

Use of Cabot Elastomer Composite Materials in Mining Applications

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From a processing point of view, mixing is the most critical process for rubber compounding. The primary functions of mixing are incorporation, dispersion and distribution of the filler and other ingredients in elastomeric polymers. Chemical reactions among the rubber components may occur as well. Traditionally, this is achieved by using batch mixing or continuous mixing of dry fillers and solid rubber or pellets, referred to as dry mixing.

During the last few decades, a great effort has been made to produce carbon black-filled polymer masterbatches by mixing liquid-state polymer latex with filler slurry and then coagulating the mixture chemically. The commercial products are generally made by a batch process. With this process, the filler dispersion generally can be improved relative to dry mixing. However, long mixing and coagulation times reduce the productivity of these processes.

Cabot Elastomer Composite (CEC) describes elastomer masterbatch produced via a unique continuous liquid phase mixing/coagulation process. During this process, filler incorporation, dispersion and distribution are completed in a very short period of time. For carbon black – filled masterbatches, it has been found that this liquid phase mixing offers the following benefits over the conventional dry mixing and wet batch processing:

- Excellent dispersion of filler independent of filler morphology;
- Improved vulcanizate properties, including significantly improved hysteresis, abrasion resistance, cut chip resistance, and flex fatigue performance, and reduced crack growth initiation and propagation; and
- Other manufacturing and commercial benefits.

The advantages of carbon black-natural rubber materials produced using this process have been discussed in several publications and patents.¹ Rubbers mixed using the CEC process and having high loadings of filler such as carbon black exhibit higher abrasion resistance than rubbers mixed using dry mixing processes. In addition, tires incorporating rubbers mixed using the CEC process exhibit lower rolling resistance and lower heat build-up than tires incorporating dry mixed rubbers. Tire tread compounds incorporating rubbers mixed using the CEC process exhibit improved cut-chip resistance, and rubbers mixed using the CEC process exhibit much longer fatigue life than rubbers produced by dry mixing.

¹ See, for example, M.-J. Wang, et al., “NR/Carbon Black Masterbatch Produced with Continuous Liquid Phase Mixing,” *KGK Kautschuk Gummi Kunststoffe*, vol. 55, 7-8/2002, pp 388-396.

The superior performance exhibited by rubbers produced using the CEC process can also benefit the mining industry. Tires abrade against a variety of surfaces, not just roads. Vehicles equipped with tires run on dirt and rock surfaces, including in mine shafts, which are not always smooth and may have jagged protrusions. As ores and slurries are transported at mining sites, they abrade against all the equipment used to move and process them, including grinding mills, hydrocyclones, pumps, chutes, conveyors, and screens. As this equipment wears, production must be paused to replace worn components. By improving wear performance, the CEC process increases the lifetime of the resulting materials, thereby reducing material, downtime, and labor costs.

This paper discusses CEC production and various mining applications in which CEC materials can provide advantageous performance.

CEC Production

The starting materials for the CEC process are an elastomer latex emulsion and a filler slurry. The particulate filler fluid may be aqueous carbon black slurry or any other appropriate filler dispersed in a fluid and selected for the intended use of the elastomer masterbatch product. In addition to carbon black and silica-type fillers, discussed in more detail below, fillers can be formed of clay, glass, or polymer particles or fibers. Additives may be pre-mixed with the particulate slurry or with the elastomer latex fluid or may be added during coagulation. Additives also can be added subsequently, e.g., by dry mixing techniques. Additives include, for example, antioxidants, antiozonants, plasticizers, processing aids (e.g., liquid polymers, oils and the like), resins, flame-retardants, extender oils, lubricants, etc.

