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Surfactants Containing Zinc Ion in Tire Compounding

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ABSTRACT

The addition of fatty acids, which react with zinc oxide during processing and curing, is the standard method to activate the cure. In addition to the cure effects there are many side benefits associated with the resulting reaction product. How to enhance these side benefits by the addition of prereacted zinc anionic surfactants will be discussed for tire compounding. The effect on filler addition, viscosity, mixing and extrusion, and physical properties will be shown for one class of fatty acid surfactant. These examples will include a discussion on the effect this class has on dynamic properties associated with tire performance.

Key words: Zinc carboxylates, surfactant, black incorporation, dispersion, dynamic properties, tire compounding.

INTRODUCTION

The use of fatty acid chemistry in rubber compounding is generally thought of in terms of the activating effect of the zinc oxide/fatty acid on the cure system [1, 1a]. The solubility of zinc carboxylate is thought to control bloom and modulus. Limited mention in these types of standard reference texts is found about how the processing or other physical properties of the rubber compound is affected by the fatty acid and its concentration or its resulting zinc carboxylate [2]. In addition to the use of fatty acid, and allowing it to react with zinc oxide during processing and curing, there are materials available where the zinc carboxylate is prereacted. These materials are made from varying acids, which include a range of naturally occurring acids with varying chain length and unsaturation. There are also materials available with synthetic acids. The structure and the concentration control the effects seen in compounding [3, 4]. Structural effects have been seen in diverse areas such as filler addition during mixing, scorch, viscosity, cure efficiency, and reversion control. In general, the response has been linear to concentration up to the studied limit of 10 phr. In commercial compounding, the stearic acid and/or the zinc carboxylate is added in the 1-5 phr range.

The role of zinc in vulcanization has been explained by its ability to form complexes utilizing the D orbits. The other effects during processing have utilized surfactant terminology [1a, 5]. With carboxylates, the surfactant is considered to be anionic. These structures are amphiphilic with a hydrocarbon end that is highly oil soluble and an ionic polar end. With the divalent zinc stearate, the solubility at room temperature is quite low because of the highly crystalline C16-C18 chain. On cooling, small micelles are thought to form which causes surface bloom and varying stiffness as a function of micelle size [1a]. In this paper, the role of a modified surfactant zinc soap with decreased crystallinity, and also containing a monovalent anionic surfactant, will be explored in compounding.

EXPERIMENTAL

The compounding mixer was a Brabender 2000 Plasticorder equipped with a head which mixes about 60 grams material. A Farrel BR size 1600 ml mixer was used to make standard batches for physical testing. The compounds were mixed by standard mixing methods. The dynamic properties were obtained with an Instrumentors MER 1100B. The blackness of the compound was determined with a Minolta Spectophotometer CM 508D. The formulations, including fillers, rubber, and cure systems, are typical of various tire compounds. The additive STRUKTOL® EF 44A is a surfactant blend of a soluble fatty acid and zinc ion.

DISCUSSION AND RESULTS

Rubber processing takes place in several discrete stages. Key to the first phase is the use of an internal mixer to mix and disperse the loose fillers and chemicals into the rubber matrix. This is followed by milling, extrusion, calendering, building, and curing into a final shape, each of which has their own process issues. Because the materials change physical state at the first stage and show non-linear viscoelastic behavior at all stages, predictions of processing are difficult. The biggest changes in material physical state occur during the filler incorporation and dispersion. The surface area, structure, and loading of the filler influence processibility issues of incorporation time, dispersion, viscosity, and die swell [6]. There is evidence that additives can influence dispersion [7] and tire grip properties [8]. The faster incorporation and dispersion affects mixing productivity, and the improved dispersion reflects in improved tire properties such as rolling resistance, tread wear, and traction [9].

Torque curves from three types of tire grade blacks show some of the differences expected (**Figure 1**). The black incorporation peak and the rate of dispersive mixing as well as the temperature rise is influenced by the black structure. When small amounts of EF 44A are added, there is a shift in the incorporation time, coupled with a significant drop in torque (**Figures 2, 3**).

The dispersion rate constant obtained from the torque curve after the incorporation peak shows a significant increased dispersion (**Figures 4, 5**). This faster rate of dispersion is reflected in the blackness [9] of the compound (**Figure 6**) and in bound rubber content (**Figure 7**). The torque curve is related to the viscosity and the undispersed carbon black (**Figure 8**) with the blank containing no additive and stearic acid used as a control.

