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Liên hệ dịch tài liệu :

[thanhlam1910\\_2006@yahoo.com](mailto:thanhlam1910_2006@yahoo.com) hoặc [frbwrthes@gmail.com](mailto:frbwrthes@gmail.com) hoặc số 0168 8557 403 (gặp Lâm)

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#### **1.5 SILICA FREE WATER**

Free water content reflects the hydrophilic nature of silica and its tendency to adsorb moisture to attain equilibrium with the relative humidity of its environment, as

#### **1.5 SILIC ĐIOXIT KHÔNG CHỨA NƯỚC**

Hàm lượng nước tự do (nước tự nhiên) phản ánh bản chất ưa nước của silic điôxit và khuynh hướng hấp thụ hơi ẩm để đạt đến trạng thái cân bằng với độ ẩm tương đối của

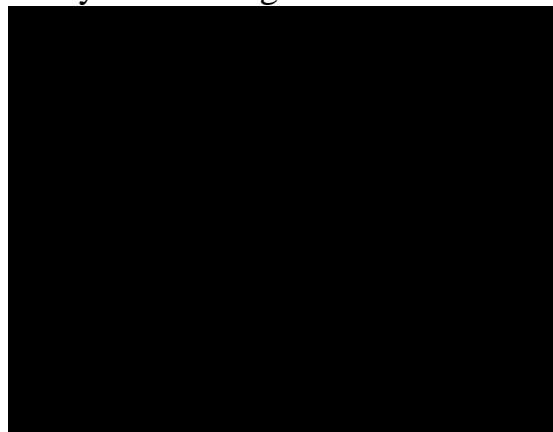
illustrated in Figure 1.3.

During manufacture, water or steam is sometimes added to the dried product to reduce electrostatic charges on fine particles and to alleviate the cure retarding effects of dry silica. The latter phenomenon is responsible for much of the processing and vulcanizate variability associated with silica reinforced compounds. Free water acts as a barrier to reduce the attachment of silica surface silanols (SiOH) to soluble zinc and hydrogen bonded materials. In particular, this removal of zinc from its cure activating function has a profound retarding effect on cure rate. Since variable amounts of free water can be lost during mixing, cure rates will, of necessity, vary. Use of permanent barrier materials such as glycols provides a partial solution to this problem. Free water content is generally determined by moisture balance at 160-200°C or in a vacuum oven at 105°C.

Unfortunately, the barrier effect of water on soluble zinc attachment is also a cause of reduced bonding of silica to elastomer. This effect is obviously a hindrance to reinforcement, and is partially the cause of lower than expected abrasion resistance and high-strain modulus in silica reinforced compounds. Later discussions of

môi trường của nó (xem Hình 1.3).

Trong quá trình sản xuất, đôi khi nước hoặc hơi nước được thêm vào sản phẩm sấy khô để giảm sự tích điện trên các hạt mịn và giảm bớt các hiện tượng chậm hóa cứng của silic điôxit khô (cure: khô, hóa cứng, lưu hóa). Hiện tượng sau đóng vai trò rất quan trọng trong quá trình xử lý và vulcanizate (lưu hóa) những biến đổi gắn với các hợp chất cường lực (gia cường) bằng silic điôxit. Nước tự do đóng vai trò như một hàng rào để giảm sự gắn kết của silanol (SiOH) trên bề mặt silic điôxit với kẽm hòa tan và các vật liệu liên kết hydro. Đặc biệt, sự loại bỏ kẽm khỏi nhóm chức hoạt hóa đông cứng của nó có tác động làm chậm tốc độ hóa cứng rất nhiều. Bởi vì lượng nước tự do mất đi trong quá trình trộn luôn luôn biến đổi, tất nhiên tốc độ đông cứng sẽ luôn thay đổi. Việc sử dụng các vật liệu chắn vĩnh viễn chẳng hạn như glycol giúp giải quyết một phần vấn đề này. Nói chung, hàm lượng nước tự do được xác định qua sự cân bằng độ ẩm ở 160-200°C hoặc trong tủ sấy chân không ở 105°C.



“zinc-free” acceleration describe a compounding approach to the barrier problem.