The CEC process is described in U.S. Patent No. 6,048,923. In brief, a slurry of carbon black or other filler and a natural rubber latex fluid or other suitable elastomer fluid are fed simultaneously to a mixing zone of a coagulum reactor. A coagulum zone extends from the mixing zone, preferably progressively increasing in cross-sectional area in the downstream direction from an entry end to a discharge end. The slurry is fed to the mixing zone preferably as a continuous, high velocity jet of injected fluid, while the elastomer latex fluid is fed at relatively low velocity. The high velocity, flow rate and particulate concentration of the filler slurry are sufficient to cause mixture and high shear of the latex fluid, flow turbulence of the mixture within at least an upstream portion of the coagulum zone, and substantially completely coagulate the elastomer latex prior to the discharge end. Substantially complete coagulation can thus be achieved without the need for an acid or salt coagulation agent.

After the substantially complete coagulation of the elastomer latex and particulate fluid, masterbatch crumb in the form of "worms" or globules is formed and discharged from the discharge

end of the coagulum reactor as a substantially constant flow concurrently with the on-going feeding of the latex and filler slurry streams into the mixing zone of the coagulum reactor. Notably, the plug-type flow and atmospheric or near atmospheric pressure conditions at the discharge end of the coagulum reactor are highly advantageous in facilitating control and collection of the elastomer composite product, such as for immediate or subsequent further processing steps. The masterbatch crumb is created and then formed into a desirable extrudate, which is then dewatered in a suitable apparatus. The resulting dewatered coagulum may be passed through a dryer or masticated and dried simultaneously. As described in PCT Application No. PCT/US2009/000732, the input of mechanical energy into the dewatered coagulum via mastication may be controlled with respect to a drying profile.

The masticated masterbatch may be dry mixed with any of the additives described above, for example, additional filler or a different type of filler (e.g., addition of silica to a carbon black-natural rubber masterbatch) or with additional elastomer, for example, butadiene rubber, as described in U.S. Patent No. 7,105,595. Alternatively or in addition, the masticated masterbatch may be fed to a cooling system or granulator as described in U.S. Patent No. 6,929,783. The granulated material may then be fed to a baler, where the granulated material may be baled more or less tightly or densely. For example, where the masterbatch will be compounded in a Banbury mixer or the like, it may be desirable to prepare a loose bale such as that described in PCT Publication WO03/042285.

Performance of CEC materials

Microscopic observation of CEC compounds and dry-mixed rubbers reveals that filler is much better dispersed in CEC compounds (Figure 1). The clumps of carbon black visible in the dry-mixed material contain carbon black that, because it is not dispersed within the rubber, cannot interact with and reinforce the rubber matrix. Rather, the carbon black simply acts as a bulk filler in the dry-mixed rubber. The superior dispersion of carbon black in the CEC compounds allows the carbon black to interact with the surrounding polymer. We typically observe 80-90% less undispersed area (i.e., the cross-sectional area occupied by undispersed carbon black) in rubbers produced by the CEC method when compared to conventional rubbers.

Figure 2 compares the bound rubber values for natural rubber-carbon black rubbers produced by the CEC method and by conventional dry mix methods, while Figure 3 compares the stress-strain curves for green compounds produced by the two methods. The higher bound rubber values for CEC compounds are indicative of excellent carbon black dispersion and minimal polymer degradation. The high stress of the CEC compounds, especially at higher elongations, demonstrates strong polymer-filler

interaction and improved dispersion with respect to dry mixed compounds having the same composition.

The high levels of reinforcement of CEC compounds are also reflected by their excellent fatigue performance. Figure 4 compares the crack initiation and cut growth performance of natural rubber-carbon black rubbers produced by the CEC method and by conventional dry mix methods. The compounds produced by the CEC method are much lower in crack initiation and cut growth than dry mixed compounds of the same composition.

CEC compounds also exhibit excellent abrasion performance, especially in comparison to dry mixed compounds. Figure 5 compares the abrasion indices at 7% slip for natural rubber-carbon black compounds produced by the CEC method and by conventional dry mix methods. Use of the CEC method allows production of more highly loaded compounds before performance declines. Even at higher loadings than optimal, compounds produced by the CEC method exhibit superior abrasion performance. Indeed, we have measured a 7-18% improvement in abrasion performance for CEC compounds with respect to dry mixed compounds. Figure 6 compares abrasion performance at 14% slip. Despite the variability in the results, the superiority of CEC compounds over dry mixed compounds is clear.

