Basic approaches to creating bonds between silica filler and rubber

K. L. Kandyrin and A. N. Karpova
M. V. Lomonosov State Academy of Fine Chemical Engineering, Moscow

It is hardly necessary at the beginning of the twenty-first century to discuss in detail the merits of vulcanisates with silica fillers. Russia is on the verge of the wide-scale use of fine colloidal silicas in tread rubber formulations, which means that the advantages of such fillers can be considered to be universally known.

Worth examining in more detail, in our view, are the shortcomings of silica fillers and the possible ways of overcoming them. As is known, the surface of silica filler particles is polar and hydrophilic, whereas general-purpose rubbers are hydrophobic and non-polar. By virtue of this, the adsorption of macromolecules on silica filler particles is difficult; furthermore, the chemical interaction of rubber and most traditional vulcanising agents with the surface of fine colloidal silica is impossible. Therefore, vulcanisates containing fine colloidal silica are inferior in the level of elastic strength properties to vulcanisates filled with carbon black with the same degree of dispersion and the same volume proportions. The loss in plastoelastic properties is normally even more pronounced, since the filler particles interact extremely actively with each other, which leads to a considerable increase in the viscosity and elastic properties of the unvulcanised composite.

The highly polar and greatly developed surface of the silica filler adsorbs vulcanising group components from the rubber mix much more strongly by comparison with carbon black. This leads to a slowing down of the vulcanisation process and to an additional reduction in the rigidity properties of vulcanisates.

To reveal the potentialities of silica fillers, it is necessary physically or chemically to modify their surface. In spite of the fact that fine colloidal silicas have been used successfully in tyre rubbers of many countries for over a quarter of a century, a modification method has yet to be developed that would satisfy both production engineers and the users of rubber products filled with silica fillers. The main properties of silica fillers and of rubbers containing them can be found in corresponding reviews [1–3].

The first attempt to improve the properties of elastomer composites containing large amounts of silica filler was by using so-called activators, including polyhydric alcohols, amino alcohols, or amines. In their presence there is an increase in the degree of dispersion of agglomerates of fine colloidal silica and consequently a reduction in the viscosity of rubber mixes and an improvement in strength properties [4, p. 368]. Furthermore, the rate and degree of crosslinking of the rubbers increase. The latter effect is connected with a reduction in adsorption of the vulcanising group by silica fillers in the presence of substances that are adsorbed more rapidly. The level of interaction of the rubber with filler increases slightly when the normal activators are replaced with cationic surfactants with long alkyl chains which cling strongly to silica filler particles and hydrophobise their surface well [5].

Organic activators are unable to ensure the properties now demanded of tread rubbers for winter or high-speed car tyres. A chief (and very serious) shortcoming of these activators is that they are unable to create chemical bonds between the filler and the elastomer, and consequently the interaction between them remains of an adsorption nature, and the main cause of improvement in the properties of the composite is an increase in the area of actual contact of the particle with the matrix as a result of easier wetting. This enables the properties of
vulcanisates to be improved, especially under accelerated test conditions, but does not make it possible to produce rubbers that are resistant to the action of elevated temperatures and water; under such conditions, non-chemical bonds are broken.

Activators and surfactants can be used only in rubbers that are not exposed to elevated temperatures, moisture, electrolytes, and solvents, and therefore the areas of their application are extremely limited. In addition, simple compatibility with the polymer is insufficient for ensuring a high combination of mechanical properties of rubbers filled with fine colloidal silica. Silica fillers are incapable of forming chemical bonds with general-purpose rubbers either in initial form or after treatment with monofunctional compounds, in contrast to carbon black (carbon–rubber gel formation). The emergence of such bonds improves considerably the mechanical properties of the filled rubbers, especially the hysteresis properties, wear resistance, and tear strength.

In “critical-application” rubbers it is necessary for interphase bonds of a chemical nature to be formed, but this presents new difficulties. It is comparatively difficult to graft onto a rubber macromolecule the desired functional group capable of reacting with an $\text{Si–O–H}$ group, but silicon bonds with nearly all other elements are not resistant to hydrolysis, and therefore the production of interphase bonds that are entirely resistant to moisture is impossible even in principle. When any organic compounds (acids, alcohols, phenols, amines, halides, epoxides, and the like) interact with silanol groups, bonds of the $\text{Si–O–C}$ type are formed on the surface of the silica filler, which are particularly non-resistant to hydrolysis. This means that, with high probability, interphase bonds produced with the participation of such compounds may be broken during tyre service, since the temperature within the tread even of a car tyre can exceed $70^\circ C$ (and significantly higher temperatures during breaking), while available water is always contained in the particles of fine colloidal silica. The main approaches to developing additives for changing interphase interaction of silica filler with rubber differ precisely in their view of the problem of hydrolytic stability of the interphase bonds.