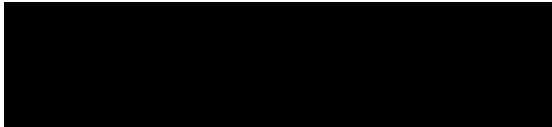
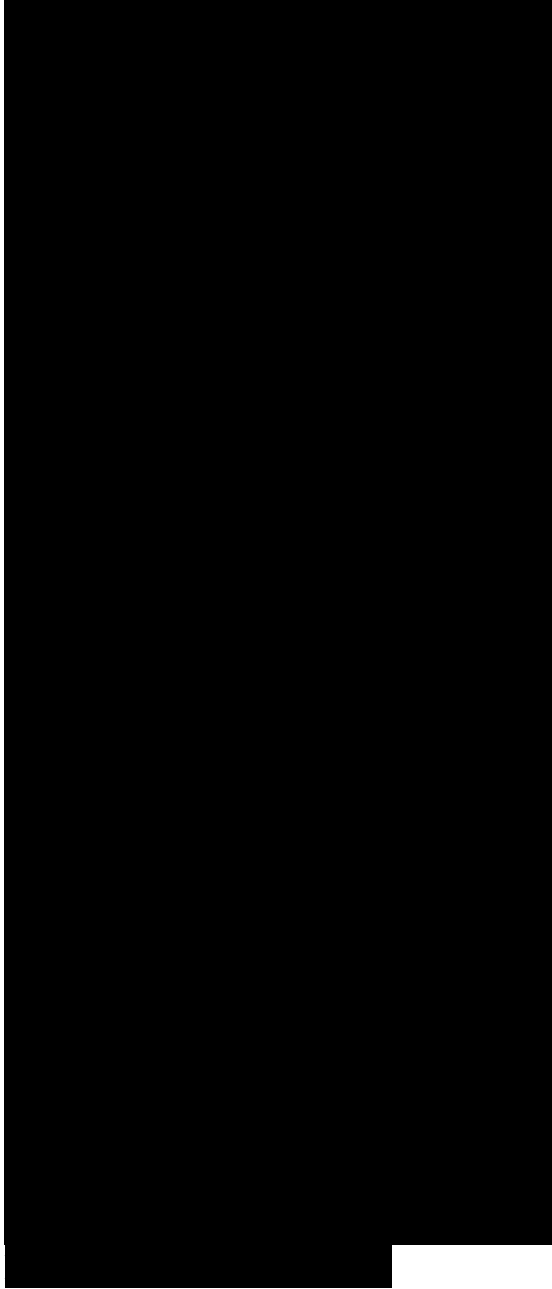
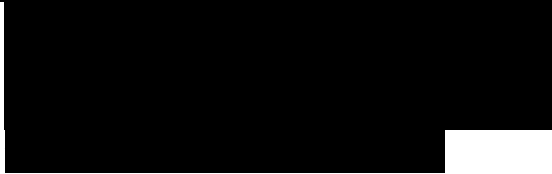
Table 1.4 illustrates the effects of free water variation in a peroxide cured natural rubber reinforced with 30 phr silica, adjusted to maintain equal SiO<sub>2</sub> content.

The major changes due to “dry” silica (less than 1% water) include increased viscosity (50% increase), reduced hardness and increased highstrainmodulus. The combination of higher viscosity and lower hardness is probably unique to hydrated silica and calls for explanation. In this case, the inclusion of silane coupling effects (compound C) and the scanning electron micrographs of these three compounds, in Figure 1.4, provide enlightenment. It is evident in Table 1.4 that an increase in viscosity with dryness involves a loss of plasticization in the absence of the cloud of water which normally surrounds the silica particle. Also, agglomerate size is reduced (Figure 1.4), possibly the result of higher shear forces during mixing. The disappearance of higher viscosity values when the silanol surface is modified by silane indicates that resulting loss in hydrogen bonded structure is the major effect. It should be noted that dry silica is defined here as water content less than 1%. Normal water content is in the range of 3 to 7%. At water

contents above 7% plasticization predominates, with a resulting decrease in viscosity, in terms of either Mooney or rheometer minimums.

In the peroxide cured compounds in Table 1.4, the contrast of increased viscosity and reduced hardness reflects the test parameters involved. The low strain deformation of durometer and 20% modulus testing of the vulcanizate is far removed from the continuous shear deformation involved in measuring the viscosity of the uncured compounds. Under the static, low strain conditions of durometer tests, hardness reduction occurs when the silanol-water structure is largely eliminated, without change in crosslinking. This structure and hardness loss is increased further when silanol bonding is removed by silanemodification of the silica surface. Reduced structure, (smaller agglomerates), is quite apparent in the Figure 1.4 photomicrographs where the average diameter size of the larger particle agglomerates is reduced from 100 to 70 nanometers with dry silica. These smaller agglomerates, together with the removal of the free water barrier, are largely responsible for the increase in 300% modulus and, frequently, abrasion resistance.