Figure 7 includes photographs of off-the-road tires produced with two section treads after road testing. The photographs show that the sections of the tread produced by the CEC method ("A") are roughly intact after testing, while the opposing sections produced by dry mixing ("B") are extensively worn.

Use of CEC Materials in Mining Applications

Rubbers prepared using the CEC method will have benefits in a wide variety of mining equipment.

For example, rubbers prepared using the CEC method, including carbon black-filled natural rubber, may be employed as the liner for a stator in positive displacement motors. In general, the rotor rotates inside a lined stator whose cross-section includes a number of lobes. Problems may be encountered with the stator when, for example, rotation of the rotor within the stator shears off portions of the stator lobes. This process, which may be referred to as "chunking," deteriorates the seal formed between the rotor and stator and may cause failure of the motor. Chunking may be increased by swelling of the stator liner or thermal fatigue. Swelling and thermal fatigue may be caused by elevated

temperatures and exposure to certain drilling fluids and formation fluids, among other factors.² Use of CEC materials in stator liners is predicted to decrease swelling and thermal fatigue, thereby decreasing chunking and improving performance lifetimes.

CEC materials may also be used to prepare liners for slurry pumps. Such slurry pump systems are used for pumping generally aggressive and corrosive liquids or slurries containing granular material such as sand, coal, ore or mining waste, sometimes at high temperatures, over generally large distances. Because of the abrasive nature of the slurry mixtures, in particular, the moving components of the pump must meet very stringent requirements.³ Centrifugal slurry pumps typically utilise a cast outer casing made in cast iron or ductile iron with an internal liner molded from a wear resisting elastomer compound. The casing and the liners are often manufactured in two parts or halves held together with bolts at the periphery of the casing. During assembly, the two liner halves must be squeezed together at their periphery to effect a pressure tight seal. The resulting joint line is a vulnerable wear area in the pump, especially as the joint line is adjacent to the impeller discharge. Once wear starts at a local spot, the continued disturbed flow pattern at the step or gap will lead to an accelerated wear point and in the worst case localized wear will cause the liner to be worn through thereby exposing the pressure containing casing to wear.⁴ In alternative designs, the liner of the centrifugal pump is manufactured in one piece, or the shape of the casing is varied. It is expected that use of CEC materials, including elastomer composites incorporating natural rubber and carbon black, can alleviate this problem.

Diaphragm pumps may also benefit from incorporating CEC materials. In such a pump, the diaphragm may be fabricated from an elastomer prepared by the CEC process. Where a pressure tank is employed in conjunction with the diaphragm pump, the diaphragm in the pressure tank may also be fabricated from a CEC material. The composition of the elastomer may be selected depending on the composition of the materials on either side of the diaphragm. For example, a halogenated elastomer may be desirable to reduce gas permeability. In addition, any seals or o-rings employed in such a pump may also employ elastomers prepared using the CEC process, as may the diaphragms, flexible membranes, flexible tubes and other resilient members employed in various configurations of slurry pumps.⁵

Grinding mills may especially benefit from the use of CEC materials. A variety of configurations of grinding mills and components such as liners, wear elements, and lifter bars, have

² U.S. Patent No. 6,604,921

³ PCT Publication No. WO2004/007961

⁴ PCT Publication No. WO2005/024243

⁵ PCT Publications Nos WO 2008/085031, WO2004/011806, WO2009/051474, WO2007/081796, WO2004/018881

been developed with the goal of improving performance, including increasing performance lifetimes.⁶ Because of the constant impact forces applied to wear elements and lifter bars when the mill is in operation, they will wear and break after a period of time (typically 6-12 months). The mill needs to be stopped while the linings are replaced. This is time consuming and labor intensive and impacts the overall productivity of the mill, especially if downtime for replacing wear components is unscheduled. The use of CEC materials, including carbon black-filled natural rubber, as materials of construction for both the liners and the lifter bars can increase performance lifetimes of the wear elements and reduce the downtime required to replace worn parts. Other lining materials, for example, liners for drums, bins, feeders, feed hoppers, vehicle platforms, and other apparatus described in this paper, may also benefit from the use of CEC elastomers.⁷