Among the many types of bond that are formed by a silicon atom, a special place is occupied by siloxane bonds $\text{Si–O–Si}$, the strength of which is extremely great, and hydrolysis occurs only under severe conditions that are not realised during tyre service. Such bonds are formed when alkoxy silanes react with a silanol group:

$$\text{Si–O–H} + \text{(C}_2\text{H}_5\text{O})_3\text{SiR} \rightarrow \text{Si–O–H} + \text{(C}_2\text{H}_5\text{O})_3\text{SiR} + \text{C}_2\text{H}_5\text{OH}$$

Even in the absence of reactive functional groups at substituent R, a monolayer of low-polarity nature is formed on the surface of the silica filler particles, which is compatible with the non-polar rubber, and chemically strongly combined with the particle itself. This on the one hand raises sharply the level of polymer–filler interaction and on the other hand lowers markedly the level of filler–filler interaction. As a result it is possible to reduce significantly the viscosity and elastic properties of rubber mixes filled with silica filler, and to improve the mechanical properties of the vulcanisates [6–8], but the interphase bond, as before, is non-chemical in nature.

It is natural that, in tread rubbers for tyres, hydrolysis-resistant interphase chemical bonds between the filler and rubber must be created. For the formation of such bonds, use is largely made of so-called bifunctional silanes (or, more accurately, substituted alkyltriethoxysilanes) which in the alkyl group contain a functional group that is capable of direct or indirect interaction with the rubber. For such bifunctional products, the term “coupling agents” is used in the English language literature. In the Russian literature, use is made of the terms “coupling agent” or “interaction promoter”, since the term “modifer”, as too broad, is inapplicable in this case.

The best example of a coupling agent of fine colloidal silica to rubber is bis(triethoxysilylpropyl)tetrasulphide (TESPT), developed by Degussa under the trade name Si-69 [9, p. 526; 10]. The tetrasulphide chain in its composition is capable, in the process of vulcanisation, of being incorporated into the general sulphur vulcanisation network (for example, by the mechanism of disulphide–disulphide exchange) or, decomposing at elevated temperatures, of interacting directly with diene rubbers. Processes of interaction with silica fillers proceed at temperatures of 120–150°C, i.e. under conditions of mixing at the first stage, while interaction with rubber proceeds at higher temperatures or longer contact times, i.e. during vulcanisation. As a result, in the process of mixing, effective hydrophobisation of the filler occurs, leading to a considerable reduction in the viscosity of the rubber mix and to a sharp reduction in its elastic properties, i.e. to a considerable improvement in its processing properties. During vulcanisation, strong polymer–filler bonds of a covalent nature are formed, the importance of which has been spoken about above. With TESPT there are practically no serious shortcomings; in its presence there is a slight reduction in scorch resistance, and its interaction with silica filler yields ethanol, as a result of which pores may arise in the vulcanisate. Furthermore, vulcanisates containing TESPT are sensitive to the manufacturing regime and, when this is disrupted, even very slightly, the properties of the mixes and of the vulcanisates may deteriorate considerably.

TESPT has performed best and has been widely used, its application being held back only by its cost (although, once the Degussa patent for Si-69 ran out, the production of analogues of this product both in the developed and in the developing countries began, and
the price of TESPT fell substantially). However, like all other triethoxysilanes, it has one further shortcoming: the reaction of the ethoxysilyl and silanolate groups is equilibrium, i.e. the $\text{Si–O–Si}$ bond formed may undergo alcoholysis by the ethanol formed. The equilibrium of this reaction is shifted to the right, but, with a considerable degree of transformation, especially if second and third alkoxy groups are affected, the reverse process begins. For this reason, the use of trialkoxysilane dressing agents cannot give the stoichiometrically calculated effect of hydrophobisation, and attempts to create a more effectively acting product are continuing worldwide. It is obvious that the use of dialkylmonoalkoxysilanes will be preferable, but such compounds are much more expensive than the traditional trialkoxysilane derivatives, and therefore the search among other organosilicon compounds is also possible.

At the same time, attempts to use organic compounds not containing silicon as the coupling agents of silica filler to rubber are continuing. Thus, recently, in a US patent [11], an interesting list of 15 non-alkoxysilane promoters of the interaction of silica fillers with rubbers has been presented, including 2,2’-dithiodisalicylic acid disodium salt, bis(succinimide) polysulphide, 3,3’-tetrathiodipropanol, hydroxyethylphenoxyacetic acid, 3,3’-tetrathiopropionitile, salicylic acid zinc and sodium salts, and compounds with maleimide groups. The authors (colleagues at the Goodyear Tire & Rubber Corporation) point out [11] that, in the presence of such additions, no ethanol, which is harmful to rubbers, is formed. It is doubtful that such an explanation is sufficient for the replacement of traditional dressing agents of the TESPT type with the proposed products, the more so as, when some of them interact with fine colloidal silicas, water is formed, which is even more harmful to rubbers. It is a different matter that additions of this kind may be useful in rubbers not experiencing extreme effects, i.e. not in car tyre tread rubbers.