The use of a peroxide cure system in exploring water effects allows the separation of filler reinforcement



mechanisms from the silica surface reactions which occur with zinc-sulfur crosslinking. As noted elsewhere, these reactions of silica with soluble zinc produce a significant increase in polysulfide crosslinks and reduced filler-polymer bonding, which in themselves are sufficient to overshadow water effects. In Table 1.5 the data for dry silica effects in sulfur cured SBR combine both crosslinking and polymer bonding effects. The doubling of viscosity together with increased 300% modulus in the dry silica compound are similar to those effects seen in the peroxide cured, zinc-free natural rubber compounds. However, other property effects here are all influenced by changes in sulfur crosslinks and fillerpolymerbonding. Higher set, modulus and durometer are all evidence of an increase in polysulfide crosslinks, the result of zinc removal from its accelerator activating function (by attachment to silanols). Increased abrasion resistance (50% improvement) and modulus indicate improved silica-polymer bonding in the absence of barrier water. Similar behavior of BR and solution SBR compounds is summarized, together with a comparison to an HAF control compound, in Table 1.6. In view of the predominantly beneficial reinforcement effects of dry silica, it is reasonable to ask why

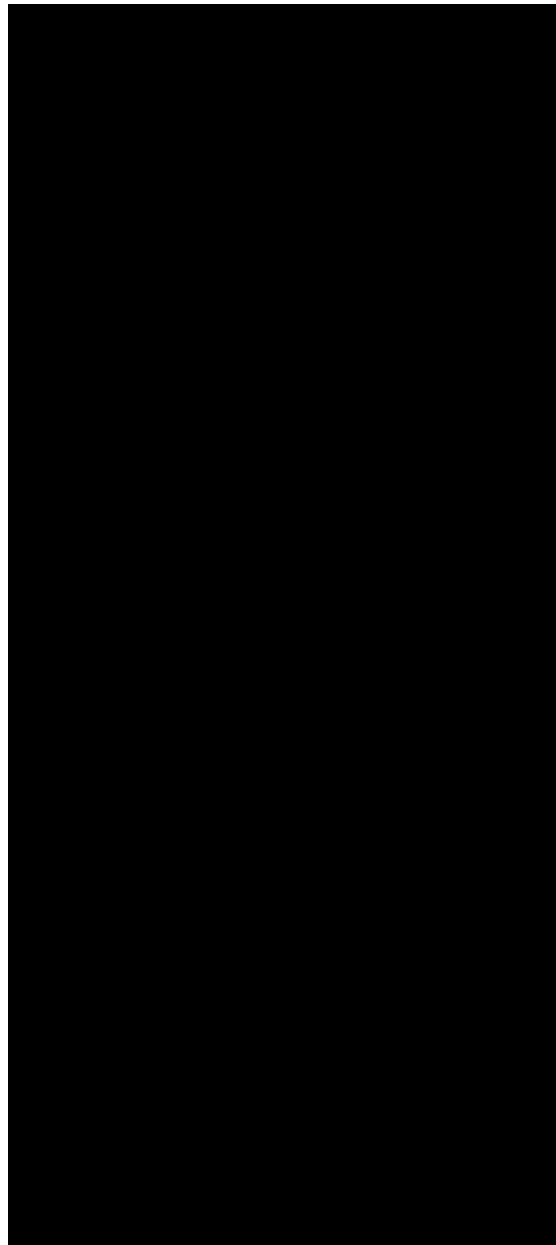
commercial products with less than 1 % free water are not readily available. Two major obstacles must be overcome. As noted above, the free water content of precipitated silica is in equilibrium with relative humidity. Since the equilibrium values vary from 1% to more than 20% over the possible humidity range, it is apparent that maintaining less than 1% water, particularly in bulk shipping, would be very difficult. The electrostatic charges and associated dusting which are characteristic of dry silicas also raise formidable problems in handling and shipping. From the compounding standpoint, cure retardation in sulfur systems with dry silica must be countered with adjusted acceleration.

### **1.7 SILICA SURFACE SILANOL GROUPS**

In contrast to the ephemeral nature of free water, bound, hydrated water is held firmly in place as silanol groups until temperatures rise above 250°C. This is well above rubber processing temperatures, and thus allows the silanol surface to be considered a permanent silica characteristic. Silanols are responsible for the hydrophilic nature of silica and its unique (versus carbon black) reactivity with water, soluble zinc and other compounding ingredients as well as elastomers. The network of

hydrogen bonded silanols leads to higher viscosity, hardness and stiffness in silica reinforced compounds, in contrast to those based on carbon black. This network is essentially a definition of silica structure. This type of structure, unlike that of carbon blacks, is not permanent, and can be significantly removed by addition of the materials described below.