Zinc soaps have been used to adjust the viscosity of rubber. This viscosity reduction is close to being linear with concentration [3]. What was not recognized then was the viscosity effects might have been due to both dispersion and micellar lubrication. The polymer (especially high Mw NR) also undergoes some shear induced breaking during processing. With EF 44A there was little difference, with or without, in molecular weight for the rubber, but the gum stock Mooney viscosity was about 18 points lower with 3 phr of EF 44A [10]. With chemical peptizers there is more chain breakage, which results in lowering of dynamic properties.

The unvulcanized filled systems show changes in tan delta during dynamic strain testing along with little change in storage modulus (**Figures 9 through 12**). These stocks show higher dissipation energy, lower viscosity, and much better processibility. The stocks with EF 44A, after a simple shear test, show the improved viscoelastic characteristics (**Figure** 13). The processing influence extends to silica filled systems [4a] (**Figure 14**), which are extensively being studied for improved rolling resistance.

The resulting compounds show excellent physical properties after cure. An example for an off the road NR formulation with N220 black and silica shows higher storage modulus and lower loss modulus with EF44A. The loss compliance (**Figure 15**) and tan delta (**Figure 16**) show this compound should produce lower heat build up and improved rolling resistance.

Even though the use of fatty acids in rubber compounding is universal because of sulfur curing requirements, the total understanding of all the things that they do physically in compounding is poorly understood. The use of surfactant type materials is thought to work through micelle formation and wetting. The rapid wetting of the filler allows for the rapid displacement of air, which increases the contact between the filler and rubber. The solubility of the soap in rubber is controlled by the nature of the hydrophobic portion of the molecule, while the wetting is controlled by the anionic strength of the cations used to make the soap. The zinc cations allow for both processing and curing interactions. These materials are generally used at low levels in the compound, but are significant in how they influence many aspects of compounding and processing.

CONCLUSION

Low levels of a fatty acid anionic surfactant (STRUKTOL® EF 44A) influences compounding and processing of tire compounds. The fillers are more rapidly incorporated and dispersed. The viscoelastic related processing issues, such as release, extrusion pressure, and flow, are greatly improved. Many of the cured characteristics required for improved tire performance are enhanced. These include heat build up and rolling resistance.

