

# CHEMICAL PROPERTIES OF FILLERS AND FILLED MATERIALS

## 6.1 REACTIVITY

The properties of filled materials are critically dependent on the interphase between the filler and the matrix polymer. The type of interphase depends on the character of the interaction which may be either a physical force or a chemical reaction. Both types of interaction contribute to the reinforcement of polymeric materials. Formation of chemical bonds in filled materials generates much of their physical properties. An interfacial bond improves interlaminar adhesion, delamination resistance, fatigue resistance, and corrosion resistance. These properties must be considered in the design of filled materials, composites, and in tailoring the properties of the final product. Other consequences of filler reactivity can be explained based on the properties of monodisperse inorganic materials having small particle sizes. The controlled shape, size and functional group distribution of these materials develop a controlled, ordered structure in the material. The filler surface acts as a template for interface formation which allows the reactivity of the filler surface to come into play. Here are examples:

The first example refers to the creation of functional groups on the filler's surface during controlled synthesis of the filler.<sup>1</sup> Silica-gel, prepared from tetraethyl orthosilicate under acidic conditions, has OH groups on its surface. A similar synthesis under basic conditions deposits alkoxy groups ( $\text{OCH}_2\text{CH}_3$ ) due to an incomplete hydrolysis of the substrate. This simple example shows the numerous

possibilities that may deposit different groups on the filler surface. More examples of formation of functional groups are given in Section 6.2.

Figure 6.1 shows the difference between physical interaction and chemical bonding,<sup>2,3</sup> although in both cases chemical bonding is involved. In the case of covalent bond formation, the link is more permanent (requires a higher energy to disrupt it) and therefore it is considered a chemical bond. Hydrogen bonding can be disso-

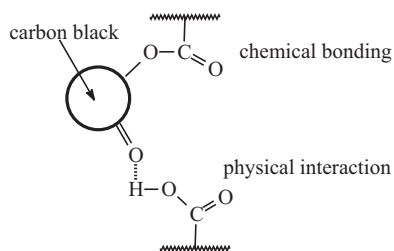


Figure 6.1. Interaction between XNBR and carbon black.<sup>2</sup>

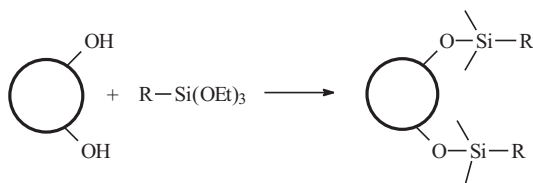


Figure 6.2. Reaction between monodispersed silica and silane.<sup>4</sup>

ciated by thermal energy (or a low level of energy) and then reformed again. Thus, hydrogen bonding is considered a physical interaction. It gives some flexibility to the system since the density of this crosslinking can be altered by changes in energy conditions.

Other physical interactions, such as van der Waals forces, have been omitted from this discussion since they are not chemical reactions. In this example, oxidized carbon black (OH and O groups on its surface) reacts with carboxylated nitrile rubber to form the product shown in Figure 6.1. This product is believed to be formed in a two-stage process. During mixing, a carboxyl group from XNBR forms hydrogen bonds with a neighboring OH group. In the second step, a molecule of water is released and the covalent bond forms later during molding. Molding assists in covalent bond formation because the process supplies sufficient energy for the reaction to proceed. This reaction is a spontaneous reaction which occurs without any special interference simply because both the correct reactants and the proper conditions are available.

Many well-controlled reactions occur when a filler and a reactant (e.g., polymer) are selected to take advantage of the chemical interaction. Reactions with silanes are typical examples of such reactions. Figure 6.2 shows an example of such a reaction.<sup>4-6</sup> Silane reactions provide a simple means of a conversion of functional groups. There may be two advantages: the possibility of forming a new functionality and a means to regulate coating thickness. Depending on the choice of R we can introduce unlimited numbers and kinds of functional groups. Depending on the effective length of the molecule R we can regulate the thickness of the monolayer coating. In one experiment,<sup>5</sup> the length of the molecule was varied from 1.92 to 13.0 nm. The length of the organic group and its concentration affects the thickness of the coating. By choosing the appropriate concentration, one can obtain monomolecular or multimolecular layers which can have further technological implications for the property of the material.

The chemical reaction can be discontinued when the silane coating has been applied or it may be continued by adding other reagents in a following step. The example described is a multistage process in which the reaction with silane is followed by many other reactions. The aim being to coat particles with *in situ* formed polymer. These reactions, called grafting reactions, may use all common organic polymerization reactions, such as radical, ring-opening, addition, etc.

Barium sulfate was first modified with 12-hydroxystearate and the product used for further grafting with acrylamide (Figure 6.3).<sup>7</sup> This experiment demonstrates that 12-hydroxystearate can be used as an initiation site for further polymerization. Also, polymer chains grow on the initiation sites formed by functional

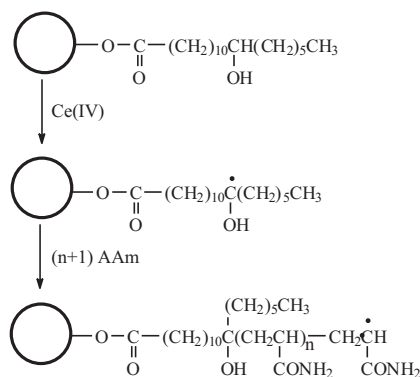


Figure 6.3. Acrylamide grafting on the 12-hydroxystearate previously reacted with the surface of  $\text{BaSO}_4$ .<sup>7</sup>

groups introduced onto the surface of fillers. Ceric ion alone can initiate polymerization of acrylamide but the conversion is low. If acrylamide is mixed with  $\text{BaSO}_4$  (without modification with 12-hydroxystearate) the conversion of acrylamide increases by about 100% but because there are no active sites available for grafting, no grafting of polymer occurs on the surface of  $\text{BaSO}_4$ . Conversion, in the presence of  $\text{BaSO}_4$  modified with 12-hydroxystearate, increases by about 220% and about 10% of the polymer formed is grafted onto the surface of the filler. The reaction proceeds according to first order kinetics (see Figures 6.9 to 6.11 in Section

6.3). Its rate is linearly increased by increasing the concentration of acrylamide, the concentration of catalyst, and the concentration of the modified filler. In summary, these reactions do not show any exceptional characteristics in comparison with the reactions without filler. But the filler's presence, and especially the presence of a modified filler, increases the initiation rate and thus the overall reaction rate. More examples of surface modification are given in Section 6.3.

Chemical reaction depends on the presence of reactive substrates and on the probability of their encounters. Thus, the possibilities of reactions can be numerous. The literature describes reactions of OH groups on the surface of kaolin with isocyanates,<sup>8</sup> vulcanization of nitrile rubber by  $\text{ZnO}$ ,<sup>9</sup> reactions of carboxyl groups on the filler surface with amines and epoxy groups,<sup>10</sup> reactions of carboxyl groups with diols,<sup>11</sup> and many others.<sup>12-15</sup> The presence of a reactant on the surface of a material particle increases the probability of chemical reaction. Other factors include statistical probabilities, surface barriers which affect contact, dilution factors, molecular mobility, and viscosity changes in the system. These are discussed in other sections of this book.

There is one particular factor which affects reactivity in systems containing fillers. This is exemplified by the work on the restriction of spin probe motions.<sup>16</sup> Nitroxyl radicals were studied in polyethylene filled with various fillers. Because of chemisorption of these radicals, their activity in the system was restricted. This phenomenon may affect the chemical reaction but in this context it is an essential mechanism which explains the somewhat disappointing performance of some UV stabilizers. UV stabilization is discussed in Chapter 11. This example is given now to show that the fillers present in a system may change performance characteristics by restricting the reactivity or the availability of system components. They may also enhance retention of components by slowing down their physical loss during processing or in subsequent exposure of the material to environmental forces.

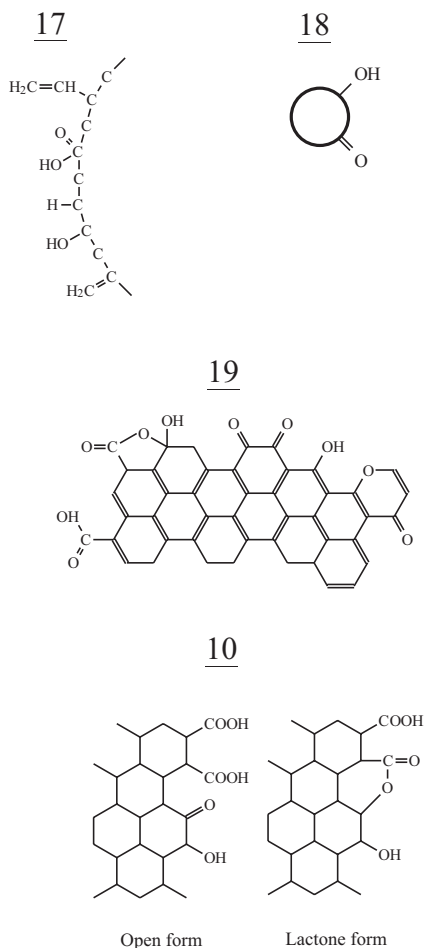


Figure 6.4. Various groups on CB surface.  
(Numbers are reference numbers).

## 6.2 CHEMICAL GROUPS ON THE FILLER SURFACE

Carbon black, because it is used so extensively, is one of the most frequently investigated fillers. However, findings have controversial elements in some of the details which attribute importance to surface groups.

Surface groups range from simple to complex structures (Figure 6.4). All agree on the presence of hydroxyl groups or oxygen on the surface but other groups such as carboxyl, lactone and unsaturations do not show on all formulas. The differences relate to the type of material tested. Some structures are typical of carbon black and some are typical of carbon fibers which differ not only in surface chemistry but also in surface morphology.

These differences in the chemical structure of the surface depend not only on the process of manufacture but also on additional treatments or processing conditions. In oxidized carbon fibers, the concentration of carbonyl and, more particularly carboxyl groups, is substantially increased at the expense of hydroxyl groups.<sup>10</sup> In the treatment of carbon fibers, several methods of oxidation are used. Liquid phase oxidation is carried out by the electrochemical and chemical methods whereas gaseous oxidation

is carried out in air, oxygen or in the presence of catalysts. Plasma treatment is also used for the surface oxidation of formed fibers. Different methods of oxidation produce different surface characteristics. For example, interlaminar strength is improved by a factor of 10 by electrolytic oxidation over crude oxidation in air.

XPS data show that adequate treatment time is needed to obtain the required concentration of functional groups on the surface of carbon black. As oxygen plasma treatment continues, the concentration of C-C bonds gradually decreases.<sup>20</sup> C-O bonds increase only during the early stages of the process, whereas both C=O and O-C=O continue to increase throughout the process. This confirms previously referred studies.<sup>10</sup> The formation of surface groups improves interfacial adhesion which contributes to reinforcement. But reinforcement also requires a strong fiber.

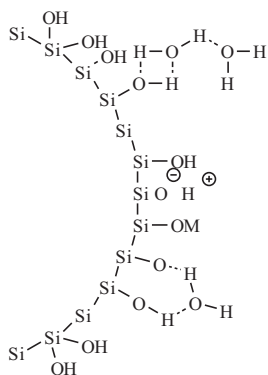


Figure 6.5. Silica, clay and talc particle.<sup>25</sup>

Fiber strength cannot be maintained if the oxidation process goes too far. It is therefore important to find a balance between fiber properties and the ability of the fiber's surface to interact with the surrounding materials.<sup>21</sup> Moderate oxidation generally gives the best performance.

IR studies give some insight into the type of chemical groups to which the hydroxyl group becomes attached. It is speculated that hydroxyl groups are parts of substituted phenols, phenols, alcohols and enols.<sup>22</sup> IR analysis also indicates that lactones, dicarbonyl compounds, carboxylic groups and carbonyl groups are present. Some of these groups are engaged in hydrogen bonding.

ESCA has been used in the surface analysis of carbon black oxidized by various methods. Again, oxidation in air contributes to the most substantial loss of C-C bonds. Keto-enol groups were detected only in the samples which were oxidized in air. When other oxidative processes were employed, the groups detected were OH, C=O, and COOH.<sup>23</sup> All other analytic methods provided similar information.