Another apparatus that can benefit from incorporating CEC materials is a downhole drilling assembly. Such apparatus are produced in a variety of configurations.⁸ For example, the assembly may be straight or may incorporate one or more bends to facilitate controlled deviation of the drilling assembly.⁸ Regardless of the configuration, the downhole drilling assembly includes a variety of o-rings, thrust bearings, seals, spacers, discs, shaft sections, and other components that may be fabricated from an elastomer. Such components can experience longer service lifetimes if the elastomer is prepared using the CEC process.

Equipment for conveying slurries, ore, or other abrasive materials may also benefit from incorporating CEC materials. Chutes and conveyors for transporting materials are frequently configured to prevent clogging as the material being transported adheres to the walls.⁹ Both the walls of the chutes and conveyors and the liners that are employed to prevent adhesion are subject to high impact and wear, and the scraper blades that are used to remove material from conveyors must be optimized to enhance material removal while preventing wear and breakage.¹⁰ Even for slurries that do not adhere as readily, transport of the material causes abrasion against the wall of the pipe during flow.¹¹ The use of CEC materials, including composites of natural rubber and carbon black, in these apparatus can improve component lifetimes and reduce costs resulting from repairs and downtime.

⁶ PCT Publications Nos. WO2006/076764, WO2006/076763, WO2006/076763, WO2009/050723, WO2009/008810, WO2007/048874

⁷ PCT Publications Nos. WO1987/004318, WO2008/087247, WO2007/138162, WO2007/085694, WO1981/001253, WO2007/063554, WO2006/132582, WO03/029114, WO99/43979

⁸ PCT Publications Nos. WO01/98619, WO99/39074

⁹ PCT Publications Nos. WO2008/105697, WO2003/086907, WO2006/031188, WO2006/131587

¹⁰ PCT Publications Nos. WO2003/035518, WO2007/043944

¹¹ PCT Publication No. WO2006/112710

Screens for separating mined materials into their various components are also subject to wear. Both the configurations and the materials of construction of screens have been adjusted to improve service lifetimes.¹² While these screens are often configured to improve service lifetimes by directing material to more wear-resistant portions, downtime could still be significantly reduced by reducing the wear on all portions of the screen, not just those components which are exposed to greater amounts of abrasion. The use of CEC materials can reduce abrasive wear on screens, allowing further optimization of configuration for other performance variables, such as flow rates or the size of the material being screened.

Hydrocyclones, sometimes termed hydrocyclone liners, are used to separate components of liquid/liquid and liquid/solid streams in a variety of mining and other applications. Even liquid/liquid streams include small particulates that will abrade against the interior of the hydrocyclone. Solid particles descending down the cone-shaped wall scrape along its surface, eventually wearing holes or even furrows through the wall that can cause leaks or even cut off the narrow portion of the cone completely. As a result, hydrocyclones require frequent repair or replacement. While both the design and the materials of construction of hydrocyclones have been adjusted in an attempt to increase service lifetimes¹³, the use of CEC materials can improve the erosion and abrasion resistance of these apparatus, thereby reducing the need for repair and downtime.

Conclusions

The CEC process has provided the first filler-natural rubber masterbatches made with a continuous liquid mixing process. This technology enables an environmentally friendly operation, simplified mixing, and lower labor- and energy-consumption. Superior filler dispersion is now possible independent of filler morphology. Due to the excellent dispersion of fillers such as carbon blacks in CEC-prepared compounds, the hysteresis, stress-strain properties, cut-chip resistance, fatigue life and abrasion resistance of the vulcanizates are significantly improved over their conventional counterparts.

