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Crystex Cure Pro: The next generation of insoluble sulfur

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Achieving better productivity and long-term operational cost savings with the next generation of insoluble sulfur: Crystex Cure Pro

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Around the globe, tire manufacturers are under growing pressure from regulators and consumers to develop more fuel efficient tires, while facing internal demands to stay competitive in an increasingly crowded market. As a result, many tire makers are tweaking their compounds while also looking for ways to get more done with existing assets. From process improvements to new technologies, tire manufacturers are trying a variety of strategies to enable productivity improvements, while enhancing the fuel efficiency of their tires.

There is a new insoluble sulfur technology that supports the creation of more complex compounds for better rolling resistance and a lighter weight, while also boosting productivity. Eastman Crystex insoluble sulfur has been the industry standard for rubber vulcanization for over 60 years. Cure Pro, the newest addition to the Crystex product line, has multiple unique features that work together to enable incremental productivity gains in the rubber compounding process that lead to meaningful operational cost savings in the long term. With faster dispersion, enhanced thermal stability, superior flow and improved efficiency (less oil and more sulfur), Cure Pro has attributes that set it apart from other rubber vulcanization agents.

Enhanced dispersion - faster incorporation provides more time for mixing

One of the characteristics that contributes to productivity and operational cost savings is the ability of Cure Pro to disperse faster than conventional products. This new technology helps minimize particle compaction while speeding incorporation of the insoluble sulfur into the rubber compound. The improved dispersion of Cure Pro contributes to better productivity and the production of higher quality tires.

To evaluate dispersion, Eastman developed a mill test to demonstrate the improved rate of incorporation along with reduced

tendencies for particle agglomeration and compaction. For the test, a rubber compound is banded on a mill and an excess of sulfur is added to exaggerate agglomeration tendencies. After a finite time of milling, the rubber is stripped from the mill and folded along the mill circumferential direction. Cross cuts are made to expose the interior of the rubber slab. By comparative analysis to conventional Crystex insoluble sulfur products HSOT20 (high stability grade IS) and HDOT20 (high dispersion grade IS) (figure 1), it is evident that Cure Pro yields better dispersion with far fewer agglomerates compared to conventional products.

Good dispersion of any material into rubber requires three successful steps. The material must become engulfed in the rubber, distributed evenly throughout the compound, and dispersed into fine particles. The last two steps cannot happen until the first step is completed. Plant scale mixing operation times are limited by “time to mix” or a “temperature-limit” fail-safe criteria; i.e., a mixer batch will be discharged either at the time limit or when the mixer thermocouple measures the temperature-limit criteria, whichever comes first. Hence, incorporation time is critical to rapid dispersion. Materials that incorporate faster have a longer time to experience the mechanical shearing action in the mixer before the batch temperature or time limits trigger the end of the mix. Using the mill test to evaluate incorporation time clarifies one of the benefits of using Cure Pro. Figure 2 shows the mill incorporation test at the completion of the Cure Pro incorporation. It can be seen that significant quantities of HDOT20 remain unincorporated when Cure Pro is completely incorporated. Incorporation can be observed in the mill study; Cure Pro incorporation time is 15% to 30% faster. Faster incorporation means more time for mixing before the mixing cycle ends, leading to opportunities for shorter mixing cycle times.

In addition to observing incorporation time, the mill test allows observations of how well the insoluble sulfur incorporates into the compound. Maximum physical properties are generally

Figure 1 - mill test demonstrating reduced tendencies for agglomeration and compaction for HDOT20 and Cure Pro