The groups present on the carbon black surface may also come from chemical treatments. In one report,<sup>24</sup> peroxide groups were introduced by radical trapping and then used for radical graft polymerization. In such a method, the entrapped radical plays the role of an initiator.

Figure 6.5 shows various functional groups which may be detected on silica, talc, and clay surfaces.<sup>25</sup> The surface character of carbon black differs in that it is mostly nonpolar whereas the surface of silica is polar. Thus carbon black is more compatible with hydrocarbon polymers which are also nonpolar. Silica and other similar fillers (talc, clay) have more affinity to each other than to nonpolar polymers. This is a major factor in the inferior performance in rubber applications where interfacial adhesion is reduced.

Figure 6.6 shows the distribution of hydroxyl groups on the surface of silicates such as aluminum, calcium, magnesium, and magnesium-aluminum silicates.<sup>26</sup> The surfaces of these fillers are dominated by silicate groups which occupy space as isolated, vicinal, geminal hydroxyl groups and sometimes form siloxane groups on the surface.

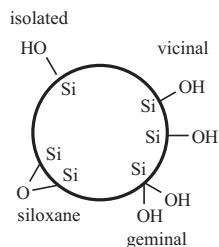


Figure 6.6. Silicate surface groups.<sup>26</sup>

The pH of the material surrounding kaolin will determine whether or not its surface will have OH groups. When the pH is above 7, the deprotonation of hydroxyl groups occurs which eliminates the active functional groups from the surface. The chemical changes are consistent with the ability of kaolin to flocculate in suspensions.<sup>27</sup>

Table 6.1: Filler modification

Modification	Reason	Typical fillers	Refs.
<i>Physical treatment methods</i> thermal (800-1050°C) thermal oxygen plasma surface oxidation (various) microwave plasma acetylene gas, plasma	improved dispersion interaction with CSPE reinforcement interfacial adhesion water resistance reinforcement	talc silica carbon fibers carbon fibers aramid fibers CaCO <sub>3</sub> , carbon fibers	33 40 20 10 48 30
<i>Acid treatment</i> hydrochloric stearic stearic stearic fatty metal soaps maleic derivatives	rubber crosslinking reinforcement surface hydrophobization dispersion dispersion interaction with H(CH <sub>2</sub> ) <sub>n</sub> H	ZnO CaCO <sub>3</sub> clay, CaCO <sub>3</sub> Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub> Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub> CaCO <sub>3</sub>	6 29 35 57 57 32
<i>Isocyanates</i> isocyanate isocyanate polyethylene glycol, isocyanate	reinforcement colloidal behavior resistance to solvents	hydroxyapatite kaolin kaolin	49 27 8
<i>Other low-molecular</i> dimeric aluminates oxyethylenes with N and S hexadecanol dicarboxylic acid anhydride doping and coating	reinforcement surface hydrophobization interaction with matrix sedimentation weather resistance	CaCO <sub>3</sub> silica silica Al(OH) <sub>3</sub> TiO <sub>2</sub>	34 45 40,41 51 59
<i>Grafting and resin coating</i> radical trapping polymerization various polymers polyethers acrylamide acrylamide maleic anhydride PP functionalized polymers polybutadiene coating resin coating	grafting initiation improved dispersion colloidal dispersion dispersability toughening, reinforcement wettability, hydrophilic coupling dispersion, adhesion chromatographic media water resistance	carbon black carbon black carbon black, silica carbon whisker CaCO <sub>3</sub> BaSO <sub>4</sub> mica, talc Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> aramid fiber	31 31 15,43 38 37 7 52-6 57 58 48

Table 6.1: continuation

Modification	Reason	Typical fillers	Refs.
<i>Silane or titanate treatment</i>			
silanes	coupling	clay	35
silanes	controlled coating thickness	silica	5
silanes	increase/decrease adhesion	silica	42
silanes	understanding surface	fumed silica	44
silanes	fire retardant improvement	Mg(OH) <sub>2</sub>	46
silanes	reinforcement	wollastonite	47
silanes	adhesion to matrix	basalt, sludge	50
silanes	whisker orientation	AlB whisker	53
silanes	coupling and adhesion	kaoline, talc, mica	54
silanes	coupling	Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub>	57
silanes	coupling	GF, silica, quartz	60
silanes	ion exchange	hydroxyapatite	6
silanes	reinforcement	natural fibers	61
silanes	nanoparticle synthesis	ceramic, metal	62
silanes	dense covering	silica	63
silanes	matrix-mineral adhesion	silica, steel, plastic	64
silanes	reinforcement	wollastonite	65
polymeric silanes	nanoparticles	silica	39
titanates	dispersion, coupling	Al(OH) <sub>3</sub> , Mg(OH) <sub>2</sub>	57
titanates	coupling, reinforcement	kaolin, silicate, CaCO <sub>3</sub>	36

Moisture is also a factor in controlling the concentration of functional groups on the filler surface.<sup>28</sup> Hydrated silicic acid has many times more OH groups than anhydrous silicic acid. The number of functional groups can also be maximized by a dispersion or particle size. For example, talc has numerous groups on its crystal side faces, therefore the number of OH groups is substantially increased with size reduction (delamination). This is consistent with the observation that fine talc gives better reinforcement of rubber than a coarse grade.

Calcium carbonate does not have functional groups (its surface is inert), therefore interaction can only be improved by chemical modification. Some hydroxyl groups can be found from admixtures such as Ca(OH)<sub>2</sub> but these admixtures may limit the ways in which calcium carbonate can be used because these admixtures increase the amount of absorbed moisture. Functional groups are frequently hydrophilic thus they attract water molecules. In many applications, moisture can either cause product instability, reduce cure rate, or reduce reinforcement. Caution is needed in selecting surface treatment to generate functional groups.

A similar analysis of functional groups in organic fillers is not feasible. These materials may be very complex mixtures (natural products) differing in chemical composition and surface organization or very diverse (man-made organic fillers).



### 6.3 FILLER SURFACE MODIFICATION

The following subjects are discussed in this section:

- Modification methods
- Reasons for employing specific method
- Examples of different fillers
- Examples of chemical reactions
- Reaction yield
- Modified material properties

Table 6.1 summarizes modification methods and reasons why such modification methods are used with the common fillers.

Table 6.1 shows that:

- Silanes are by far the most popular materials used for filler modification
- Silanes are also the most versatile (useful in modifying many types of fillers)
- Reinforcement and improvement of interface adhesion are the most frequent reasons for filler modification

Several approaches are used to modify fillers. One approach aims at increasing the number of active sites on the filler surface. This is usually done either by physical treatment or by acid treatment.

A second (and largest) group of methods includes the reaction of existing active groups to change their chemical composition. Acetic treatment, isocyanation, grafting, addition of other low molecular weight substances, and silane modifications fall into this category.

When modified by one of these methods, fillers become reactive with other chemical groups (a change in functionality) or change in surface character from hydrophobic to hydrophilic (and *vice versa*). Fillers are usually hydrophilic and do not easily combine with most polymeric materials which are usually hydrophobic. Such modification not only contributes to reinforcement but is also very useful in increasing the interaction of particles to impart rheological properties, prevent sedimentation, aid dispersion, or prevent agglomeration. These reactions deposit different coating densities. Coatings can be monomolecular or consist of numerous interacting layers. Coating thickness can also be varied by the length of the grafted polymer chain.

If functional groups are not available on the filler's surface, the filler's surface cannot be modified. This is the case with calcium carbonate. It may be coated with a layer of stearates, reacted with carboxylic acid, or exposed to a pyrolytic process (acetylene gas, plasma treatment) which forms reactive surface groups. Other fillers may be coated with a layer of polymer or a low molecular weight substance. This method is used frequently with fibers to either protect them against damage during processing (carbon fibers and glass fibers are fragile) or to assure that they will be wetted by the polymer matrix.



Calcium carbonate is a useful filler for the reinforcement of poly(vinyl acetate). Unlike other fillers, calcium carbonate can react with the carboxylic groups of poly(vinyl acetate). Stearic acid treatment is similar. Stearic acid is bound to the surface molecules to form insoluble calcium stearate. It is estimated that 3.2% of stearic acid covers only 40% of the surface. For 100% coverage, 8% stearic acid is needed.<sup>29</sup> The acid used for this reaction must be chosen with care. Best results are obtained from acids with hydroxyl group (hydroxyundecanoic acid).<sup>33</sup> This occurs due to hydrogen bonding between neighboring groups. The grafting ratio of hydroxyundecanoic acid ( $4.3 \text{ mol/nm}^2$ ) is better than that of stearic acid ( $3.5 \text{ mol/nm}^2$ ). Note that the concentration of acid in this experiment<sup>33</sup> was a magnitude lower than in the previously discussed experiment.<sup>29</sup> The density of the surface coverage is essential for orientation of the matrix chains on the filler's surface. If there is no coating on the calcium carbonate surface, it will have a high surface energy. This attracts some segments of the polymer chain to cover the filler surface. Most polymer structures do not interact with the filler surfaces. If a moderate coverage of fatty acid is applied, a polymer interacts with the surface of filler in between fatty acid chains. This gives a more dense and a more uniform interaction and better orientation of the polymer chains on the filler's surface. A further increase in coverage by fatty acid (more than 5%) does not leave enough space for the polymer to interact with the filler's surface which reduces the reinforcing effect of the filler.<sup>35</sup>

Several interesting and unusual methods are used to treat carbon black. Polymer radicals formed during the decomposition of peroxide polymers may be trapped on the surface of carbon black.<sup>31</sup> Such radicals reacted on the surface to form natural sites for further polymerization. This is because trapped radicals function as an initiator to initiate further polymerization reaction of methyl methacrylate on these sites. Polymerization of isobutyl vinyl ether gave very good grafting yields (23.5% and 16.2) when hydroxyl and carbonyl groups were first converted to sodium phenolates or carboxylated or by amine groups, respectively.<sup>15</sup> Methyl-2-oxazoline gave even higher grafting yields (24.8 to 32.9%).

Properties of carbon fibers were modified by oxygen plasma. Figure 6.7 shows changes in the O/C ratio versus the duration of the plasma treatment.<sup>20</sup> The amount of oxygen increases rapidly during the first minute of treatment. This is accompanied by a very rapid increase in carboxyl group concentration which later becomes stable. Other functional groups such as hydroxyl and carbonyl are stable throughout the first 3 minutes of the treatment. Only 10% of the original tensile strength is lost during the first 3 minutes of the treatment.

This discussion refers to modification of carbon whisker.<sup>38</sup> Ring opening polymerization of cyclic ethers was used to modify the whisker surface. To increase the number of functional groups, the whisker was also pretreated with  $\text{HNO}_3$  which increased the concentration of hydroxyl and carboxyl groups by about 50%. Figure 6.8 shows that increasing the grafting temperature decreased the grafting yield.

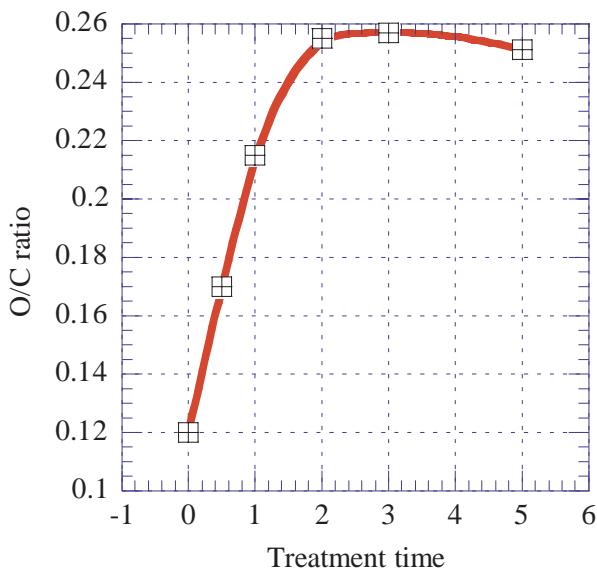


Figure 6.7. Variation of O/C elemental ratio as a function of treatment time. [Adapted, by permission, from Byung Suk Jin, Kwang Hee Lee, Chul Rim Choe, *Polym. Int.*, **34**, No.2, 1994, 181-5.]