¹² PCT Publications Nos. WO2006/068590, WO2007/105227, WO2008/140394, WO2003/082484, WO2006/031176

¹³ U.S. Patents Nos. 5,819,955; 5,266,198; 7,011,219; 4,358,369; 6,540,918; PCT Publication No. 2009/089589 ; U.S. Patent Publications Nos. 2005/0236324 ; 2004/0134852

Figures

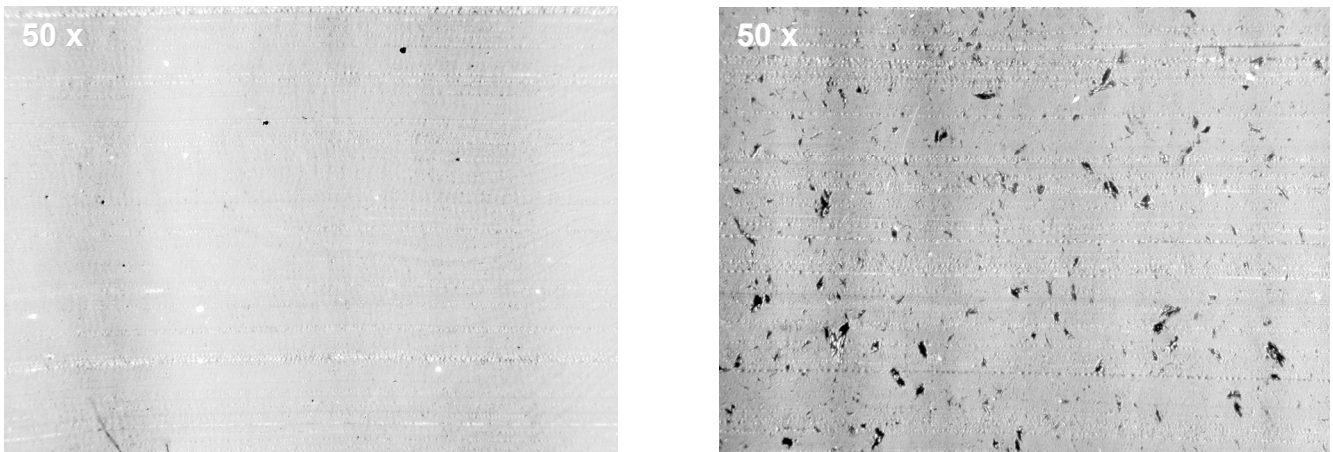


Figure 1: Optical micrographs of sections of rubber (50 phr N134 in natural rubber) prepared by the CEC method (left) and two stage dry mixing (right)