In the presence of dithiodipropionic acid, an interphase chemical bond can be formed between a filler particle and rubber, but, if interaction with the rubber occurs by a mechanism practically identical to the interaction of rubber with TESPT, then a sequence of the $\text{Si–O–C}$ type is formed with the silica, with all the consequent effects. Nonetheless, such a coupling agent seems to be finding practical application, especially as 3,3’-dithiodipropionic acid can be used not only independently but also in mixtures with TESPT and other silane dressing agents [12].

Among the other organic promoters not containing silicon it is possible to name such compounds as tetrathiodipropionic acid [13] and also nicotinamide, in the presence of which, under conditions of accelerated tests, there is an increase in the strength and wear resistance of fine colloidal silica filled vulcanisates and a reduction in hysteresis losses. The nature of the interphase bond in this case may not be chemical; it is assumed that a hydrogen bond of nicotinamide with silica particle is formed, and van der Waals forces of interaction with the rubber [14]. Other nitrogen-containing compounds are also effective, for example, amides of aliphatic and aromatic carboxylic acids, including e-caprolactam and diethyltoluamide [15]. A description has been given of the use in this capacity of zinc, sodium, and ammonium salicylates [16], bis(hydroxy) compounds such as hydroxyethylphenoxyacetate [17], and also other bifunctional compounds containing hydroxyl, carboxyl, sulphonate, and thiooctanate groups, halides, etc. [18]. The use of alkylphenoldisulphide–formaldehyde resins is possible [19], but in this case the interphase bonds that arise are not resistant to hydrolysis.

The use of phosphites as coupling agents of silica filler to rubber is interesting [20], leading to the formation of bonds of the $\text{Si–O–P=}$ type, which differ in properties from both types of bond examined above. It is questionable, however, whether these bonds are resistant to hydrolysis.

Epoxy compounds, including epoxidised natural rubber, have a favourable effect on the properties of composites filled with silica filler. The independent use of epoxy oligomers and diglycidyl derivatives as coupling agents of fine colloidal silica to rubber is possible, but they are more effective in the presence of TESPT [21]. Interesting results can be obtained in the presence of liquid epoxidised oligobutadienes with a degree of epoxidation of 2–30% [22]. Epoxy compounds are preferable to alcohols, amines, and other organic substances of this kind, since they are capable of simultaneously reacting with other neighbouring silanol groups, i.e. of creating a more reliable bond of filler with rubber. Thus, the development of coupling agents of fine colloidal silica to rubber is possible on the basis of epoxy compounds, preferably with a high degree of residual non-saturation, including epoxidised oligodienes. In spite of the fact that the activity of the epoxy group in epoxidised polyisoprenes is much lower than in normal epoxy resins [9, p. 480], the chemical interaction of epoxidised natural rubber with the filler surface can be considered to have been proven [23]. Epoxidised natural rubber has recently attracted the fixed attention of researchers both as the polymer base for the corresponding vulcanisates and as a coupling agent for general-purpose rubbers with silica fillers [24]. The formation of chemical bonds between silica fillers and rubbers containing functional groups (nitrile, ester, hydroxyl, etc.) is possible, but the reliability of these bonds will not be high. The direction of the modification of elastomers with the formation of graft silanol, halosilane, or alkoxy silane groups, and, possibly, also groups containing tin [25, 26], can be considered promising, but today it is uncompetitive; furthermore, rubber containing functional groups of this kind can be crosslinked during storage [9, p. 531; 27].
Attempts to produce synthetic elastomers with polar groups that are adsorbed by silica filler or chemically react with it are worth mentioning [28, 29–31]. In spite of the fact that in the composites produced the interphase bonds between the filler and matrix have the same nature (Si–O–C) and are not resistant to hydrolysis, the polymer nature of the adhesive (in the present case, the matrix) makes it possible to treat this more leniently, but only when the functional groups in the modified rubber are located over the entire length of the macromolecule and are not end groups.