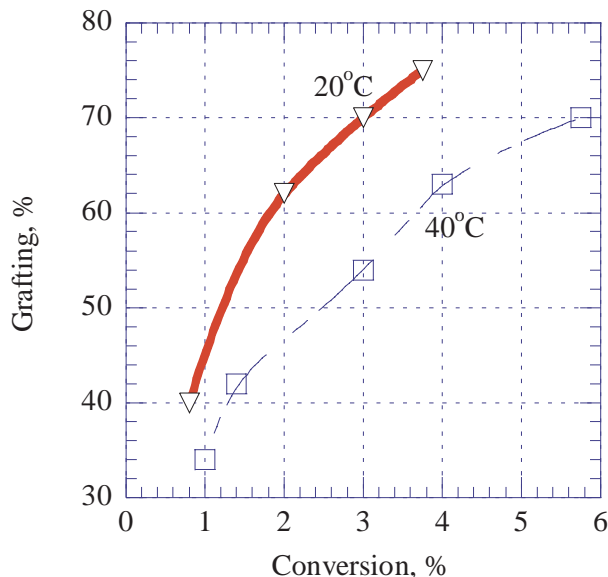


Figure 6.8. Effect of temperature on the grafting of poly(THF) onto carbon whisker. [Adapted, by permission from, Tsubokawa N, Yoshihara T, *Coll. & Surfaces*, **81**, 1993, 195-201.]

More ungrafted polymer is formed at higher temperatures because the higher temperatures facilitate chain transfer in the growing polymer cation.

Surface modification of silica is much easier than that of calcium carbonate because silica has numerous surface groups. It is not the greater reactivity of the sil-

ica which makes it easier but also the way in which silanes or titanates orient on the surface. Calcium carbonate, which does not have active sites, is coated with a random layer of modifying compounds. In silica, the modifier molecules are oriented perpendicular to the filler's surface.<sup>36</sup> There is a growing interest in methods of preparation of monodispersed particles of colloidal silica with grafted silane. These become sites for further polymerization. Alternately, polymeric silane is used for modification.<sup>5,39</sup> The nanoparticles had sizes of 11 or 42 nm and they were reacted with polymeric silanes, such as trimethoxysilyl-terminated poly(maleic anhydride-styrene) (PM-ST), PMMA or PS. On small particles, 8.6 molecules of PM-ST were bound to a particle compared with 590 molecules bound to larger particles.<sup>39</sup> The polymeric modifier (PM-ST) is a relatively rigid molecule and can be stretched to a molecular length of 15 nm which is relatively large compared to the smaller particle size (11 nm). This suggests that polymer chains are in a sterically crowded condition on the surface of small particles and the modifier encounters strong steric repulsion forces resulting in lower coverage. A broader study included 6 different low molecular weight silanes, polymeric silanes and further polymerization on the silane initiated sites.<sup>5</sup> The aim of the study was to control the thickness of the coating. For much larger particles of silica (with a diameter of 450 nm), the thickness of the coating varied from 0.6 to 73.1 nm depending on the modifier type and its concentration. It was not possible to control coating thickness by consecutive radical polymerization over previously initiated sites. But the use of some low molecular coupling agents enables the layer thickness to be controlled by concentration. Synthesis is simple, involving a simple mixing of reagents in solution with the filler. The temperature (from 0°C to reflux) and the time of reaction depend on the reactivity of the reagents. The yield of the reaction is also influenced by these conditions. Treatment by silanes is often conducted in bulk in which all the ingredients (including polymer) are present. This is a convenient method but results are not nearly as precise as those discussed above where silica is modified under controlled conditions.

The modification of a filler surface with isocyanates is a simple process which involves the reaction of hydroxyl groups on the filler surface with monomeric isocyanate. 2,4-toluene diisocyanate or hexamethylene diisocyanate are commonly used.<sup>8,27,49</sup> Since isocyanates are bifunctional they can be further reacted with polyols to form a coating on the surface or they can be used for the reinforcement of polyurethane. A strong covalent bonding can be verified by controlled extraction with the solvent. Bound material will not be removed from the filler's surface.

Mica, because of its platelet structure is a very useful filler. Its performance is improved by increasing the compatibility between filler and polymer. Silane modification is one simple and frequently used method. An alternative method involves a polymeric modifier which, in the case of polypropylene formulations, is polypropylene modified by maleic anhydride.<sup>52,56</sup> Such modifiers act more as compatibilizers. They are added in small amounts to a system containing both mica

and polypropylene. The polymeric component of the compatibilizer mixes with the polymer interphase and reacts with the filler. Similar technology is used for PP filled with talc.<sup>55</sup> These types of reactive compatibilizers (or polymeric modifiers of the filler surface) are of growing interest, considering that rather small additions of inexpensive material (relative to the cost of silane treatment) give the required reinforcement.

Wollastonite and kaolin are most frequently modified by silanes.<sup>35,47,54</sup> Several water-borne products are now available for this purpose, including those with functional amines, diamines, and vinyl-amines.<sup>54</sup>

Surface grafting of barium sulfate is interesting from the point of view of the kinetics of such reactions.<sup>7</sup> Barium sulfate like calcium carbonate, is an inert filler. So it is necessary to modify its surface. First, barium chloride is reacted with sodium sulfate in the presence of a small amount of sodium 12-hydroxystearate. This introduces a controlled number of hydroxyl stearate sites onto the barium sulfate surface. The reaction is followed by a redox graft polymerization of acrylamide initiated by the hydroxyl stearate groups and ceric ion as a catalyst. Figures 6.9 to 6.11 show the effect of reaction substrates concentrations on polymerization rate.

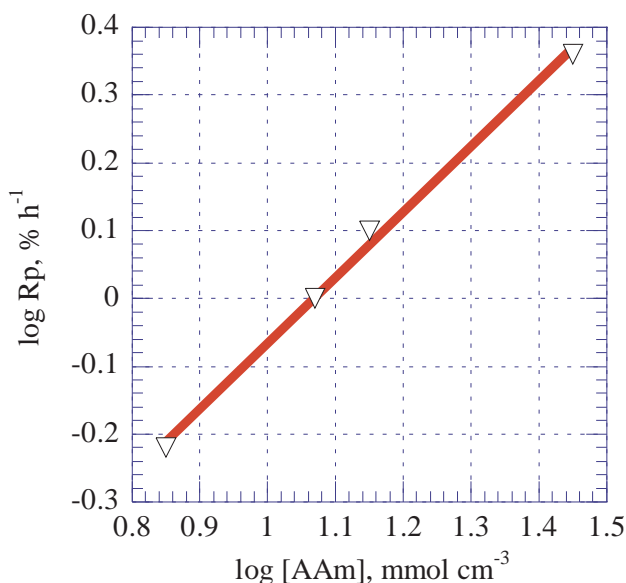


Figure 6.9. Polymerization rate,  $R_p$ , versus acrylamide concentration. [Adapted, by permission, from Tsubokawa N, Seno K, *J. Macromol. Sci. A*, **31**, No.9, 1994, 1135-45.]

In addition to the data included in Figures 6.9 to 6.11, it should be mentioned that grafting only occurs when all three of the ingredients are present (active site, monomer, and catalyst). The grafting reaction constitutes about 12% of the total

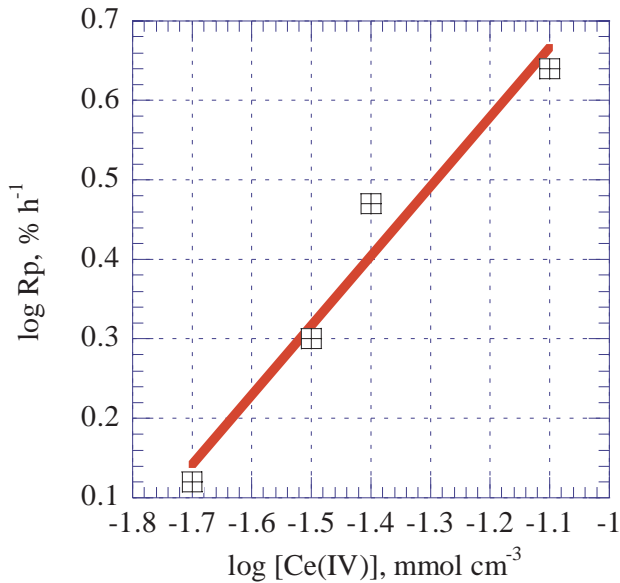


Figure 6.10. Polymerization rate,  $R_p$ , versus ceric ion (catalyst) concentration. [Adapted, by permission, from Tsubokawa N, Seno K, *J. Macromol. Sci. A*, **31**, No.9, 1994, 1135-45.]

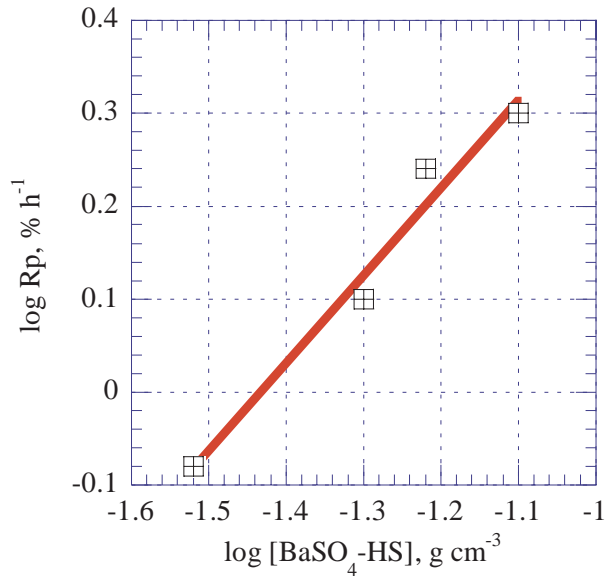


Figure 6.11. Polymerization rate,  $R_p$ , versus  $\text{BaSO}_4$  12-hydroxystearate modified concentration. [Adapted, by permission, from Tsubokawa N, Seno K, *J. Macromol. Sci. A*, **31**, No.9, 1994, 1135-45.]

polymer produced. The remaining polymer is not attached to the filler particles. The graphs show that the following kinetic equation is valid:

$$R_p = k[A\text{Am}][\text{Ce(IV)}][\text{BaSO}_4 - \text{HS}] \quad [6.1]$$

The modification of aluminum hydroxide by dicarboxylic anhydride has similar kinetics (Figure 6.12).<sup>51</sup> Figure 6.13 shows that the linkages formed are durable since they withstand of 30 h Soxlet extraction with n-hexane. Only when more than 1% of dicarboxylic anhydride is used does it becomes associated with the filler through physical forces. In this condition it can be removed by extraction. The concentration of reactive functional groups on the filler surface has a strong influence on the modification processes.

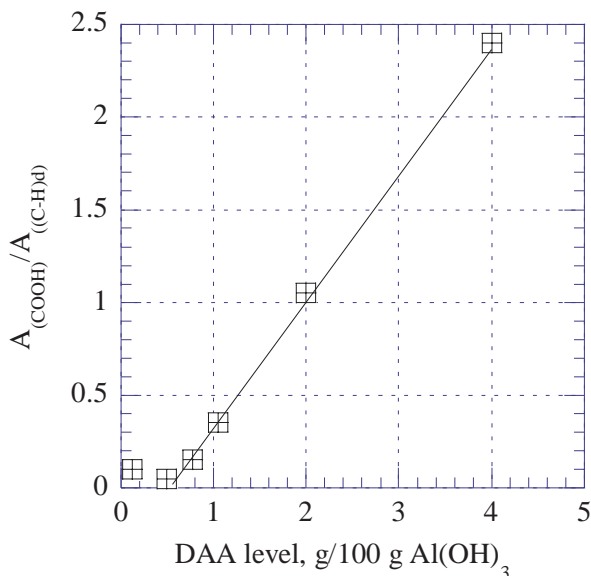


Figure 6.12. Carboxyl group IR absorption versus amount of dicarboxylic anhydride used for modification. [Adapted, by permission, from Liauw C M, Lees G C, Hurst S J, Rothon R N, Dobson D C, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.4, 1995, 211-9.]

Titanium dioxide can be improved by doping with metals. Titanium dioxide participates in photochemical processes. Its mechanism involves the formation of positive holes in the valence band and electron promotion to the conductive band irradiated by UV. Both electrons and holes react with the surrounding material. By doping TiO<sub>2</sub> crystals with various metals, electron and hole recombination centers are formed. Also, the crystal is coated with a layer of hydrous oxides which decompose hydroxyl radicals. This is applied to various grades of TiO<sub>2</sub> which gives them a unique performance in applications where UV durability is required.