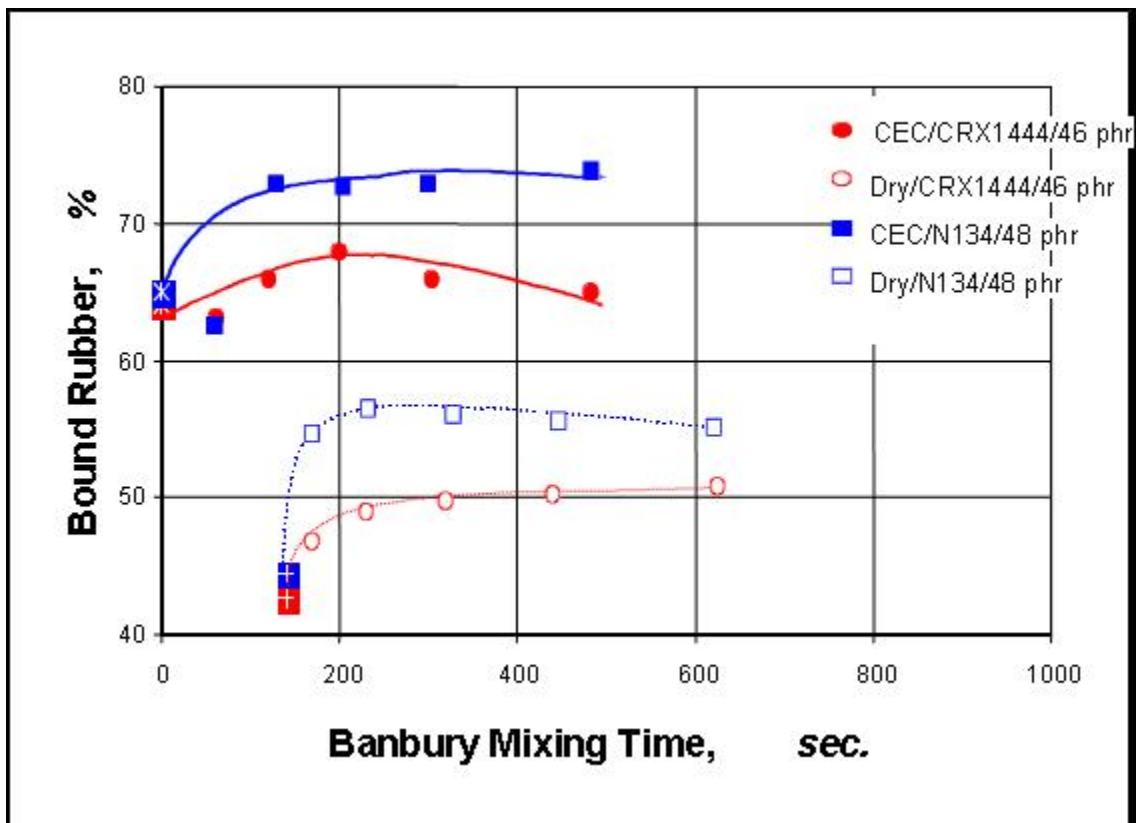


Figure 2: Variation in bound rubber (%) with mixing time in an internal (Banbury) mixer for two grades of rubber produced by the CEC method and two stage dry mixing

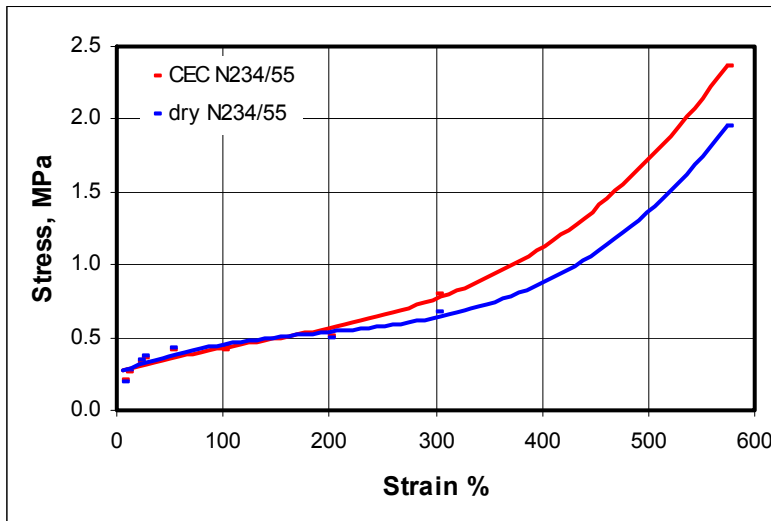


Figure 3: Stress-strain curves for rubber composite (55 phr N234 in natural rubber) prepared by the CEC method and two stage dry mixing

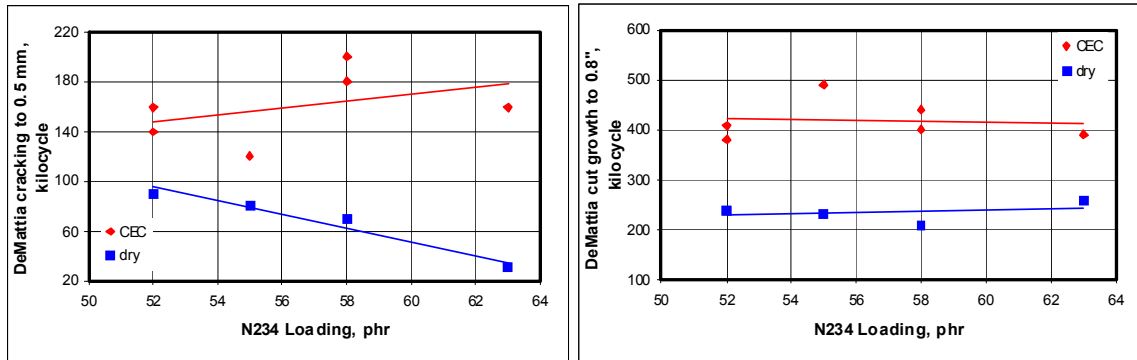


Figure 4: Variation in DeMattia cracking (left) and DeMattia cut growth (right) with loading levels of N234 in natural rubber prepared by the CEC method and two stage dry mixing