Examination of a model that contrasts the surface make-up of silica and carbon black [2] reveals the source of their widely divergent behavior in rubber. As illustrated in Figure 1.1, silanol groups provide a hydrophilic surface; carbon black is hydrophobic, and therefore more compatible with organic polymers. Silanols react readily with oxygen- or nitrogen-containing compounds such as glycols, water, alcohols, amines, divalent metal salts and with each other. Among these reactions, that with soluble zinc is the major source of silica's unique compounding characteristics. The reaction, as shown in Figure 1.5, takes place in two steps. First, reaction of zinc oxide with a fatty acid produces soluble zinc ion; second, zinc becomes securely bound to one or two silanols. Zinc attachment displaces part of the free water and creates a heterogeneous surface in which the ratio of zinc-to-water is variable. This ratio will increase when water is driven off by high mixing temperatures or when



zinc oxide is added early in the mixing schedule. The ratio will decrease when the addition of glycols or other buffering chemicals compete with soluble zinc for silanol attachment. High ratios of zinc-to-water lead to a loss of soluble zinc from its cure activating function and lead to reductions in cure rate, mono and disulfide crosslinks, and high strain modulus. These effects are accompanied by excessive elongation, set and heat build-up. At the same time, the presence of zinc on the silica surface reduces silica-polymer bond strength with a resulting loss in abrasion resistance. A zinc-free cure system used with solution polymers has been effective in overcoming these characteristic silica compounding problems. Alternate compounding solutions are discussed in subsequent chapters. Determination of silanol content is made by incineration above 900°C, a method somewhat complicated by the loss of volatile salts.

Other methods include reacting silanols with a variety of organic compounds [3]. The surface of precipitated silica is considered to be completely saturated with silanol groups. At 200°C these are present in the range of 4 to 5 per square nanometer (some determinations at lower temperatures put the value between 8 and 12). Of greater importance to rubber reinforcement



is the position of -OH in respect to a surface silicon. Analysis with photoacoustic FTIR by J. R. Parker [5] has done much to reveal the nature of the silica surface. Three positions are recognized: isolated, vicinal and geminal, modeled in Figure 1.6. A vicinal grouping refers to adjacent silanols (-SiOH), hydrogen bonded. Geminal refers to two -OH groups attached to one silicon. The isolated silanol is the most reactive, and is the principal location for bonding to soluble zinc, amine derivatives, glycols and other additives. The photoacoustic infrared spectrum of silica in Figure 1.7 identifies the silanol types and other surface groups.

Most commercial precipitated silicas show little difference in the relative amounts of these three silanol types. A possible exception is the product Zeosil® 1165. A comparison of the infrared characterization of this silica with that of a silica of comparable surface area show fewer than normal isolated silanols. This difference might explain the higher MDR (moving die rheometer) crosslinks and 300% modulus found in many sulfur cured compounds based on 1165. Fewer isolated silanols result in less removal of soluble zinc from its crosslinking function. Of greater interest is the possible influence of reduced isolated silanols on surface area

measurements. Both CTAB and BET procedures give subnormal values for 1165 in respect to its actual agglomerate size in vulcanizates. The Figure 1.8 scanning electron micrographs of 1165 and other silicas in a zinc-free BR/NR formula show that only the silica with an average CTAB area of 170 m<sup>2</sup>/g (Hi-Sil® 190G) has agglomerates similar in size to those of the CTAB 155 m<sup>2</sup>/g Zeosil 1165. BET single point (N<sub>2</sub>SA) values show a wider gap of 217 to 173 m<sup>2</sup>/g. The inference here is that a reduction in silanol reactivity (fewer isolated groups) has also reduced surface area values. Confirmation of this failure of surface area to predict particle size is seen in Table 1.8 in a comparison of the processing and vulcanizate properties of 190G and 1165 compounds. There are no significant differences between the two silica compounds. In this case (Table 1.8) the normal prediction that high surface areas produce small agglomerates and high reinforcement is completely at odds with the data. That prediction appears to be valid only for silicas of similar silanol type distribution. Fortunately, this is still the situation for most commercial silicas. The “zinc-free” formula used in Table 1.8 uses a cure system which excludes soluble zinc, that is, one without fatty acid. It has been effective in solution polymers, raising the abrasion resistance of

silica reinforced compounds very close to that of comparable carbon black compounds. Zincfree curing systems are discussed at length in Chapter 4 on solution polymers.