Silanes play an important role in the modification of fillers. Silanes are coupling agents. Coupling, in technical terms, means a device for connecting things. Here, coupling means chemical or physical bridging of two different chemical materials which otherwise would have had a weaker association. Coupling depends on:

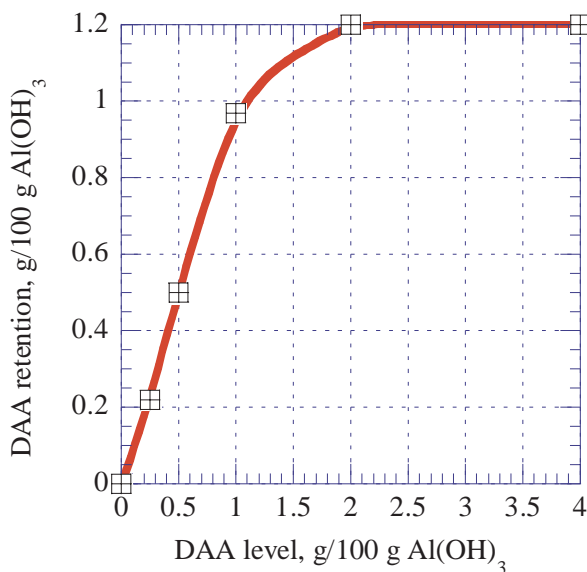


Figure 6.13. Retention of dicarboxylic anhydride after Soxlet extraction of modified  $\text{Al}(\text{OH})_3$  versus amount of modifier. [Adapted, by permission, from Liauw C M, Lees G C, Hurst S J, Rothon R N, Dobson D C, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.4, 1995, 211-9.]

- The chemical structure and mechanism of action of the coupling agent
- The character and chemical composition of the filler surface
- The chemical composition and, thus, the reactivity of the polymeric material
- The surface tension of the material being coupled
- The effect of system rheology
- The mechanism of physical and chemical adsorption of the coupling agent on the filler surface
- The molecular coverage and molecular orientation of the coupling agent
- The mobility of the coupling agent and other components of the system
- The effect of pH, solvent, etc. on adsorption
- The effect of filler surface preparation on adsorption and bond stability
- The reactivity of the organic part of the coupling agent with the polymer

From this list, the complexity of the coupling phenomenon can be estimated. It has taken forty years of practical experiments to develop our current understanding of these processes.

The chemical formula of the coupling agent can be written as follows:



where:

- $R$  a group responsible for polymer binding
- $X$  a group which combines with a filler
- $A$  a four-valent central atom connecting both groups in one chemical moiety.



Silicon, titanium, and zirconium, members of the IVth group of the periodic table, are the elements used as a central atom of the coupling compound. They are able to form four-valent compounds. The above structure is sometimes written in the more detailed form of a chemical compound able to perform six functions:<sup>84</sup>

$$(Y - R_1 - Z - O)_n AX_{4-n}$$

[6.3]

- where:
- Y

provides bonding reactivity with the polymer
- R<sub>1</sub>

provides van der Waals attraction and entanglement via long carbon chains
- Z

provides antioxidant effect, acid resistance, and corrosion protection via chemical groups involved (alkyl, carboxyl, sulfonyl, phenolic phosphate, etc.)
- X

hydrolyzable portion of molecule able to combine with filler
- A

provides transesterification and transalkylation catalytic activities, as well as affects other processes simultaneously performed in the system (curing, foaming, etc.)
- n

controls functionality of each substrate involved in the coupling reaction (filler and polymer).

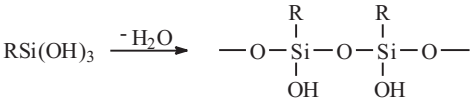
Table 6.2: Physical properties of some organofunctional silanes

Formula	Mol. weight	Density, g/cm <sup>3</sup>	n <sub>D</sub> <sup>25</sup>	Boiling point, °C
CH <sub>2</sub> =CHSi(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	190.3	0.894	1.397	161
CH <sub>2</sub> =C(CH <sub>3</sub> )C(O)O(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	248.1	1.045	1.429	255
EpoxyCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	236.1	1.069	1.427	290
HS(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	238.3	1.072	1.440	212
H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	221.3	0.942	1.420	217

This chemical formula describes the functions of coupling agents. The functional groups in available compounds, containing titanium, zirconium, and silicon, can be identified in corresponding catalogs of these products.<sup>66,67</sup> Several hundred compounds are available and discussed in these catalogues<sup>66,67</sup> which list prospective coupling agents. Table 6.2 outlines the basic properties of organofunctional silanes which have found broad application in industry. The chemical structure of these compounds influences the mechanism in which they are involved. The first involves hydrolysis, according to the following equation:

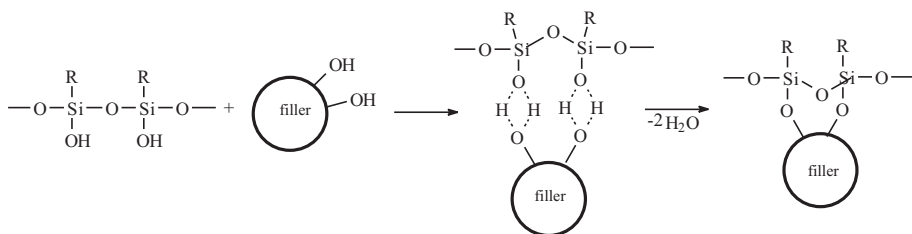


Because the X group is usually either alkoxy or chlorine, HX denotes alcohol or hydrogen chloride. In the next stage, the hydrolyzed silane undergoes a condensation according to the following reaction:



This stage is probably the most important contributor to coupling success. If the reaction occurs just as the silane is added or, later during material storage, it may retard silane mobility in the system (as the molecular weight of the silane increases, its rate of migration to the surface is slowed). This results in a less efficient silane use or in system instability. Here, the silane is used for the production of homopolymer entangled in the polymer chains, rather than for forming an interface between the filler and the polymer.

It has long been known that the rate of silane homopolymerization is increased by pH or metal salt catalysis and decreased by increased concentration and higher temperature. Most silanes are hydrolyzed most rapidly at pH between 3 and 5. Solution stability depends on the rate of homopolymerization to siloxane polymer. This is affected by pH, the presence of soluble salts of lead, zinc, iron, etc., and silane concentration. A pH in the range of 4 to 5 generally favors the monomeric form and retards polymerization. The formation of homopolymer can be detected as silane loses solubility and forms a gel which is not active in the coupling process. It is, then, desirable to retain silane in the monomeric or dimeric form. In the next two steps a bond is formed with the substrate (e.g., filler).



The first step is hydrogen bonding followed by bond formation and then by release of water which hydrolyzes other molecules should there be a shortage of water in the system.

The character of the deposition of  $\gamma$ -(methacryloxy)-propyl-trimethoxysilane (MPS) on the surface of clay and calcium carbonate was studied.<sup>68</sup> While most of MPS resists tetrahydrofuran washing when deposited on clay, MPS is removed by THF from calcium carbonate. Physico-sorbed layers can be removed by a solvent, whereas chemisorbed layers cannot be. Calcium carbonate does not contain hydroxyl groups (only some are available in admixtures), unlike clay which has a surface composed of Si-OH and Al-OH functionalities capable of covalent bond formation with silanol. Clay retains 66% of the silane applied, whereas only 19% of silane remained on the surface of calcium carbonate.

Further experiments have been done to determine the molecular weight of silane oligomers formed on the surfaces of various fillers and the amount of silane retained after THF washing. Table 6.3 shows how the retention of silane compares with the pH of the filler slurry. Neutral pH favors retention of silane, whereas a ba-

**Table 6.3: Silane retention percentage on various fillers after THF washing<sup>69</sup>**

Acidic	Neutral	Basic
Iron(III) oxide (pH=1.9) 82% Zirconium oxide (3.1) 78% Aluminum oxide (3.3) 100% Clay (4.1) 77% Tin (IV) oxide (4.1) 77% Tungsten oxide (4.8) 45% Tin oxide (5.3) 100 Iron(II) oxide (5.7) 100 Copper(II) oxide (6.1) 18%	Aluminum silicate (6.6) 87% Titanium oxide (6.6) 84% Amorphous silica (6.9) 83% Nickel oxide (7.0) 96% Kaolin (7.1) 96% Zinc oxide (7.6) 100%	Calcium hydroxide (12.3) 57% Magnesium oxide (11.1) 98% Glass spheres (10.7) 32% Barium hydroxide (10.5) 46% Lead oxide (10.0) 80% Wollastonite (9.9) 21% E-glass (9.5) 50% Calcium carbonate (9.4) 19% Calcium metasilicate (9.4) 34% Mica (9.3) 55%
Average = 74%	Average = 89%	Average = 49%

sic species does not favor retention. A pH of 4-5 is needed to stabilize a monomeric form.

At neutral pH, high molecular weight silane structures are obtained which provide more protection against chemical and water attack at the interface, but they also reduce interpenetration of resin into the silane layers (a similar effect was discussed above for calcium carbonate coating density).

The reversibility of the reaction is another important feature of coupling by silanes, titanates, and zirconates. The bond formed in the second stage (see chemical reaction above) is not a permanent bond but is an equilibrium reaction which depends on the amount of water in the system. This is the most important concept in the coupling mechanism. Bonds can form, break, and reform. Water immersion affects the interface, causing bond breakage. Bonds can be reformed again if the internal stress in the polymer matrix does not cause permanent delamination which separates the surfaces.

The third stage involves the reaction of the organic part of the silane molecule with a polymer, if such mechanism is available; e.g., when the organic part contains groups which can react with the polymer in question. The reactive group of the organic part of silane must react with the polymer. But, it is also very essential when this reaction occurs. If the rate of this reaction is too high, the polymer binds silane before it can reach the filler surface, thus silane mobility is retarded. This silane molecule will never participate in interface formation but will remain entrapped in the system, forming an inefficient bond.

In summary, depending on polymer type, amino, mercapto, epoxy, or vinyl are the most common functional groups which react with the polymer. Alkoxy or chlorine groups are often used to react with the filler surface, chlorine being less popular because it produces hydrogen chloride, a corrosive material.

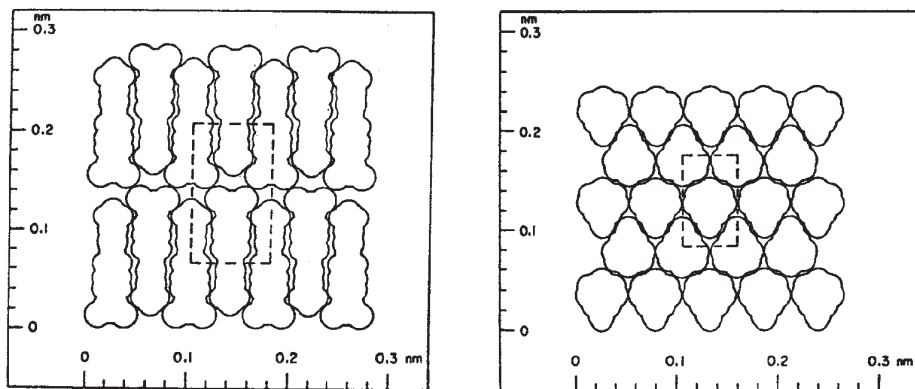


Figure 6.14. Closely-packed molecular configurations for silanetriol oriented parallel (left) and perpendicular (right) to the substrate surface. [Adapted, by permission, from Miller J D, Ishida H, *Surface Sci.*, **148**, 1973, 601.]

Efficiency is determined by the wetting characteristics of coupling agents, the surface area of the filler occupied by the coupling agent, the molecular mobility of coupling agents, their effect on viscosity, the effect of solvents on adsorption, the molecular orientation of coupling agents on the filler surface, their configuration, and molecular packing. The effect of coupling depends on the density of bonds formed on both sides of the interface, which primarily depends on the availability of the coupling agent at the interface. Critical surface tensions of most silanes are generally much lower than those of the surfaces (glass, fillers, metals) which they wet, indicating that surface wettability does not create a barrier.