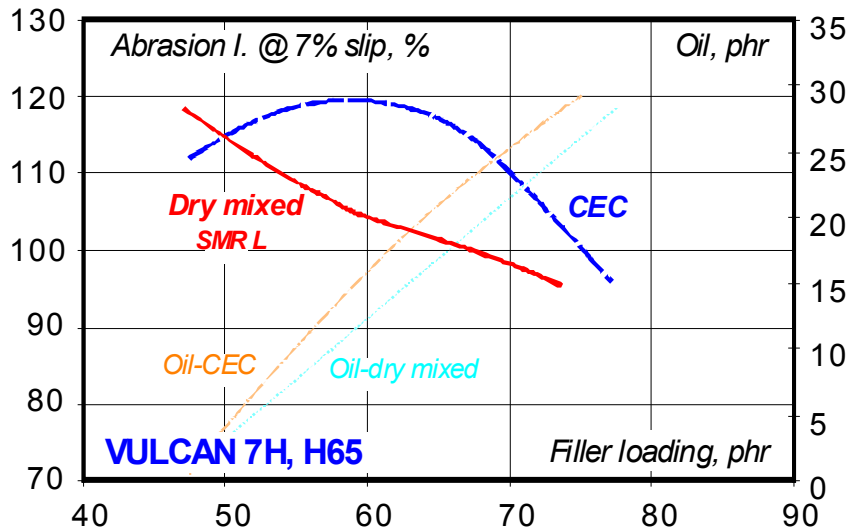


Figure 5: Variation with respect to filler loading in the abrasion index (%) at 7% slip for compounds prepared with Vulcan® 7H carbon black. All compounds prepared to the same (65 Shore A) hardness; the graph also indicates how much oil was added to the compounds to achieve the hardness level.

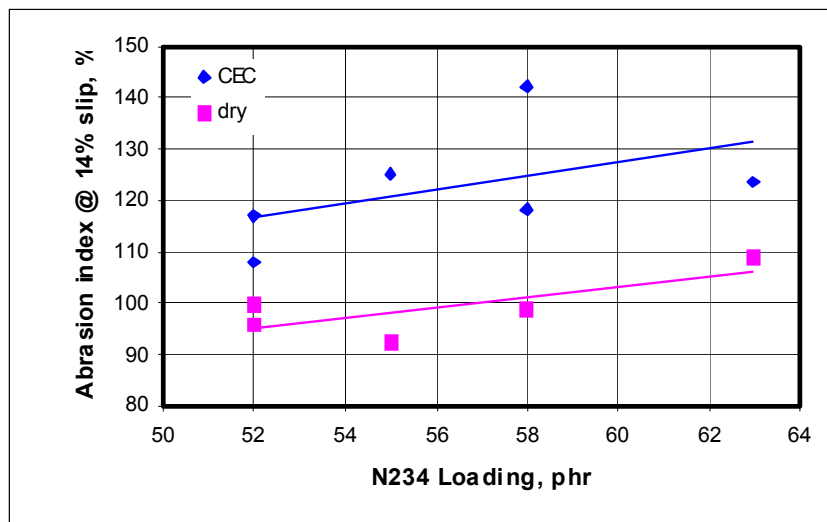


Figure 6: Variation with respect to filler loading in the abrasion index (%) at 14% slip for compounds prepared with N234 carbon black.



Figure 7: Photographs of tire prepared with two-section tread, showing condition of tire after off-the-road use.