Homogeneous Silanization and Optimum Loading with PDPB Silane

Technical Note

預分散偶聯劑橡膠母粒的均勻偶聯化及使用劑量優化的研究

Common practice on the application of the silica-silane filler system involves in-situ modification of silica with the silane during the mixing process. This in-situ modification requires, in addition to an optimal dispersion, the precise control of the subsequent silanization (chemical reaction between silanol group on silica surface and silane) in the mixer.

白炭黑填充膠料需要在混煉過程中使用硅烷偶聯劑。偶聯劑可使膠料與白炭黑發生化學反應(偶聯)形成結合橡膠。結合橡膠的動靜態模量及物性良好。尤其耐磨性更為顯著。本實驗探討預分散偶聯劑橡膠母粒在促進白炭黑填充膠料均勻偶聯化的效果。從而使結合橡膠交聯性最佳化。達到使用劑量及混煉操作時間上經濟的效果。

Deteriorated Reinforcement from Non-uniform Silanization
非均勻白炭黑偶聯化導致補強質量降低

There are some serious problems if a complete silanization proceeds before a good dispersion established between silica and silane. First, it could lead to a non-uniform silanization on the accessible outer surface of the silica particles, but once the silane is consumed, no silane is left to modify the surface formed during the ongoing dispersion process. Such an inhomogeneous silanization results in a higher non-modified silica-silica network and a deteriorated reinforcement.

在混煉過程中白炭黑偶聯化(白炭黑/偶聯劑反應)的速率若快於偶聯劑在白炭黑的分散速率容易導致非均勻白炭黑偶聯化。進而造成補強質量上的一些問題。非均勻白炭黑偶聯僅使部份的白炭黑得到偶聯。尚有大比例的白炭黑表面未能得到適當的浸潤。因而無法產生所需要的白炭黑偶聯效果。

Secondly, due to the fact that the silanes have three ethoxy groups, intermolecular condensation reaction between neighbored silanes can also occur (secondary reaction). This secondary reaction results in a further crosslinking of the silanes on the silica surface. A dense inhomogeneous silanization could increase this intermolecular condensation in the presence of moisture in the rubber matrix and

results in the formation of polysiloxanes. These polysiloxanes deteriorate an optimal reinforcement and lead to a poor wear and abrasion resistance. Because of this deficiency, compounder need to increase liquid silane dosage to compensate this material lost to meet the needed physical properties.

除此之外。非均匀白炭黑偶聯造成過多偶聯劑聚集於局部的白炭黑中。此聚集的偶聯劑或者自相形成縮合反應（偶聯劑降解）或殘存於白炭黑結構裏。無法達到均匀全面的偶聯效果。進而導致耐磨性及補強質量降低。因此配方中常需追加偶聯劑使用劑量以彌補因非均匀白炭黑偶聯所造成的缺失。

Optimum Loading through Homogeneous PDPB Silanization
均匀全面的白炭黑偶聯化反應有助於使用劑量的優化

Pre-dispersed polymer bound silane (PDPB silane), unlike liquid silane, requires shorter mixing time to achieve a good dispersion. It guarantees a subsequent uniform silanization and completed primary reaction. The homogeneous silanization achieves advantages on optimized loading dosage and mixing time to meet the needed physical properties.

預分散偶聯劑橡膠母粒相對於液体偶聯劑需要較短的混煉時間。保証在良好的分散狀況下進行均匀全面的白炭黑偶聯化反應。從而使白炭黑交聯性最佳化。 同時近乎所有使用的偶聯劑參與反應。沒有偶聯劑降解或殘存偶聯劑。可達到使用劑量及混煉操作時間上經濟的效果。

Monitoring Silanization Process and Optimum Loading Determination
驗証均匀白炭黑偶聯化反應及使用劑量優化

Two experiments were discussed to validate the quality of homogeneous silanization from PDPB silane and determine the optimized equivalent loading in applying PDPB silane.

1. Measuring the quality of homogeneous silanization from PDPB silane

   The quality of the homogeneous silanization reaction during mixing can be monitored by measuring the dynamic Payne effect. Homogeneous silanization with better dispersion and subsequent silanization shows a lower Mooney viscosity and better dynamic properties. Non-linearity under small strains and tanδ values are substantially reduced with homogeneous silanization. The shear/strain curve demonstrates that PDPB silane has a significant lower shear

modulus and a homogeneous silanization at the 1st mixing stage. On the other hand, liquid silane application has a high modulus and a large portion of unmodified silica at the 1st mixing. It needs multiple no-productive mixing steps (2nd and 3rd mixing stages) to achieve a lower modulus before a required homogeneous silanization achieved. The homogeneous silanization thru PDPB silane eliminates the need for multiple re-mill steps and intermediates cooling.

2. Loading reduction study with rubber compounds containing PDPB silane

We compared the modulus at high strain to determine the optimum amount of PDPB silane necessary to disperse and reinforce silica-loaded rubber. A lower modulus at high strain indicates a better efficiency of the silica silanization as well as a better reinforcement. PDPB silane shows a lower modulus than any multiple re-mills using liquid silane at equivalent loading. There is a need to increase liquid silane dosage to compensate the material lost from deficient silica silanization in using liquid silane. to obtain In order to achieve the same level of reinforcement, compounder need to increase liquid silane dosage to compensate this material lost. The homogeneous silanization from PDPB silane optimizes loading dosage to meet the needed physical properties

下列實驗驗証預分散偶聯劑橡膠母粒在劑量及混煉操作時間上經濟的效果,

1. 確認預分散偶聯劑橡膠母粒達成的均勻白炭黑偶聯化反應

硫化膠的動態剪切模量試驗可用於觀察白炭黑/膠料, 白炭黑/白炭黑間的作用力。本實驗比較預分散偶聯劑橡膠母粒以及液体偶聯劑的動態剪切模量。以決定白炭黑偶聯化反應的均勻性。剪切模量和應變關係曲線顯示預分散偶聯劑橡膠母粒在第一次混煉後便具有顯著的低剪切模量。這結果表明均勻白炭黑偶聯化反應發生並形成結合橡膠。液体偶聯劑在第一次混煉後仍存有極高的剪切模量。必須經過多次混煉才能達到如預分散偶聯劑橡膠母粒的低剪切模量。這代表液体偶聯劑需要較多次混煉過程才能達到預分散偶聯劑橡膠母粒相同的分散性。使用預分散偶聯劑橡膠母粒有助於混煉操作時間上經濟的效果。

2. 驗証預分散偶聯劑橡膠母粒在劑量上經濟的效果

白炭黑偶聯率可由高應變力時的剪切模量決定。實驗結果表明液体偶聯劑都具有較高的剪切模量。即使經過多次混煉仍無法達到類似預分散偶聯劑橡膠母粒的低剪切模量。為達到與預分散偶聯劑橡膠母粒相同的低剪切模量。配方上必須追加液体偶聯劑劑量以彌補較低的白炭黑偶聯率。使用預

分散偶聯劑橡膠母粒沒有殘存偶聯劑或偶聯劑自身降解。近乎所有的偶聯劑參與白炭黑偶聯化反應。可達到使用劑量上經濟的效果。