The molecular mobility of the coupling agent is probably the single most important factor which contributes to the efficiency of its action. Two aspects of the mobility are equally essential: the reactivity of chemical groups in the coupling agent with chemical groups on the system components, and the mobility of the coupling agent, which depends on its physical interaction with the mixture components. The coupling agent must undergo a chemical reaction with the reactive group of the polymer or any other component of the mixture. But such a reaction should occur only when the reactive molecule is delivered to the interface which must be improved. To accomplish this requires planning of the mechanisms such that the rate of migration of the coupling agent is much higher than the rate of its reaction with the organic component. If this mechanism is not provided, more of this expensive component must be added and polymer properties will be modified. In this situation, the pot-life of the reactive system may affect the adhesion. Better adhesion will be obtained in a freshly prepared mixture than in the same system after storage, as a result of the partial reaction of silane.

Orientation of  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS) was studied in detail.<sup>70</sup> Two approaches were adapted: one was experimental, using FTIR with a hemispherical diffuse reflectance attachment, the other involved molecular model-

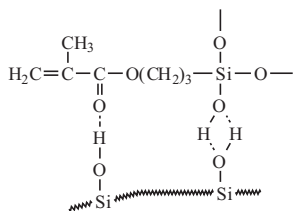


Figure 6.15. Silane arrangement on substrate surface.<sup>70</sup>

ling. Two molecular projections were analyzed, as displayed in Figure 6.14. Calculations showed that at a parallel orientation to the substrate, the MPS occupies a surface area of  $0.55 \text{ nm}^2$ . At a perpendicular orientation to the substrate surface one molecule of MPS occupies a surface area of  $0.24 \text{ nm}^2$ . From spectroscopic data it was calculated that the MPS molecule occupies  $0.6 \text{ nm}^2$  on clay and  $0.59 \text{ nm}^2$  on lead oxide which indicates that the molecules are in a parallel orientation (Figure 6.15).

These experiments show that the silane molecule must be held on the surface by hydrogen bonding at two centers of the molecule. The hydrogen bonding interaction with a clay surface is stronger than that with a lead oxide surface, as suggested by the  $9 \text{ cm}^{-1}$  difference in the frequency shift. The hydrogen bonding appears to be related to the ability of the surface to donate protons.

The close similarity of the data from modelling and experiments suggests that silane, if allowed to migrate to the surface of the filler, forms a closely packed monomolecular layer. The surface area occupied is related to the orientation of the molecule and its size, rather than to the type of substrate (filler) on which it is deposited. According to other studies,<sup>71,72</sup> silane molecules can also be oriented horizontally, and their actual orientation probably depends on the method of application (concentration, type of solvent, etc.).

The data in Table 6.4 have been developed from many years of practical experience. It provides information on the suitable types of coupling agents differentiated by the organic portion of the molecule. In polymers which are not reactive, such as polyethylene, polypropylene, etc., adhesion is built up by hydrogen bond formation. Methacrylosilanes provide this effect with these materials. Experimental work is always recommended to evaluate each combination of coupling agent, substrate, and polymer. So many diverse factors are involved that theoretical predictions are not always reliable.

**Table 6.4: Preferred silanes for certain resins**

Resin	Silane functional group
Epoxy	Epoxy, amine
Melamine	Amine
Polyamide	Epoxy, amine
Phenolic	Epoxy, amine
Polybutadiene	Vinyl, methacryl, mercapto
Polyester	Vinyl, methacryl
Polyethylene	Vinyl, methacryl
Polypropylene	Methacryl
Polyvinylchloride	Mercapto, amine
Urethane	Methacryl, mercapto, amine

Several new developments in silanes have been reported recently.<sup>64</sup> One deficiency of existing silanes was that they were not applicable to high-temperature polymers such as polyimides, either because they were not thermally stable or because they did not facilitate adhesion. A new aromatic imide silane was synthesized with two silane groups attached to the terminal phenyls in the molecule. A

**Table 6.5: Changes in material properties caused by use of modified filler**

Property change	Filler	Modification	Refs.
Reinforcement	glass beads	silane	73
Increased impact resistance	glass beads graphite fiber	compatibilizer polymerization	74 75
Increase in tensile strength	clay silica	silane	26 42,76
Decrease in elongation	talc	phosphate coating hexadecanol, silica	77 76
Increase in interlaminar shear strength	carbon fiber	thermal & epoxy oxidation	78 10
Increase in tear strength	clay CaCO <sub>3</sub>	silane	26 28
Increase in abrasion resistance	clay	silane	26
Increase in flexural modulus	talc	phosphate coating	77
Improvement in shear stress transfer	cellulose fibers	maleic anhydride	79
Decrease in Mullins' effect	silica	hexadecanol, silanes	76
Decrease in compression set	clay	silane	26
Increase in heat resistance	clay	silane	26
Decrease in sedimentation	Al(OH) <sub>3</sub>	dicarboxylic anhydride	51
Improvement in colloidal stability	kaolin carbon black	polyurethane coating grafting	8 11
Improvement in dispersion	carbon whisker	grafting	38
Decrease in viscosity	clay Al(OH) <sub>3</sub>	silanes dicarboxylic anhydride	26 51
Increase in melt flow	CaCO <sub>3</sub>	stearate	80
Effect on rheological properties	sepiolite	thermal treatment	81
Control of particle size and coating	colloidal silica	grafting	5
Improvement in whiteness	CaCO <sub>3</sub>	stearate	80
Lower electric conductivity	graphite	polymerization	72
Increase in polymer MW	graphite	polymerization	75
Transcrystallinity occurs	cellulose fiber	maleic anhydride	79
Increase in rubber-filler bonding	carbon black	oxidation silane	82 83
Converts hydrophilic to hydrophobic	montmorillonite	grafting	84

**Table 6.5: continuation**

Property change	Filler	Modification	Refs.
Reduction in water uptake	montmorillonite	grafting	84
Increase in crosslink density	silica CaCO <sub>3</sub>	hexadecanol, silanes maleic derivatives	76 32
Decrease in filler-filler interaction	silica	hexadecanol, silanes	76
Increase in solvent resistance	kaolin	polyurethane coating	8
Decrease in specific interaction	fumed silica	silanes	44

new polymeric silane was also developed. This has a polyethyleneimine backbone. It has film forming properties and can be used for the reinforcement of the interphase. Silanes have recently been used in the fabrication of integrated circuits where it adheres to polyimide, silicon and the layered metal patterns. Other area of developments in silane technology involve various methods of polymerization. Two relatively new methods are: photograft polymerization (photosensitive silane) and plasma polymerization of organosilanes. There are many new applications which use mixed silanes which allow various properties to be optimized.

**6.4 EFFECT OF FILLER MODIFICATION ON MATERIAL PROPERTIES**

Modification of fillers alters their properties. This section discusses:

- The types of changes which can be expected from modifications
- The extent of such changes

Table 6.5 lists the properties affected by various filler modifiers. Table 6.5 is not given as a comprehensive list of applications of these fillers. Fillers and specific properties of filled materials are dealt in detail in other parts of the book. The table summarizes the types of changes which can be expected from modifications.

The extent of changes caused by modifications is illustrated by the specific cases discussed below. Figure 6.16 shows the influence of modification of glass beads with 3-aminopropyltrimethylsilane by maleic anhydride grafted polypropylene (Exxelor PO2011) on the notched Charpy impact of polypropylene containing a compatibilizer and a non-functionalized rubber (EPM). The addition of glass beads to PP caused a reduction of Charpy impact from 6 to 4 kJ/m<sup>2</sup>. Yield stress was reduced from 32 to 18 MPa. This is caused by poor interfacial adhesion between PP and amine functional beads. The addition of a maleic grafted PP compatibilizer increased the yield stress to 31-32 MPa in the concentration range of compatibilizer. The Charpy impact improved at the lowest level of compatibilizer and remained constant. Although glass beads are coated with only 0.02% 3-aminopropyltrimethoxysilane, this is sufficient to react with the smallest amount of compatibilizer (no more reactive sites left). If EPM is dispersed as a separate



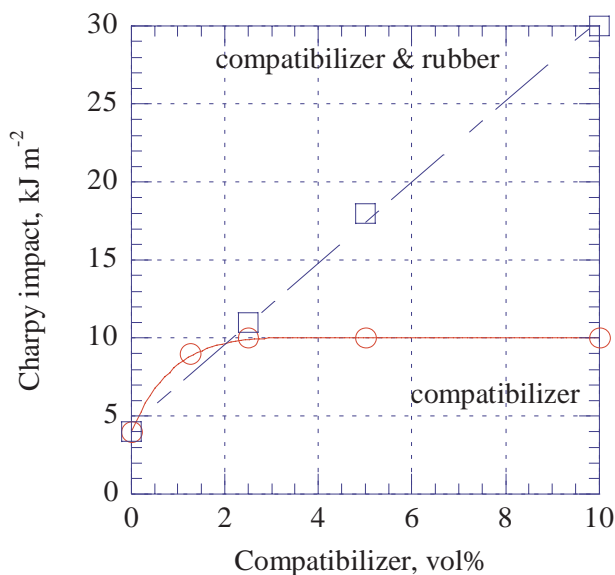


Figure 6.16. Charpy impact of PP containing 30% glass beads, compatibilizer (PP-g-MA) and rubber (EPM). [Data from ref. 74.]

microphase, its Charpy impact can be dramatically improved with a slight loss of yield stress. This shows that it is not just simple surface modification but complex interaction of the several components of the formulation and the reactive processing. The results of a good composition design can surpass the performance of the matrix polymer.

Figure 6.17 shows that crystalline dimensions affect interlaminar shear strength. Crystalline dimensions on the surface of carbon fibers can be measured by Raman spectroscopy. The ratio of intensity of two bands ( $1355$  and  $1575\text{ cm}^{-1}$ ) is proportional to the crystalline dimensions on the surface. The crystalline width increases considerably from 3 to over 12.5 nm when the temperature of manufacture of carbon fibers is increased from 1000 to 3000°C. The increase in band ratio correlates with an increase in interlaminar shear strength.

The amount of carboxylic anhydride used for modification of  $\text{Al}(\text{OH})_3$  determines the sedimentation rate of filler particles and the increase in water-based slurry viscosity.<sup>51</sup> A limiting value of viscosity is attained at relatively low levels of modifier. This amount of modifier is sufficient to react with the available sites on the  $\text{Al}(\text{OH})_3$  providing conditions for the breakdown of the aggregates and a separation of individual particles. Since the reaction decreases particle-particle interaction these processes are likely to occur. The sedimentation volume curve can be explained in the same way.

At low levels of addition, aggregates breakdown with simple shaking (before measurement) and later reaggregate as they settle. These data show the effect of

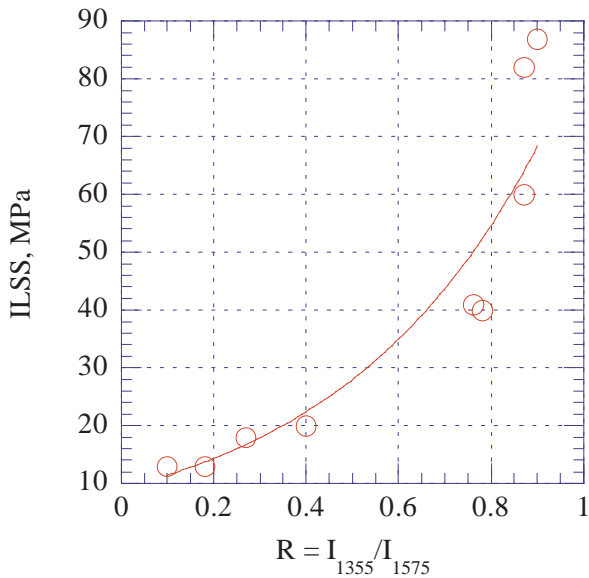


Figure 6.17. Ratio of Raman peak intensities at 1355 and 1575  $\text{cm}^{-1}$  vs. interlaminar shear strength of composites containing carbon fibers of different origin. [Data from Tang L-G, Kardos J L, *Polym. Composites*, **18**, No.1, 1997, 100-13.]