ACKNOWLEDGMENTS

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LIST OF FIGURES

Figure 1. Mixing charts for various carbon blacks in s-SBR

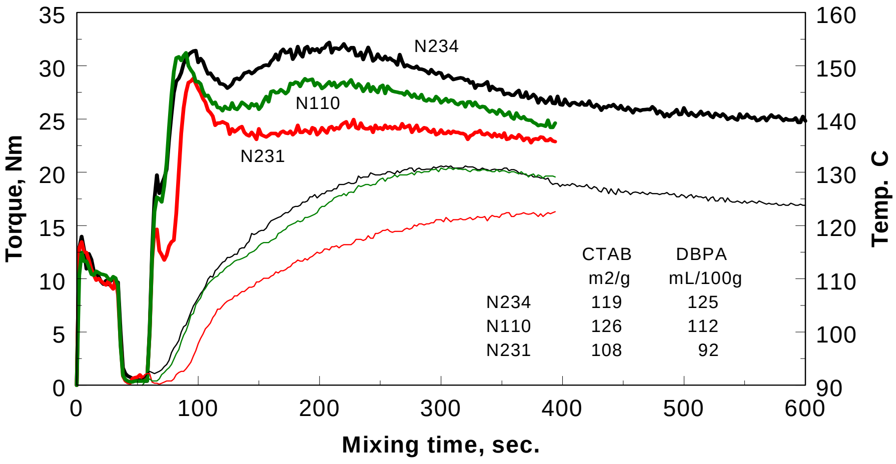


Figure 2. Brabender mixing charts for SIR 20 and N110 with EF44A

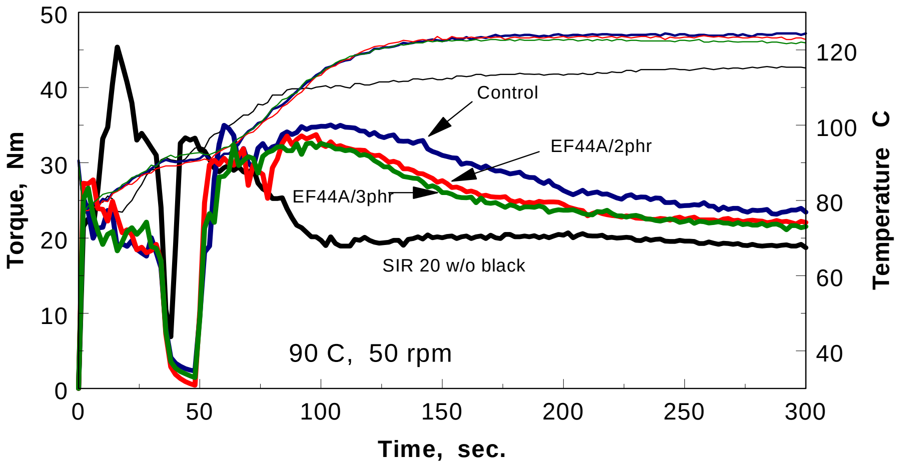


Figure 3. Brabender mixing charts for SBR/BR/NR blend N110 with EF44A

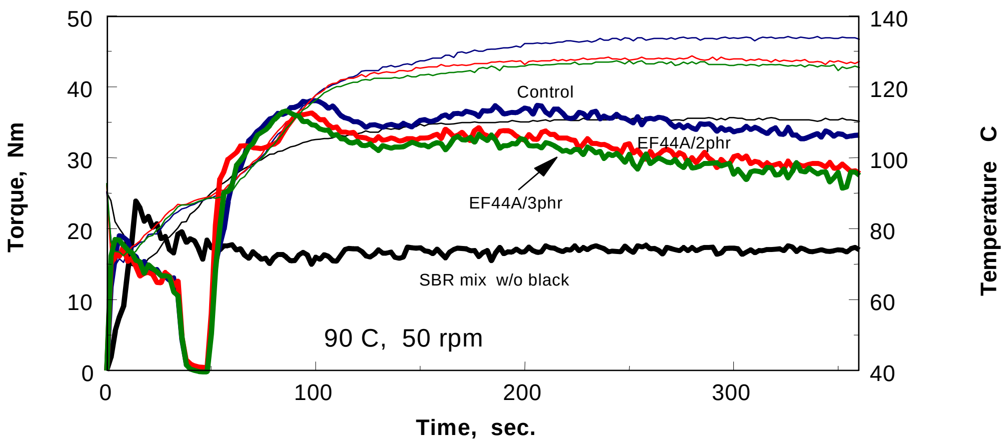