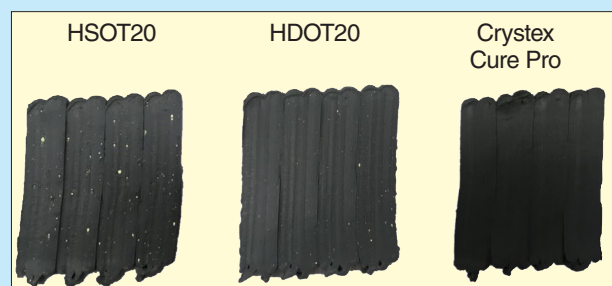
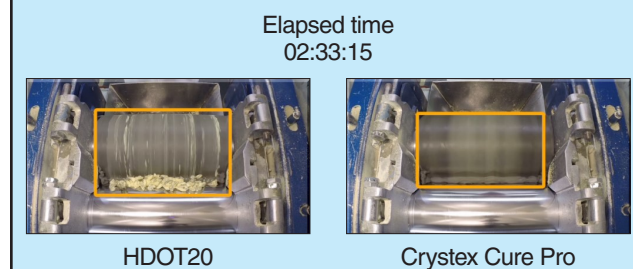


Figure 2 - timing incorporation in mill mixing demonstrates that Cure Pro provides significant improvements to incorporation time



observed when all the ingredients of a compound are both distributively and dispersively mixed well. Distributive mixing refers to a more macroscopic, but uniform, distribution of material in the compound. For distributive mixing, uniformity in material concentration or distribution on a typical scale of cubic centimeters is the most critical factor. That being the case, replicate rheometer testing will show little variation in cure characteristics within a sample set from the same well-distributed mixer batch. Dispersive mixing refers to a more microscopic or even nanoscopic scale. In poor dispersive mixing, larger particles, agglomerates, aggregates or concentrations of materials or chemicals within a small localized region of the compound are observed. These small regions can be about 25-100 microns or larger for fillers and other nonsoluble additives, or 100-500 microns or larger for other additives, such as polymers (gels), curatives, resins and other materials that have the potential to dissolve during the mixing and curing steps of the process. Melting point and aggregate size become important for soluble materials. If the material can completely dissolve and diffuse within the compound during mixing, shaping and forming operations, then there will likely be no irregularities in compound characteristics. Compounds without irregularities are the building blocks of better performing tires. If soluble material is not dissolved by curing time, and the vulcanization rate competes effectively with the steps of dissolving and diffusing of that material, the compound could have localized areas that vary in network uniformity. When the localized modulus increases around such a nonuniformity, e.g., filler or crosslink density, the area can behave as a stress-riser in a strain field. As such, these nonuniformities may manifest themselves as critical flaws, which may give rise to initiation of a crack, tear or abrasion. These nonuniformities manifest themselves as changes in the variances or averages of physical properties, such as fatigue life or tensile strength. Cure Pro enables compounds to be distributively and dispersively mixed in a shorter period of time, while helping to reduce the likelihood of critical flaws in tires.

Using tensile strength measurements to assess dispersion

It is helpful to review articles discussing the influence of curative dispersion on physical properties in sulfur vulcanized rubber (ref. 1). Such a review shows how the large particle size of accelerators can reduce the average tensile strength of a compound, or how populations of undispersed sulfur greater than 100 microns can reduce fatigue life. Tensile testing is very useful in understanding dispersion quality. However, adequate testing requires high numbers of replicates in both mixes and tensile pulls to reliably quantify dispersion quality. To test sulfur dispersion in the Eastman laboratory, scientists use eight replicate mixes that are prepared using a short mixing sequence. Cold natural rubber masterbatch, which has had a resting time of more than one week, is loaded into a 1.6 L Kobelco mixer equilibrated to 155°F, equipped with four-wing H rotors (rotating at 35 rpm), over 30 seconds, providing a fill factor of 67%. The sulfur and accelerators are added with the last piece of rubber. The ram is lowered (pressure 60 psi) and the batch is mixed for 75 seconds; then it is discharged. The rubber is passed (without banding) through a mill equilibrated to 70°C with gap setting of 0.090" and removed

immediately. The rubber is folded twice lengthwise (keeping the mill width dimension intact). It is passed a second time through the mill, again without banding, and removed immediately. From the sheet, samples are cut which nominally fill a tensile mold, as described in ASTM D-412. The samples are cured at 170°C for the time determined by the MDR rheometer to reach maximum torque at 170°C. Dumbbell-shaped tensile samples (50 per mix) are die cut using Die C, as described in ASTM D-412, and then they are tested accordingly. The sample results are analyzed as a survival experiment using Weibull statistics generating the Weibull alpha (α) and beta (β) parameters. Survival plots can be constructed using tensile at break or elongation at break as the abscissa, and the fraction or percent samples remaining as the ordinate.