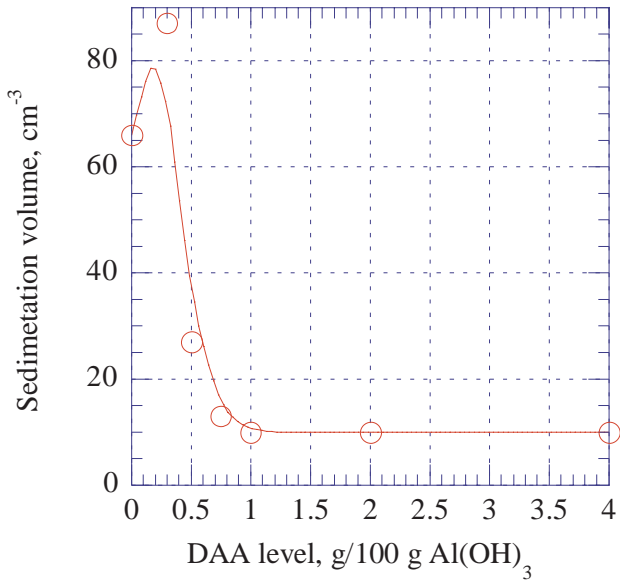


Figure 6.18. Sedimentation volume of  $\text{Al(OH)}_3$  vs. amount of dicarboxylic anhydride used for its modification. [Adapted, by permission, from Liauw C M, Lees G C, Hurst S J, Rothon R N, Dobson D C, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.4, 1995, 211-9.]

modification on particle-particle interactions. Not only rheological properties but other properties such mechanical properties, Mullins' effect, etc. are affected.

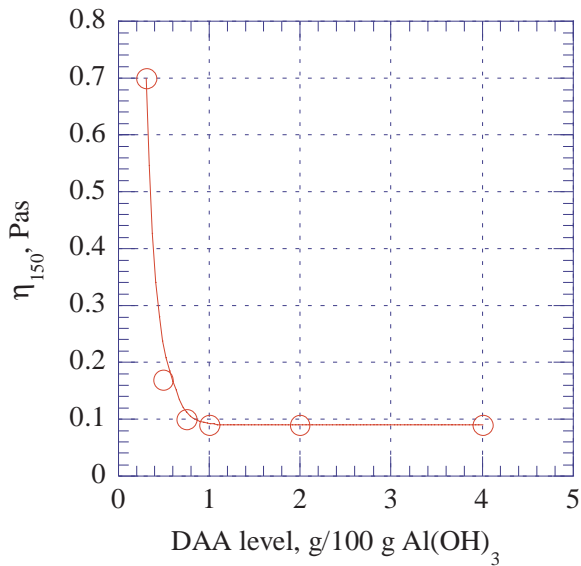


Figure 6.19. Slurry viscosity vs. amount of dicarboxylic anhydride used for  $\text{Al}(\text{OH})_3$  modification. [Adapted, by permission, from Liauw C M, Lees G C, Hurst S J, Rothon R N, Dobson D C, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.4, 1995, 211-9.]

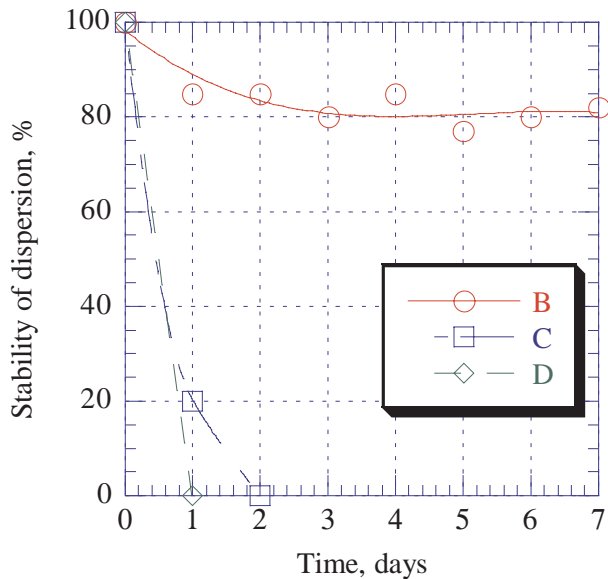


Figure 6.20. Stability of grafted carbon black (A), carbon black with physically absorbed polymer (B) and untreated carbon black (C). [Adapted, by permission, from Tsubokawa N, Hosoya M, Kurumada J, *Reactive & Functional Polym.*, **27**, No.1, 1995, 75-81.]

Carbon black grafting has a similar effect on dispersion stability (Figure 6.20).<sup>11</sup> Modified carbon black is substantially improved. The graphs show that

there is a substantial difference between the physical dispersion of the polymer and grafting. The absorption of polymer on the surface does not give improvement over untreated carbon black. Direct condensation of carboxyl groups on the surface of carbon black with N,N'-dicyclohexylcarbodiimide, followed by the reaction with the polyol gives substantial improvement. Grafted polymer chains inhibit aggregation and contribute to the formation of a stable colloidal dispersion.

The same results were obtained when polytetrahydrofuran was grafted onto carbon whisker.<sup>38</sup>

## 6.5 RESISTANCE TO VARIOUS CHEMICAL MATERIALS

The literature on the subject of chemical resistance of fillers and filled materials remains sparse but some essential data can be reported. A comparison was made between E-glass and Kevlar with respect to their resistance to acids and bases.<sup>85</sup> E-glass is severely attacked by most acids. The most aggressive is nitric acid. Two weeks immersion causes a loss of more than 90% of its original strength. E-glass is resistant to acetic and phosphoric acids. Only 39% of its original strength is retained in ammonia and 64% in NaOH. In all these cases, the samples were immersed for 2 weeks in 2M solutions. Kevlar in most cases resists acids very well with a loss of only 10% of its original strength. The exceptions are HCl (a loss of 4%) and HNO<sub>3</sub> (loss of 60%). Other immersions, such as in H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and NaOH cause losses of about 30%.

Morphological studies explain the mechanisms of E-glass corrosion.<sup>86</sup> According to these studies, acid corrosion of E-glass is caused by calcium and aluminum depletion which varies depending on the acid type, fiber type, and acid concentration. Oxalic and sulfuric acids are more corrosive than nitric and hydrochloric acids. This difference is due to the fact that, in oxalic acid, precipitated products are formed which decrease the concentration of leachates in solution. In addition to the loss of mineral content, fibers develop axial and spiral cracks. Crack formation depends on the rate of material depletion.

CaCO<sub>3</sub> is not resistant to the attacks of H<sub>2</sub>SO<sub>4</sub> and HCl because the products of reaction are water soluble. Polyolefins filled with CaCO<sub>3</sub> experience a rapid loss of weight on acid immersion which depends on the concentration of filler. This loss of mass causes increased porosity of the filled materials.<sup>87</sup> The effect of TiO<sub>2</sub> on corrosion resistance was also evaluated. Different grades varied in their degree of interaction with the binder. If the interaction decreases, the corrosion resistance also decreases. The corrosion damage in salt spray was proportional to the concentration of TiO<sub>2</sub>.<sup>88</sup> Filled epoxy resins used in food contact applications were evaluated by SEM. Introduction, even in small concentrations (10%), of filler causes inhomogeneities in the fracture zone but the surface remains similar to unfilled material. But, under high magnification, all surfaces had small (about 9 nm) microcracks which might permit reagents to diffuse. Larger particle sized fillers

(barium sulfate and iron oxide) caused more inhomogeneity in the filled material than did smaller particles. Small particles were well coated with resin.<sup>89</sup>

Solvents produce different effects than do corrosive chemicals. Both silica and carbon black filled natural rubbers were more resistant to solvents than unfilled rubber.<sup>90</sup> Also, the cure time was important, indicating that the bound rubber plays a role in the reduction of a solvent sorption. The diffusion coefficient of solvents into rubbers decreases with longer cure times and higher fillers loadings. Polychloroprene rubber swollen with solvent has a lower compression set when it is filled with carbon black.<sup>91</sup>

## 6.6 CURE IN FILLER'S PRESENCE

This section contains information on the cure response of UV-curable and thermosetting polymers in the presence of fillers. The discussion includes:

- Advantages and disadvantages of the use of fillers
- How fillers interfere with cure

The kinetics of reaction is discussed in Section 6.10 and polymerization reactions in Section 6.7. Grafting is discussed in Section 6.8, crosslink density in Section 6.9, and bound rubber in Chapter 7. Here, UV-curable materials, epoxy resins, polyurethanes, rubbers, polyesters, and phenolic resins are discussed.

The application of fillers in light-curable resins is considered a sensitive issue because filler particles are known to reflect and absorb light radiation which may potentially affect curing rates. This makes it an interesting subject to evaluate. Several fillers were studied in this context.<sup>92-95</sup> Silica was used to fill 2,2'-bis[4-(-methacryloxy-2-hydroxy-propoxy)-phenyl]-propane – a material used for restorative purposes in dental applications. Figure 6.21 shows the degree of conversion vs. silica content. The increase in conversion rate depends on the path length of UV radiation through the material. Multiple radiation scattering by the filler causes a better use of light energy due to the complex path that the light beam is forced to take and by better light distribution throughout the material. In order to take full advantage of scattering, the size of particles must be half of the wavelength of the activating light. Silica particles are very small (0.04  $\mu\text{m}$ ) but they form agglomerates which are larger (0.2  $\mu\text{m}$ ). The size of these agglomerates is close to half of the wavelength of the activating light (0.4-0.5  $\mu\text{m}$ ).<sup>92</sup>

Printing inks and wood fillers also take advantage of light curing.<sup>93</sup>  $\text{Al}(\text{OH})_3$  is the usual choice in this application. Materials were cured by a mercury lamp and results evaluated by differential photocalorimetry and UV-visible spectroscopy. The sample weight and amount of filler were the essential variables. Addition of filler increased UV cure rate. At a low filler concentration (13.2%) the rate was only ~10% more than with no filler. At a medium filler load (19.7%) the rate was doubled. At very high loads (56.5%) and in larger specimens used for the evaluation of wood fillers, the curing rates tripled over products filled with the more conventional  $\text{CaCO}_3$  and clay. These increased rates of cure are due to a filler more

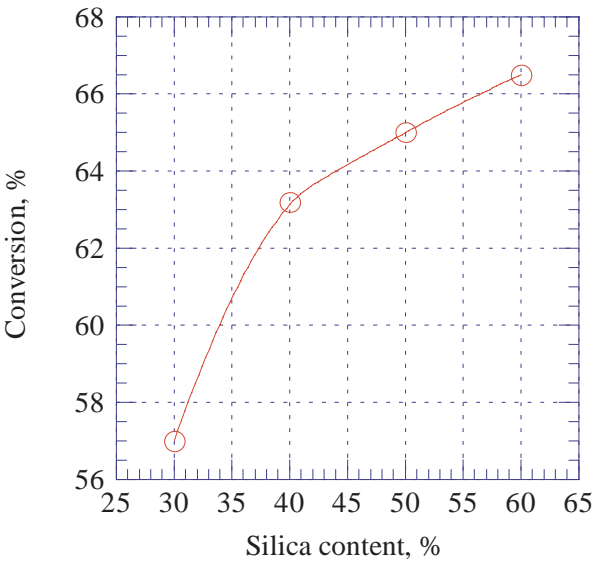


Figure 6.21. Degree of conversion as a function of silica content. [Adapted, by permission, from Kim S, Jang J, *Polym. Test.*, **15**, No.6, 1996, 559-71.]