Figure 4. Derivation of dispersion rate constant, k of NR/N110 with EF44A

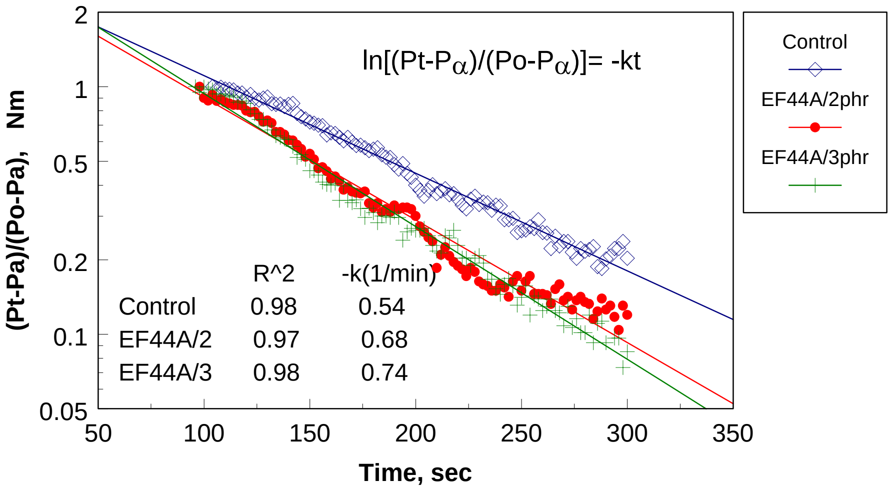


Figure 5. Derivation of dispersion rate constant, k of SBR/BR/NR/N110 with EF44A

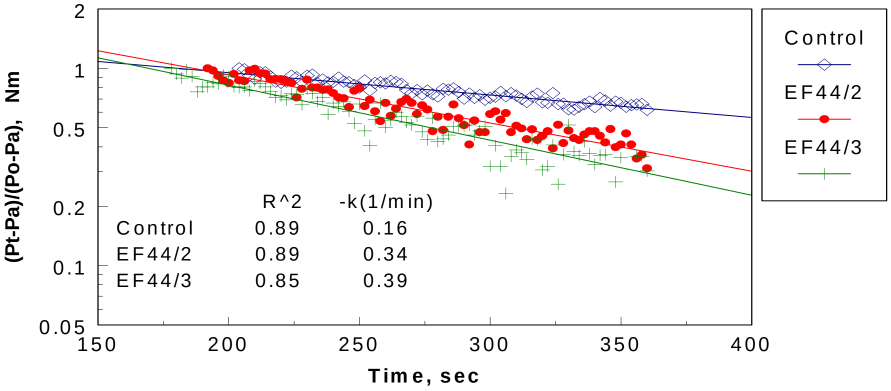
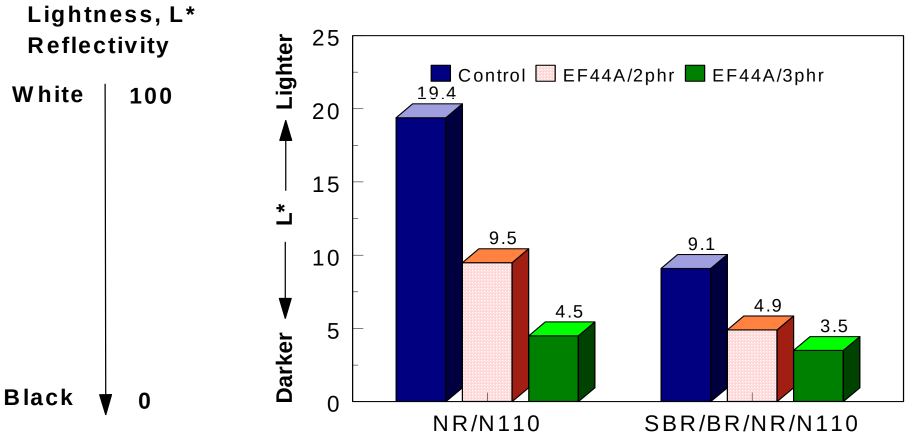
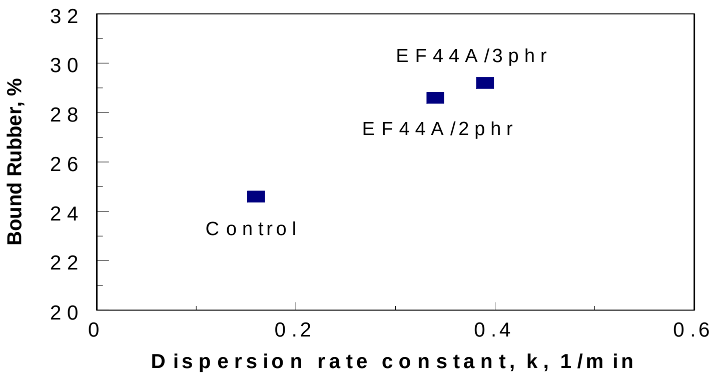


Figure 6. Dispersion rating by Spectrophotometer, Lightness(L*)



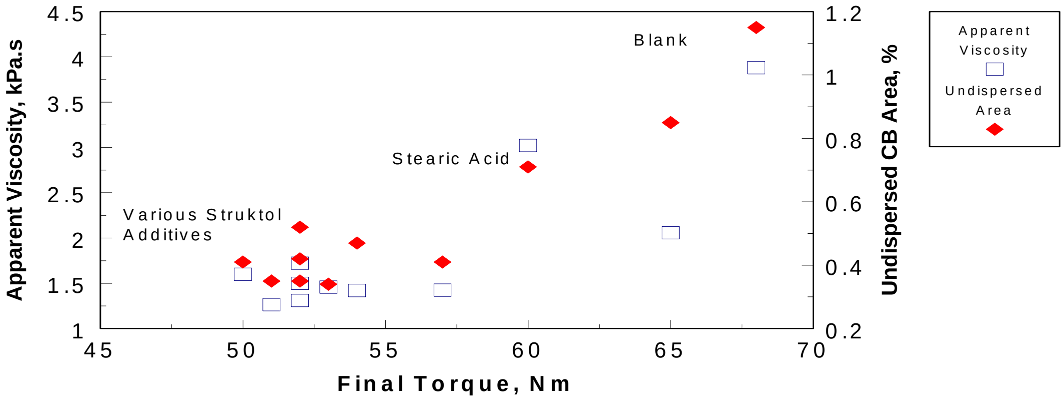
5 min. mixing for NR, 4min. for SBR blends