With ideal behavior, the entire population of samples reaches a high ultimate tensile strength and then fails over a narrow range. When the only difference in the tests is the curative, it is assumed that differences in the survival plot reflect the differences in the dispersion kinetics of the curative. Thus, the state of dispersion for a given time or energy of mixing is evident. Cure Pro tensile samples generally reach higher tensile strength under these short mixing conditions. The narrower spread of tensile strength of Cure Pro demonstrates its superior dispersion. Since these materials were mixed under the same conditions, this demonstrates the opportunity to achieve better dispersion with less mixing time, thus enabling better productivity.

To further demonstrate the dispersion of Cure Pro, optical imaging was used to evaluate agglomerates. Figure 3 shows uncured material after mixing. Cure Pro appears to have a higher population of light spots, but they are, for the most part, smaller than the larger spots observed in the HDOT20 image. Because it has fewer agglomerates, the Cure Pro sample demonstrates better dispersion and compound performance.

Improved thermal stability

Another attribute of Cure Pro that enables productivity enhancements and operational cost savings is its thermal stability. The thermal stability (figure 4) of Cure Pro is better than other products currently available to the industry. HTS is reported as the percent IS remaining after heating a sample of IS in an inert mineral oil for 15 minutes. The typical specification range for

Figure 3 - optical microscopy of uncured rubber compound after mixing curatives

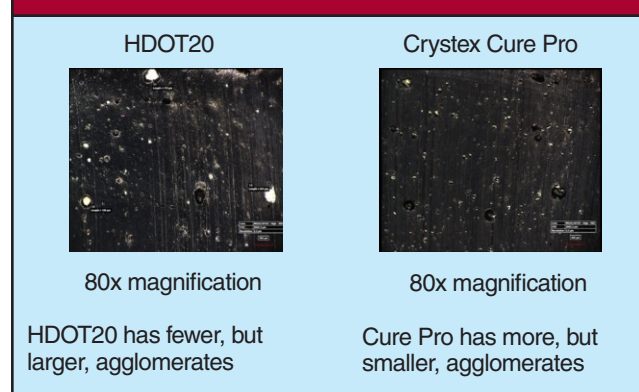
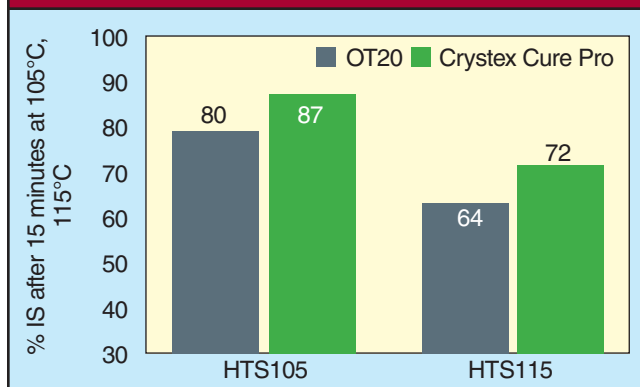


Figure 4 - thermal stability characteristics of Cure Pro compared to typical insoluble sulfur products



insoluble sulfur heat stability at 105°C spans from about 75% to 80%. For Cure Pro, the thermal stability at 105°C will be more than 85%, and typically about 87%. Thermal stability at 115°C is similarly improved. Typical commercially available material will be about 60% to 64%, but Cure Pro will be sold to a minimum sales specification of 70%. Typical HTS115 will be about 72%.

