Finally, the loss compliance graph proved the control Buna[®] mix with more mixing time to be the best. This compound started with the highest loss compliance and only improved throughout the 15 hours of the cycling process. Loss compliance increased during cycling for all four specimens, but the control with extra mix time had the greatest increase. This proves that with more mixing time, making the tires less rugged, improves

dry traction in both polymer types and mix methods. However, the control polymer proved better with a peak in loss compliance near the end of the test, around 5×10^5 cycles.

Therefore, rolling resistance and dry traction actually improve during the main part of the fatigue test, associated with mechanical softening from filler-filler break-down, and would improve during service. However, after about 3×10^5 cycles mechanism involved a more permanent, non-recoverable, damage associated with tangent delta increase and modulus decrease. Storage modulus worsened and was lost for all four compounds during cycling. As a conclusion on the mix time, it is seen that the longer mix time gives a reduction in tangent delta, which good for rolling resistance, but has a slight loss in wet and ice traction, handling, and treadwear. The functionalized Sprintan[®] compounds offer advantages in winter traction and fuel economy but the control Buna[®] compounds offer advantages in dry handling and treadwear. The figures indicate one compound does not offer advantages over the other in ice traction, wet traction, and dry traction.

References

1. Jonathan E. Martens, Edward R. Terrill, and James T. Lewis, Paper No 71 “Effect of F-S-SBR in Silica Tire Tread Formulation” Presented at the Fall 180th Technical Meeting of the Rubber Division American Chemical Society, Cleveland, OH, October 11-13, 2011.
2. Shipeng Wang, Fazhong Zhang, Xiuying Zhao, Liqun Zhang, Li Liu, “Filler Network of SiO₂/NR(SBR) Composites under Fatigue Process” Presented at the Spring 181st Technical Meeting of the Rubber Division American Chemical Society, Spring, 2012.

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