Figure 7. Bound rubber vs. dispersion rate constant for SBR/BR/NR/N110



SBR/BR/NR

Figure 8. Correlation of apparent viscosity and undispersed area to final mixing torque



96001, s-SBR/N234

Figure 9. Storage modulus G' on unvulcanized SBR/BR/NR/N110 componds

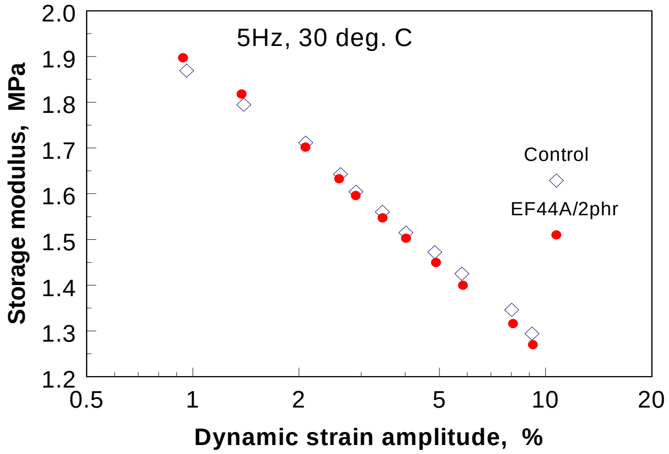


Figure 10. Tan delta on unvulcanized SBR/BR/NR/N110 componds

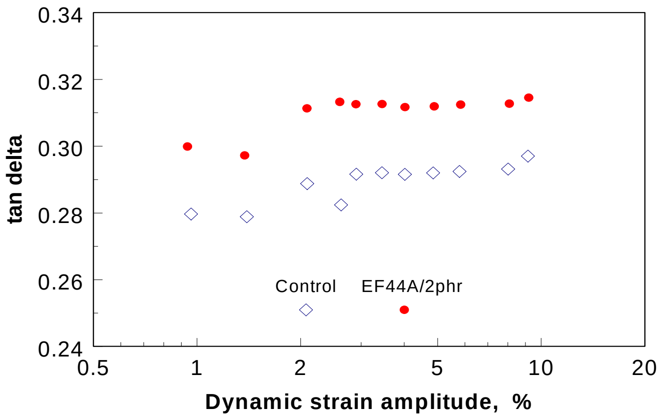


Figure 11. Storage modulus G' on unvulcanized NR/BR blend with N330 carcass compounds, double shear test at 50 deg. C, 2Hz, 80% DSA

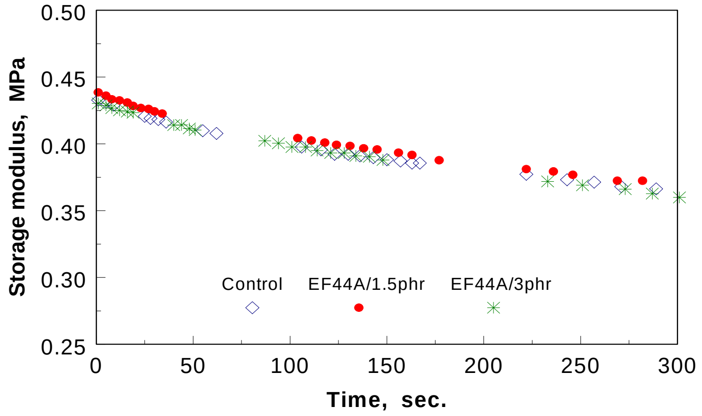


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Figure 12. Tan delta on unvulcanized NR/BR blend with N330 carcass compounds, double shear test at 50 deg. C, 2Hz, 80% DSA