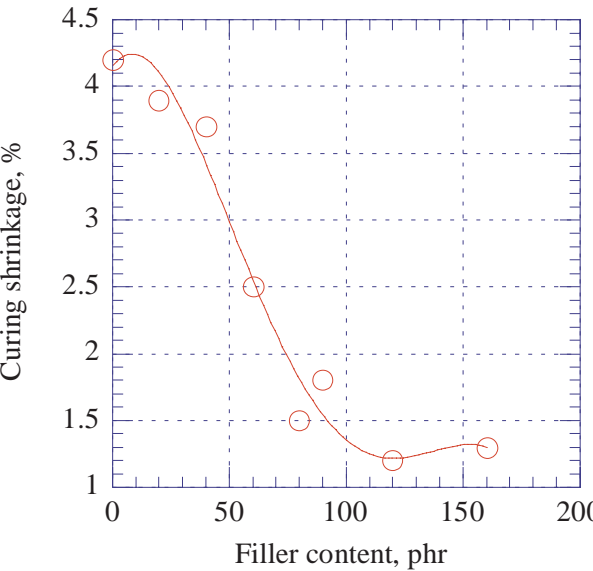


Figure 6.22. Curing shrinkage of UV curable adhesive vs. filler content. [Adapted, by permission, from Murata N, Nishi S, Hosono S, *J. Adhesion*, **59**, Nos.1-4, 1996, 39-50.]

transparent to UV light than is the resin which causes the increase in UV flux and penetration depth. This conclusion is further reinforced by other data presented.<sup>94</sup> The evaluation of light transmittance through a sample of a filled polymer (UV-

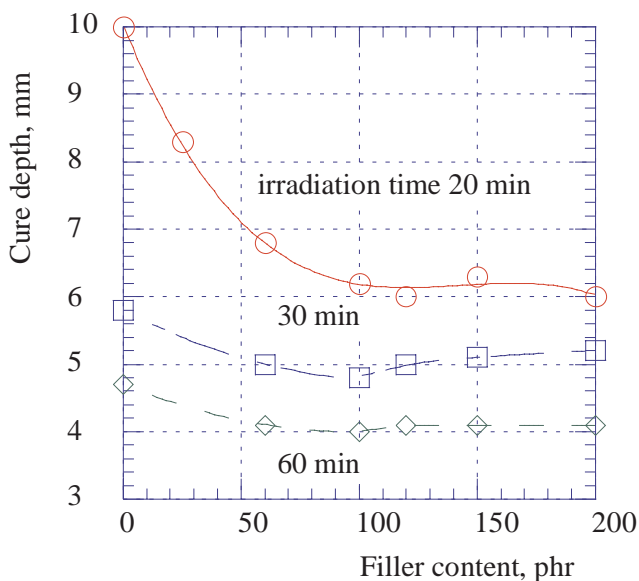


Figure 6.23. The effect of quartz filler on the depth of cure at three irradiation times. [Adapted, by permission, from Murata N, Nishi S, Hosono S, *J. Adhesion*, **59**, Nos.1-4, 1996, 39-50.]

cured polyurethane) shows that the unfilled polymer has the same transmittance as a polymer filled with  $\text{Al}(\text{OH})_3$  but the filled polymer has substantially improved diffuse transmittance over the neat polymer. Thus, more light is used in a process which accelerates the cure. Particle size does not seem to have any influence on transmittance nor on cure.

Quartz was used as a filler in the manufacture of optical devices from epoxy in a UV-curable system.<sup>95</sup> Figure 6.22 shows that addition of a filler can substantially reduce curing shrinkage which is highly desirable in the precise manufacture of these materials. Reduced shrinkage is the result of a low thermal expansion coefficient of quartz in comparison with the resin.

The presence of a filler does not significantly affect cure depth (Figure 6.23). Small quantities of a filler in a system with very long cure times have some influence. But this is irrelevant considering that the best optical and mechanical properties are obtained at filler loadings of 100-150 phr. Several metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{ZnO}$ ) were tested in brominated epoxy resins cured at elevated temperatures.  $\text{Fe}_2\text{O}_3$  was found to have a catalytic effect on the cure. This is due to the reaction of terminal epoxy groups with surface hydroxyl groups on the filler. Adding  $\text{Al}(\text{OH})_3$  also caused an increase in the rate of cure. This is attributed to an accelerated homopolymerization of epoxy on the alumina surface.  $\text{ZnO}$  gave the greatest acceleration of cure rate but no explanation is yet known. All three fillers affect reaction rates, reaction orders, activation energies, and reaction exotherms.



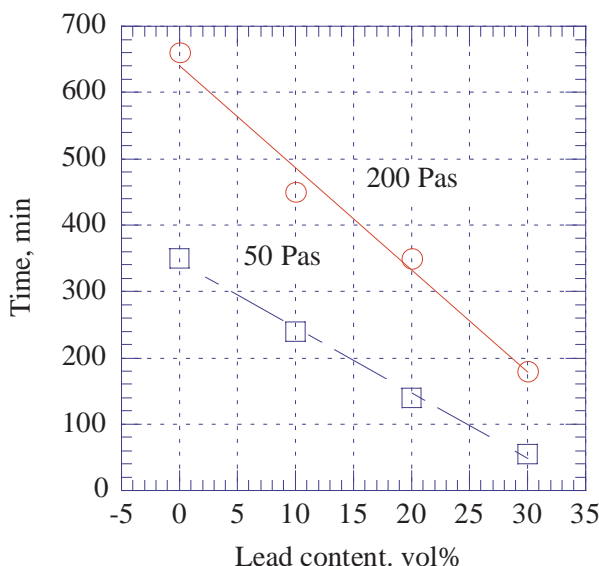


Figure 6.24. Polyurethane formation in the presence of lead powder. Reaction time to reach certain viscosity. [Adapted, by permission, from Caillaud J L, Deguillaume S, Vincent M, Giannotta J C, Widmaier J M, *Polym. Int.*, **40**, No.1, 1996, 1-7. ]

Lead powder was used as a filler in polyurethane.<sup>97</sup> It is clear from the graph (Figure 6.24) that the addition of metal catalyzes the curing process. The reasons for this catalytic effect are unknown. It is suspected that surface impurities may act as a system catalyst but which impurities is not known.

Densified polyurethane foam was used as a filler in rubber in an attempt to recycle this material.<sup>98</sup> Small additions (up to 30%) did not much affect the cure rate but as the quantity was increased the rate of vulcanization slowed probably due to the effect of dilution and increasing viscosity.

In interpenetrating polymer networks, chemical crosslinking and phase separation and their timing affect properties. Fumed silica, alumina, and carbon fiber were used in a network developed from polyurethane and polyesteracrylate.<sup>99</sup> The presence of fillers affected many properties. Conversion rates were higher in the presence of fillers. Also, microphase separation was affected. As a result of these two changes the filled material was unrecognizable from the unfilled material.

In rubber, fillers play a role in the vulcanization process. These fillers are not considered here. The effect of carbon black on the vulcanization rate is still a matter of some dispute. Older papers presented data indicating that carbon black slows down the vulcanization rate. A more recent study<sup>100</sup> shows that the vulcanization rate of rubber actually speeds up with the addition of carbon black. The proposed explanation suggests that changes in the mechanism of vulcanization occur in the presence of carbon black. Addition of ground rubber together with carbon black did not affect the vulcanization rate.<sup>101</sup> In ferromagnetic applications, ferrites were

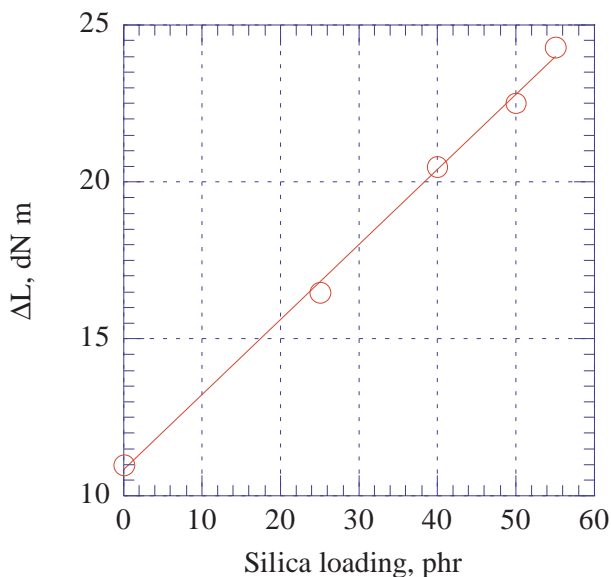


Figure 6.25. Torque difference vs. silica loading. [Adapted, by permission, from Cochrane H, Lin C S, *Rubb. Chem. Technol.*, **66**, No.1, 1993, 48-60.]

added to rubber.<sup>102</sup> Cure rates were substantially faster especially in the presence of barium ferrite.

Silicone polymers are unique in that they require a filler to improve their properties. The filler discussed here (silica) is similar in functionality to the polymer.<sup>103</sup> Figure 6.25 shows the difference between the initial and the final torque which is a measure of crosslink density. The reaction rate is proportional to the silica loading. This indicates that both the filler and polymer contribute to the measured property. Also, properties depend on the number of hydroxyl groups on the filler's surface since they participate in the reaction.

$\text{Al}(\text{OH})_3$  inhibits the curing reaction of allylester resin.<sup>104</sup>  $\text{CaCO}_3$  and glass fiber exert a similar effect on the cure of unsaturated polyesters.<sup>105,106</sup> Both the reaction rate constant and the activation energy are higher in the presence of a filler than in the neat resin. Many papers have been published dealing with the rate of reaction in the presence of these fillers. There is no consensus. Some report acceleration, some no effect, others rate reduction. The reasons are also inconclusive. It is difficult to say if cure inhibitions reported in recent papers are a special case or if the results reported depend on factors which are still to be determined.

Lignin fillers decreased the cure rate of phenol-formaldehyde resin.<sup>107</sup> Here, the filler acts as a diluent and does not have the ability to affect the reaction kinetics by interaction with the polymer. Glass fibers also decreased the rate of cure of a phenolic resin in another study.<sup>108</sup>

In conclusion, the effects of particulate fillers differ from those of high aspect ratio fillers. Particulate fillers seem to increase cure rate in most cases, especially if they contain active groups on their surface which either may react with the resin or change reaction mechanism. High aspect ratio fillers seem to decrease the reaction rate due perhaps to their more localized influence. Questions still remain as to how accurate these findings are. Reactive systems have been studied by rheological and physical methods and little is known about the mechanisms of reaction or kinetics determined by following the concentrations of substrates during the reaction. Physical and rheological methods give information on the entire system as determined by changes in viscoelastic properties or in thermodynamic properties. These depend not only on the chemical reaction but also on the association, crystallization, and orientation which are properties unrelated to cure.

## 6.7 POLYMERIZATION IN FILLER'S PRESENCE

Catalytic polymerization on solid surfaces is becoming a more attractive method for the production of polymer filler composites.<sup>109-111</sup> The process involves three major stages: preparation of filler, surface activation of filler, and polymerization on the filler surface. Fillers usually tested for this application include kaolin, tufa, dolomite, perlite,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaSO}_4$ , mica and wollastonite. The best results were obtained with  $\text{CaSO}_4$ , wollastonite,  $\text{Al}_2\text{O}_3$ , dolomite, and kaolin. Before the filler can be used, it must be dried because the deposition of catalyst requires moisture-free conditions. The catalyst is a combination of Al/Ti/Mg in different proportions each of which gives a different efficiency. The deposition of catalyst is a simple process involving the treatment of filler particles with solvent solutions of organometallic compounds. The polymerization of ethylene in a slurry is a highly efficient process. This is sometimes called polymerization filling. There is no elaborate process mechanism nor is the morphology or chemistry well understood, but the results of this synthesis surpass all conventional mixing techniques. The products from this process have better elongation than unfilled polymers and show improvements in almost all mechanical properties.

Montmorillonite is an effective complex with the initiator in the polymerization of methyl methacrylate.<sup>112</sup> It not only accelerates the polymerization but also improves such mechanical properties as hardness and compression strength. Pentabromobenzyl acrylate was mechano-polymerized in the presence of  $\text{Mg}(\text{OH})_2$ .<sup>113</sup> The polymerization occurred at a reduced temperature and a flame retarded product was produced.

Figure 6.26 gives information on the effect of carbon black loading on the polymerization efficiency of pyrrole. The polymerization rate was reduced as the loading of carbon black was increased. The reduced rate is caused by the oligomer coupling on the surface of the carbon black and by the absorption of the chemical oxidant needed for polymerization.<sup>114</sup>

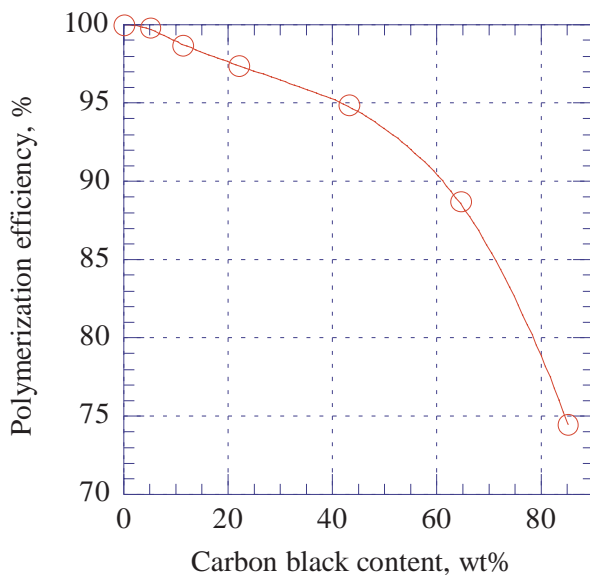


Figure 6.26. Effect of carbon black on polymerization efficiency of pyrrole. [Data from Wampler W A, Rajeshwar K, Pethe R G, Hyer R C, Sharma S C, *J. Mat. Res.*, **10**, No.7, 1995, 1811-22.]