This improvement in the HTS (high temperature stability) provides increased insurance against bloom during processing. Processing temperature and time of a rubber compound can be referred to as its thermal history. Insoluble sulfur has an inherent thermal budget, or the processing temperature and time at which point reversion occurs to generate soluble sulfur in sufficient quantities that would be prone to bloom. Given the HTS values, it is possible to calculate thermal conversion rate constants for a conventional product and for Cure Pro. From the rate constants, it is feasible to calculate how much time is required at a given temperature to reach levels of reversion which represent a potential to form bloom. For reversion at 115°C, the time to reach the bloom threshold in the rubber compound containing Cure Pro is about 15 minutes; but for the conventional product, 10 minutes. The data are outlined in figure 5. This suggests there may be about five additional minutes of process safety for compounds employing Cure Pro insoluble sulfur. With this added protection

Figure 5 - reversion as a function time at constant temperature; Cure Pro offers about five extra minutes of processability at 115°C

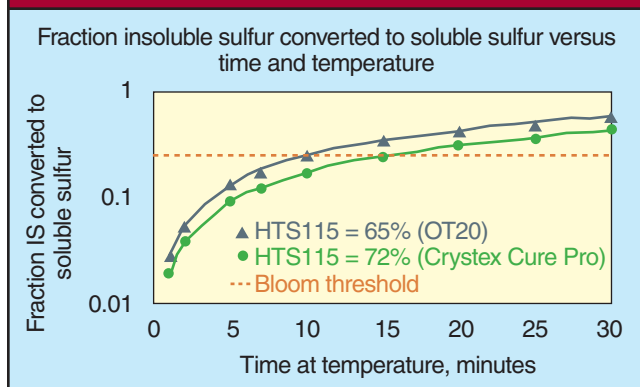
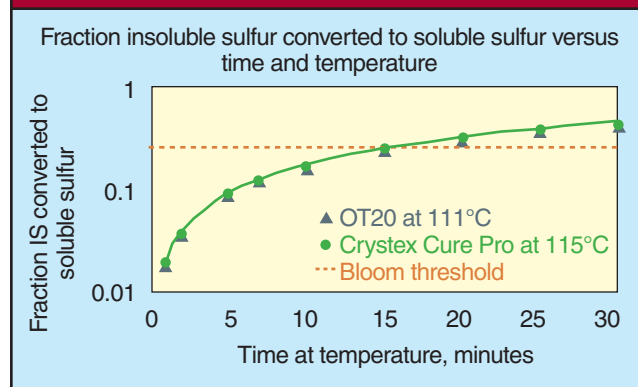


Figure 6 - iso-reversion as a function of time, matched decomposition for Cure Pro requires about +4°C



against bloom, tire manufacturers can expect fewer bloom events and less scrapping of both steel and rubber, which can cost hundreds of thousands of dollars per occurrence.

Knowing the rate constants, it is easy to derive from the Arrhenius equation decomposition rates at different temperatures. Solving for an iso-decomposition rate against time, it is possible to infer what additional process temperature could be achieved with the enhanced thermal stability of Cure Pro. The solution to the iso-reversion condition suggests Cure Pro provides about 4°C to 5°C of thermal safety in processing (figure 6).

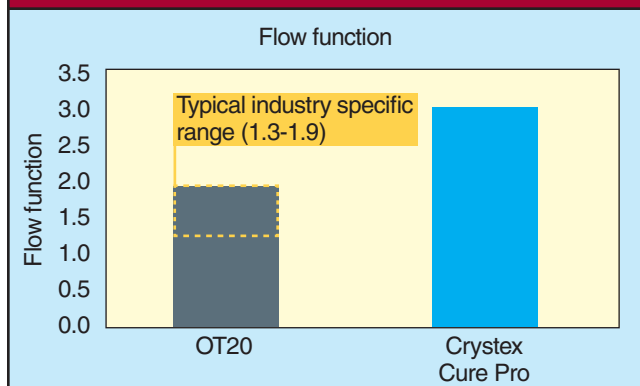
The additional thermal safety becomes beneficial for optimizing processing rates in manufacturing. One of the biggest problems in processing mass quantities of rubber relates to viscous heating as a result of mechanical shear, along with the heat transfer required to dissipate the generated heat. To prevent “hot spots” in the mixer and other processing equipment, common practice is to process at slow rates to avoid localized reversion of insoluble sulfur. Allowing a few extra degrees of thermal stability could provide opportunities to process compounds containing insoluble sulfur at faster rates, affording shorter times and increasing plant capacities. When decreasing mix times, it is critical to allow adequate distributive mixing. With improved heat stability, adequate distribution can be ensured by mixing at a higher rpm to compensate for the shorter time in the mixer. The added thermal stability of Cure Pro contributes to better productivity and operational cost savings by allowing shorter mix times while guarding against bloom.