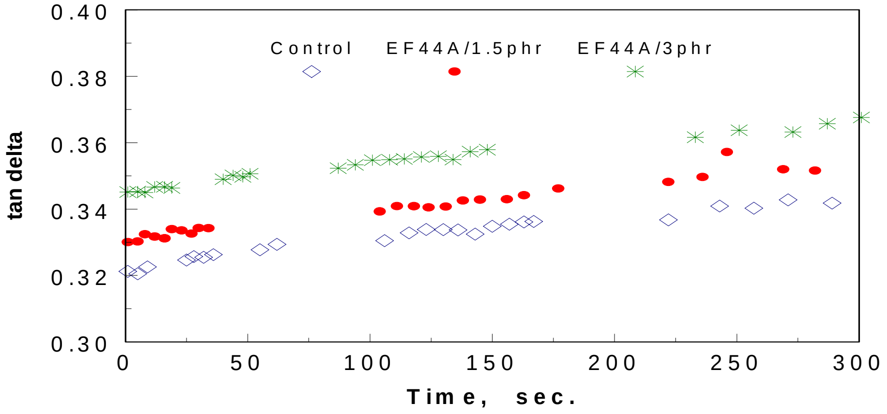

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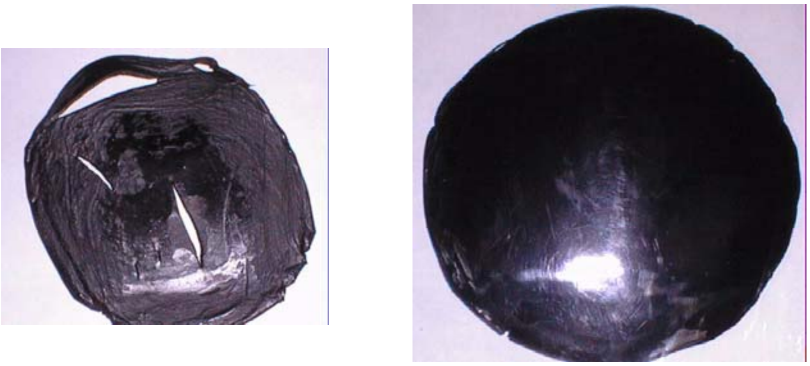
Figure 13. Surface appearance for SBR/BR/NR/N110 compounds

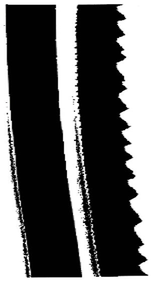


Control

EF44A/3phr

Figure 14. The comparison on extrudates of silica compounds

- 80 phr silica
- cold extrusion
- 70 rpm
- Pressure bar
  - EF44A : 43
  - Control : 54
- Surface appearance
  - EF44A : 9A
  - Control : 5B



EF44A Control

Figure 15. Loss compliance data for cured OTR tread from dynamic compression test at 100C, const. stress, 0.39 MPa

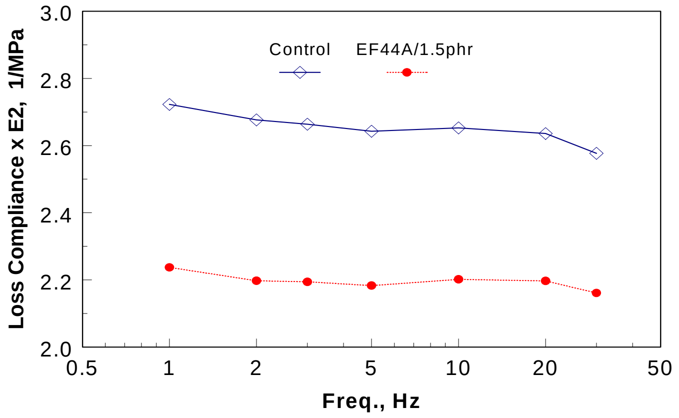


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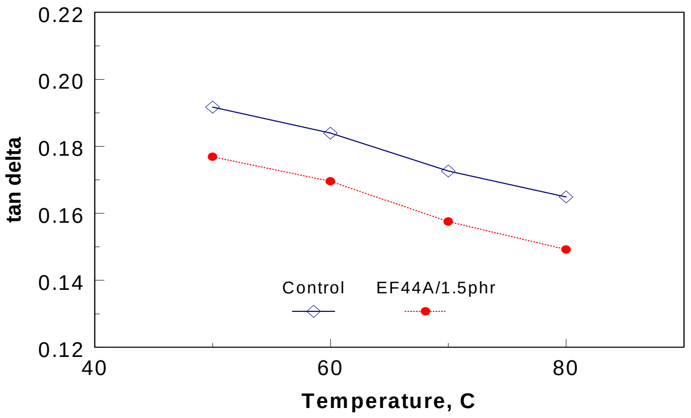
Figure 16. Tan delta data for cured OTR tread from dynamic compression test at 5 Hz, const. stress, 0.29 MPa



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