The range of organosilicon coupling agents of fine colloidal silica to rubber is not so broad, since, as already mentioned, it is difficult to outdo TESPT. A new product, more active than TESPT – 3-octanoylthio-1-propyltriethoxysilane – may possibly find industrial application [32]. Alkylmercapto-substituted trialkoxysilanes are known to have been used up to this point [6, 33, 34]. However, rubber mixes containing such additions are characterised by reduced scorch resistance [9, p. 528]. The highly effective coupling agent SILCAF (triethoxysilane with a carbamoylazoformate substituent), far more efficient than TESPT, is unstable during storage [9, p. 527]. When the main problem is the processing properties of the composite, primarily its viscosity, and the dynamic properties are not so important, so-called monofunctional silanes are used successfully, in particular alkylalkoxysilanes, which are extremely effective as water repellants. Such compounds are also effective as additions to TESPT [35]. Mention is often made of the use in composites filled with fine colloidal silica of unsaturated organosilicon compounds, in particular vinyltriethoxysilane. The chemical interaction of the simple vinyl group with rubber, even in the presence of sulphur, is unlikely, and consequently in this case it can only be a matter of the effects of hydrophobisation. The participation of unsaturated hydrocarbon substituents at the silicon atom in the formation of an interphase bond is possible either with a greater length of such a substituent [36] or in the case of the activation of such a bond by a neighbouring electronegative group [37]. Trialkoxysilanes with other substituents are used much less frequently on account of their low reactivity in relation to elastomers. It is possible to cite a neat example of the use as a promoter of the interaction of filler with rubber of γ-aminopropyltriethoxysilane AGM-9, which is capable of reacting with acid groups formed during the bulk hydrolysis of cyano groups of Reziplast rubber [38]. Unfortunately, AGM-9 does not improve the processing properties of the composite and, in addition, is more expensive than the Si-69 analogues. Furthermore, such a method is suitable only for rubbers containing a considerable number of acid functional groups in explicit or latent form. Another explanation of the effects observed is possible: nitrile groups are capable of forming hydrogen bonds with the silanol groups of the fine colloidal silica, which promotes disaggregation and dispersion of the filler [39].

Compounds of aluminium, titanium, zirconium, and other elements of groups III and IV of the periodic table that contain trialkoxysilylalkylene substituents have been proposed as additives that improve the properties of composites containing silica fillers [40]. Such compounds are quite likely to have a positive effect on the processing properties of fine colloidal silica filled rubbers, but it is unclear how they improve upon the much more readily available and cheaper analogues based on silicon. Slightly more accessible are organotin products [41], but they, too, are unduly expensive and in the near future will barely find practical application.

Asymmetric silane dressing agents, containing, along with trialkoxysilane groups, a benzthiazolyldisulphide substituent, and a maleic acid monoamide derivative have been proposed [42]. Whereas the mechanism of action of the first additive is clear (the disulphide group reacts with the rubber with the participation of a benzthiazolyl or benzthiazolylsulphide radical), in the second case it is difficult to expect the formation of a chemical bond directly with the rubber, although the interaction with different functional groups (aldehyde, amine, carboxyl, and like groups), which are always present in technical-grade rubbers in small quantities, is not ruled out.

Finally, mention must be made of a new approach proposed by the present authors to the formation of chemical bonds between fine colloidal silica and rubber, which consists in using two individual compounds, only one of which is an organosilicon compound capable of reacting with the surface of silica particles [43, 44]. Here, the second component of the system is selected such that it may combine the functional groups formed on the surface of the silica particles with macromolecules of the rubber. If the organosilicon component is used at the first stage of mixing, and the second component at the final stage, it is possible to avoid negative factors connected with the incompleteness of occurrence of chemical processes during mixing, and also with premature vulcanisation.

Thus, in spite of the fact that different additions belonging to different classes of chemical compounds can be used as coupling agents of fine colloidal silica to rubber, only organosilicon compounds capable of directly or indirectly interacting with general-purpose rubbers may find practical use in tyre rubbers. Among the products known today, these are triethoxysilylpropylpolysulphides, primarily di- and tetrasulphides. In spite of this, work in the area of creating other organosilicon promoters of interaction is urgent, since all products used at present have a number of shortcomings, and are also costly.

For rubbers working in less severe conditions than tyres (sole rubbers, light mechanical rubber goods

---

*International Polymer Science and Technology, Vol. 33, No. 2, 2006*
operating under mild temperature conditions, and so on), the use of organosilicon promoters is not essential and a greater proportion of the examined coupling agents of fine colloidal silica to rubber is possible.

The scope of this review has not made it possible to discuss in detail the mechanism of action of promoters of the interaction of silica with rubber, especially as this is discussed in detail in a number of papers by Noordermeer et al. [45–47] who have devoted long years to the investigation of this question.

REFERENCES

42. US Patent 6465581, MKI 5 C 08 L 005/544, 2002.

(Received 7.12.2004)