Superior flow

Cure Pro has superior flow, a characteristic that contributes to its ability to deliver productivity and operational cost savings. Engineered to flow faster and easier than traditional insoluble sulfur products, Cure Pro allows easier material handling, less compaction, and better accuracy and efficiency in automatic dosing systems.

The typical industry specification range for OT20 is 1.3 to 1.9 for flow function. In contrast, the flow function for Cure Pro is 3.0 (figure 7). In the Eastman lab, scientists determined flow function with the standard test method for shear testing of powders using the Freeman Technology FT4 powder rheometer

Figure 7 - typical flow function of insoluble sulfur



shear cell.

Eastman scientists also tested flow by placing 150 grams of insoluble sulfur in a hopper and measuring the time required to transfer the material by an auger. For OT20, the transfer took 340 seconds, while Cure Pro transferred in just 150 seconds. Figure 8 demonstrates that Cure Pro is less prone to bridging in hoppers.

Because Cure Pro has measurably better flow characteristics, it makes handling easier, conveys from a hopper faster, and enables faster fill times. The labor savings enabled by Cure Pro help tire manufacturers increase productivity and reduce costs.

Plant experiment to demonstrate better thermal stability and faster mixing can lead to significantly improved productivity

To demonstrate the potential savings that Cure Pro brings to tire manufacturing, Eastman partnered with a tire manufacturer to test the dispersion and thermal stability characteristics in a plant environment. The results demonstrated the potential for incremental productivity and operational cost reductions that can provide meaningful savings over time.

It is important to begin with a clear understanding of mixing conditions and the balance tire manufacturers must strike between mixing speed and achieving adequate distributive mixing. Factory mixing generally relies primarily on thermocouple-

Figure 8 - Crystex Cure Pro conveys from a hopper in half the time as OT20

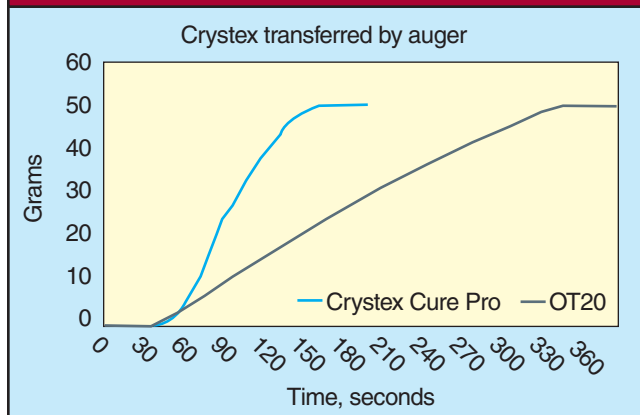
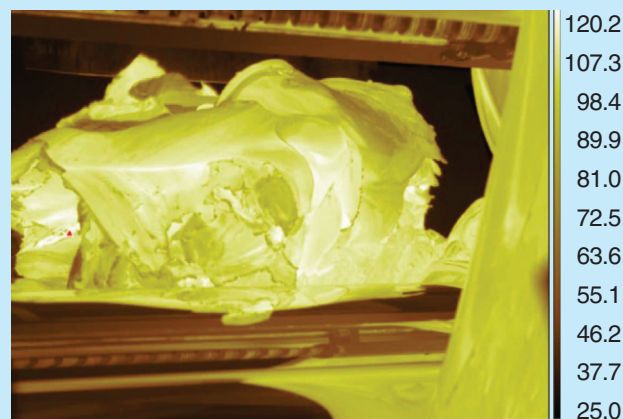


Figure 9 - thermal image of a final compound batch on the drop mill after mixing; rubber temperature ranges from about 85°-120°C in this mix

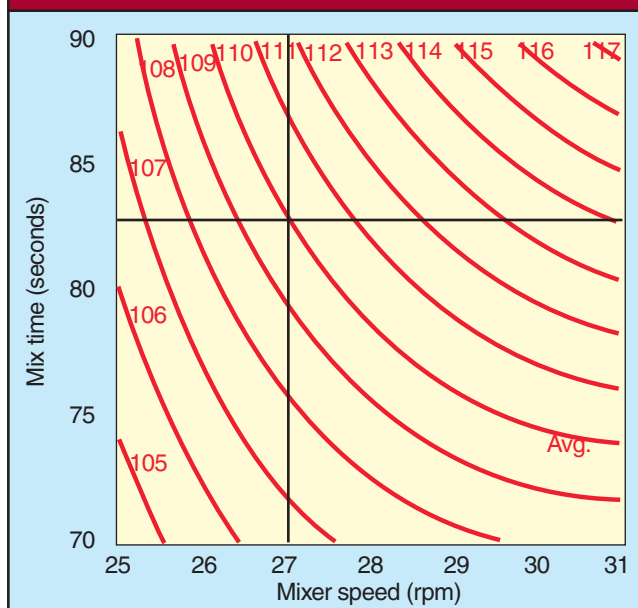


measured temperature to monitor mixing conditions or progress. Typical factory mixing processes are generally programmed with two finishing criteria. The first criterion is usually a mixing time limit, and the second criterion, being a fail-safe, is a batch temperature limit. Typical final mixes containing insoluble sulfur have mixing specifications often ranging from 60 to 120 seconds at various mixing speeds, with a batch temperature limit of about 100°C to 105°C. Slower mixer speeds provide less viscous heating, thereby reducing the demand on the mixer cooling system to dissipate the heat. However, slower mixer speeds also require more time to achieve effective distributive mixing.

Higher mixer speeds would allow higher mixing capacity, a need in any tire factory. But higher mixer speeds produce more viscous heating and can lead to hotter batch temperatures. Understanding the thermal properties of the mix can help productivity optimization. Thermal imaging (figure 9) enables tire manufacturers to readily assess the temperature profile of a batch. Doing so allows the optimization of mixer efficiency, batch homogeneity and mixer productivity.

Using a designed experiment, it is possible to profile mixing characteristics as a function of time and speed (rpm). Using thermal imaging techniques, various thermal functions of the batch can be calculated and studied. Properties such as average temperatures, maximum temperatures and portions of the mix above a given temperature can be estimated. Figure 10 shows a response surface of maximum temperature from the batch thermal image as a function of mixer speed and mix time. The design of experiments in this case was mixed with each condition and replicated five times. The mixer was a Kobelco 262 L mixer equipped with four-wing N rotors, and the rubber compound was an apex compound. Starting at 25 rpm and 90 seconds (37.5 mixer turns), the maximum rubber temperature in the batch reaches about 107°C. Mix time reduction from 90 to 70 seconds would be highly desirable in any situation should the material have the process safety for such a change. To achieve similar distribution of compound ingredients, it is imperative to operate the mixer at approximately 31 rpm (36 mixer turns). The mixer

Figure 10 - response surface for a final mix; mix times ranged from 70 to 90 seconds (Y-axis) with mixer speeds of 25 to 31 rpm (X-axis); the maximum temperature ranged from about 104°C to 117°C over these conditions



response surface indicates that the batch temperature is likely to be on the order of 109°C to 110°C, an increase of 2°C to 3°C.

The control mix for this compound was 25 rpm and 90 seconds. The average temperature for the control was 107°C, with a

Figure 11 - survival plot for the apex compound plant mixing experiment; the red line is HDOT20 mixed for 90 seconds at 25 rpm; the blue line is Cure Pro mixed for 70 seconds at 31 rpm; the control curve contains data from 1,768 tensile pulls from 20 replicate mixes; the Cure Pro curve contains 450 tensile pulls from five replicate mixes

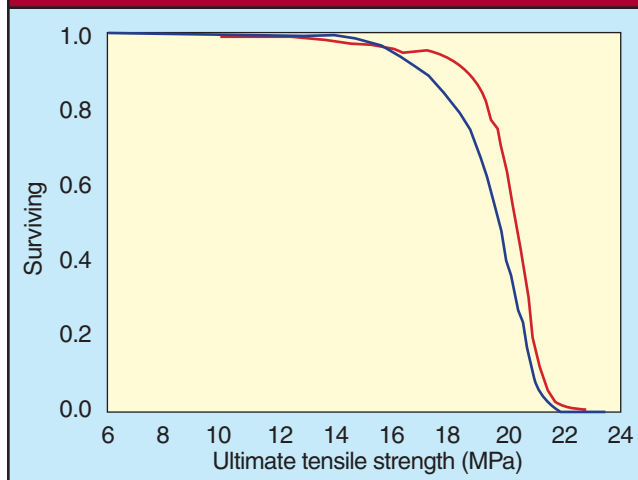


Table 1 - Weibull statistics for the tensile dispersion experiment

Label	Parameter	Estimate	Lower 95%	Upper 95%
Control	α	20.848565	20.793976	20.902955
Control	β	18.651327	17.961796	19.353504
Cure Pro	α	21.311133	21.234010	21.387509
Cure Pro	β	26.991518	25.064285	28.988565

standard deviation of 2°C for 20 mixes. Test mixing conditions set to 30 rpm and 70 seconds provided a batch temperature of 108.7°C, with a standard deviation of 1.1°C for five batches, or an increase of about 2°C. The compounds were tested for wt% soluble sulfur to determine how much of the insoluble sulfur was converted to soluble sulfur. The control compound contained 0.23 wt% soluble sulfur compared to 0.16 wt% soluble sulfur for the compound containing Cure Pro.

Tensile dispersion testing of these two conditions shows that Cure Pro provided better dispersion in the shorter mixing time compared to the control. The survival plot for these mixes is shown in figure 11. The Weibull parameters α and β for this experiment are given in table 1. The Weibull β value for the Cure Pro sample is significantly better than that for the HDOT20, and the α parameter is improved as well, demonstrating, in this case, that shorter mix time provided better dispersion than the control sulfur product.

The mix time reduction from 90 to 70 seconds in this experiment provides an improvement in mixing capacity of about 15% when loading and unloading the mixer is considered. This improvement allows tire manufacturers to achieve better efficiency during finish mixing operations. Conversion of insoluble to soluble sulfur was reduced from about 0.23 wt% to 0.16 wt%, providing more than a 25% reduction in soluble sulfur. This improvement shows the better thermal stability of Cure Pro could reduce or limit costly bloom events. The improved thermal stability, coupled with faster dispersion, provides opportunities to mix at higher rpm and shorter mixing cycle time, which can contribute to increased efficiency and operational savings over time. When mixing to equal soluble sulfur content, mixing time was reduced to 50 seconds, achieving about a 30% improvement in mixer capacity for this compound.

Conclusion

Eastman Crystex Cure Pro insoluble sulfur utilizes a combination of performance improvements over conventional insoluble sulfur, such as faster dispersion, improved thermal stability and superior flow. These engineered characteristics come together to create the opportunity for incremental operational cost savings by improving productivity of the compounding operation. Tire manufacturers can use Cure Pro to upgrade their compounding process to achieve better productivity, thereby building in cost savings that become meaningful over time.

References

1. Frederick Ignatz-Hoover and Byron H. To, presentation at the 178th Technical Meeting of the Rubber Division, ACS, Milwaukee, WI, October 12-14, 2010.