The free radical polymerization of styrene initialized by iniferter is influenced by chemical binding of iniferter on the surface of the silica.<sup>115</sup> This reaction is used for grafting the polymer onto the surface of the silica. A similar approach is used when carbon whisker is incorporated during the graft-polymerization of methyl methacrylate.<sup>116</sup> Depending on how the whisker is prepared, surface conversion can be increased up to twelve times compared to a polymerization with no whisker present. The addition of graphite to the polyesterification reaction doubles the molecular weight of the polymer.<sup>117</sup>

The presence of a filler in a polymerization reaction can often produce an improved material. Now, the challenge is to take advantage of these new findings and develop cost effective commercial processes.

## 6.8 GRAFTING

Grafting has already been discussed in this chapter. These additional remarks highlight the technology. Three general types of grafting have evolved. Grafting to specific, well defined substrates, grafting to natural products and grafting during another primary or secondary process such as during mixing. Most of the processes discussed above fall into the first category.<sup>7,15,31,37,38,43</sup> A well-controlled process must begin with a filler with appropriate functional groups which permit further synthesis. But the conditions of grafting must be very strictly met because the polymerization of organic monomers requires tight control. In the majority of cases discussed in the literature, the technology is developed for laboratory conditions. Grafting is a simple one- or two-step process. The first step is the conversion of

functional groups to form initiating sites for polymerization. The second step involves chain extension. Typically, grafting is performed in solvent slurries which is an expensive process. The results of these syntheses show that products meet requirements and that the process can be controlled to obtain the designed thickness and distribution of coverage. Now, such synthesis is limited in practice to very expensive products because at this time processes are technologically too complex, too expensive, and frequently environmentally undesirable. This research, has helped significantly in improving our understanding of the range of properties offered by grafted fillers but has made little contribution to the mainstream processing of plastics for which the associated costs are too high.<sup>41,84,118,119</sup>

The second type is a group of processes which involve grafting onto natural materials or waste products.<sup>120,121</sup> Here, the goal is to utilize these materials in a simple and economical fashion. The conditions of grafting are not well controlled because of the complex nature of the substrates. This affects results. Products of these grafting processes are useful to merely fill polymers without detracting from their properties. This work will prove useful, particularly in the recovery of materials from recycling streams. At the same time, a substantial effort will be required to develop these processes with an economical application in mind.

The third group is the most promising because grafting during material processing adds only the cost of the raw materials. Two options are available for the development of these processes: a third additive is used to react with the filler and interact with the polymer (e.g., reactive compatibilizer)<sup>32,52-8</sup> or the filler surface is modified by a simple process (e.g., silanization) to allow reactive grafting during the manufacturing process.<sup>74</sup> Both routes are already in use and new applications and research will contribute to the further improvement of materials.

## 6.9 CROSSLINK DENSITY

In some cases, the crosslink density of a polymer can be affected by the filler. These include:

- The filler particle contains several functional groups which react with different polymer chains
- The filler surface is modified to contain a group which can react with polymer chains
- The modification of the filler surface reacts with a similar group on another filler particle

All of these mechanisms which affect crosslink density were confirmed by experimental studies. The classic case of a reactive particle filler is silica filled polysiloxane (Figure 6.25).<sup>103</sup> Silica particles have numerous OH groups which react with the crosslinking component of polysiloxane. Modification of silica by silanes reduces reinforcement.

Modification of the silica surface with mercaptosilane makes it reactive with rubber, resulting in an improvement in mechanical properties.<sup>122</sup> Modified, precipi-

tated cellulose can reinforce butadiene-acrylonitrile copolymer by forming covalent bonds.<sup>123</sup> Maleic derivatives of EPM react with  $\text{CaCO}_3$  to increase crosslink density.<sup>32</sup> There are other examples where a variety of functions can be utilized to modify the crosslink density.

One of the reactions which occurs on the surface of filler particles is that involving silanes. Vinyl silanes and mercapto silanes being typical examples. Kaolin modified with an isocyanate can react with polyols.<sup>8</sup> Magnetic resonance spectroscopy was used to identify various crosslinks involving the filler<sup>124</sup> and this shows that crosslinked rubber chains were attached to the surface of the carbon black.

Zinc oxide is a reactive filler commonly used in rubber vulcanization. The crosslink density of rubber can be doubled by reaction of  $\text{ZnO}$  with  $\text{HCl}$ .<sup>9</sup> Only a few specific fillers have the catalytic activity to promote crosslinking but fillers can take part directly in crosslinking processes initiated by an external source such as  $\gamma$ -radiation.<sup>125</sup> Generally, fillers reduce the effect of radiation. But  $\gamma$ -rays are not screened by the filler so the protection given by fillers comes from reduction in chain mobility which lessens the probability of photoconversion.

In summary, fillers have a very limited effect on matrix crosslinking except when they are used as crosslinkers or when the effect is caused by the physical properties of the filler (e.g.,  $\text{Al}(\text{OH})_3$  in UV crosslinked systems).

## 6.10 REACTION KINETICS

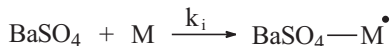
The kinetics of reactions which occur when fillers are present depend on the reaction type and on the analytical methods used to follow the kinetics of such reactions. A few examples of kinetic modelling are given below.

Figures 6.9–6.11 provide a data set of a grafting reaction of acrylamide onto the surface of barium sulfate which had been previously reacted with 12-hydroxystearate.<sup>7</sup> The steps of this reaction are given below:

Primary radical formation:



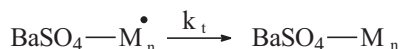
Initiation:



Propagation:



Unimolecular termination:



The following equation applies according to the steady-state principle as applied to active intermediates:

$$R_p = K \frac{k_p k_i}{k_t} [AAm][Ce(IV)][BaSO_4 - HS] \quad [6.5]$$

where:

$R_p$	reaction rate
AAm	acrylamide concentration
Ce(IV)	catalyst concentration
$BaSO_4 - HS$	reactive site concentration

This equation is typical of most bimolecular reactions studied by the analysis of substrates and reaction products.

The equation is a simple case of a mechanistic model. Models such as this may give better predictions but may not always apply because of the complexity of the reactions. Phenomenological models are expressed by simple rate equations which ignore the details of the reaction. Phenomenological models are typically used to follow cure rates in polymeric systems which are difficult to follow by chemical analysis. This is because reaction products become insoluble during the course of the reaction and, consequently, are not detected in an analysis of the solution.

A model which can be applied to reactions involving fillers is expressed in the simplest form given as an equation of the  $n$ th order:<sup>126</sup>

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad [6.6]$$

where:

$\alpha$	cumulative conversion at given time $t$
$k$	rate constant which obeys Arrhenius dependence (Eq 6.7)
$n$	reaction exponent

The Arrhenius temperature dependence is:

$$k = k_o \exp(-E / RT) \quad [6.7]$$

where:

$E$	activation energy, kJ/mol
$R$	universal gas constant
$T$	temperature

These equations can be used to calculate the reaction rate and activation energy of the process. The equations are simple and cannot account for the complexity in each reaction stage nor for all of the physical processes such as phase separation, gelation, or vitrification which determine the outcome of reaction. Several other variations of these equations have been developed to deal better with these complexities.

The order of the reaction can be calculated with more precision using the following equation:

$$\ln \frac{\alpha}{(1 - \alpha_i)^n} = -\frac{E_\alpha}{RT_i} + \ln(k_o) \quad [6.8]$$

where:

$\dot{\alpha}$	conversion rate
$\alpha$	conversion
$E_{\alpha}$	activation energy
$k_o$	Arrhenius frequency factor

If fillers are involved, the expression is changed to:

$$\frac{d\alpha}{dt} = (k_1^* + k_2^* \alpha^m)(1 - \alpha)^n \quad [6.9]$$

where:

$k_i^*$	functions of filler content
m, n	reaction exponents

The filler presence affects constants which can be used in comparison with the unfilled system.

There are other equations derived from these which have a close relationship to them but deal with other aspects of the complexities.

## 6.11 MOLECULAR MOBILITY

Chain mobility should be considered from both a chemical and a physical standpoint. Chemical reactions require reagents to be physically in contact. The morphology of the interphase organization restricts chain motions which might be considered either a chemical or a physical phenomenon.

There are three types of chains or chain segments which may be involved in filler-polymer interactions:

- A chain segment which is restricted in its motion because it has been adsorbed on the surface of the filler and has possibly reacted with it
- Adjacent segments because they are restricted by a proximity of the bound segment
- Chains which belong to the polymer bulk since they behave as they were in the unfilled polymer.

The first two types cannot be dissolved in a good solvent whereas the third type can. The first type can be designated to be in a tight region and is called a rigid segment. The adjacent segments form elastic loops and they belong to the loose region and are called elastic segments. From the point of view of chemical reactivity, the rigid segment is the one which has either undergone one of the chemical reactions discussed above or it has been absorbed on the surface by very strong physical interactions. This chain segment can participate in other chemical reactions if the energy level is sufficient to rupture its connection to the filler surface or if the action of binding to the surface of the filler changes its configuration. Elastic segments have the ability to participate in reactions but the probability of such reactions are less than that of the unrestricted polymer chain.

Several analytic techniques can contribute information on molecular mobility with NMR being the most useful. Two spin-spin relaxation times are observed: short (tight region) and long (loose region). The values and ratios for materials of different compositions can give an insight into the behavior of these two segmental



types. Modification of the surface of silica with hexadecanol decreases the ratio of loosely bound to tightly bound signals when it is dispersed in natural rubber. This shows first that rigid segments are formed in the reaction of rubber with silanol groups. Second, it shows that the compatibility between rubber and modified silica was greater than between rubber and unmodified silica. The signal of loose segments is three times stronger.<sup>41</sup> Similar studies on many different systems confirm the validity of observations using a spin-spin relaxation time,  $T_2$ .<sup>124</sup>

A study of SBR rubber showed a difference in the behavior over the temperature range of 20-70°C between the unfilled rubber and rubber filled with carbon black.<sup>127</sup>  $T_2$  changes by a few tens percent for filled rubber in this temperature range and it almost doubles in the unfilled rubber. The increased temperature contributes to the increased molecular mobility but this effect is retarded by the bound segments in the filled rubber.<sup>127</sup>

Monte Carlo simulations show the differences between chains on elongation.<sup>128</sup> Restricted chains (chains attached to the filler's surface) have a modulus similar to free chains when the elongation is small whereas a substantially higher modulus is observed when restricted chains are subjected to large deformations. These simulations produce results which are borne out by experimental work. NMR studies suggest that fixation (attachment) of one monomeric unit to the filler's surface hinders random motions (a characteristic of free chains) of approximately 4 monomeric units on both sides of the contact point.<sup>129</sup> On the other hand, the diffusion of free chains is progressively reduced as the number of the adsorbed segments is increased. If the filler has a low potential for bonding (e.g.,  $\text{CaCO}_3$ ) then the system is not affected by the concentration of interacting components because a sufficient number of functional groups does not exist to make any observable difference.

Dynamic mechanical analysis of filled systems confirms analytical observations.<sup>130</sup> The thickness of the restricted mobility region in carbon filled rubber is proportional to the activity of the carbon black.

The mobility of low molecular weight additives in the presence of fillers is important for the same reasons. Recent studies show that UV stabilizers are immobilized on the surfaces of filler particles. Nitroxyl radicals were used as spin probes in silica filled polymers.<sup>131</sup> Experimental work confirms that absorption occurs on the OH groups of silica but it was shown that a certain minimum concentration of filler is required to trigger this absorption effect.

The forces which come into play in a filled system are not restricted to affecting the mobility of chains. They also influence the filler particle distribution. The migration of filler particles has been modeled for an injection molding process.<sup>132</sup> A spectacular effect was observed when jute fiber was used as a filler.<sup>133</sup> As the moisture level of jute was increased, the fibers rotated about their axes. This changes the distribution and orientation of the jute fibers and has an effect on the properties of the composite.

In summary, the molecular mobility of high molecular weight substances in the presence of fillers is very different from the mobility of low molecular weight materials (most especially, in liquid systems). The effect of these phenomena on chemical processes and reactions is limited. The most pronounced effect on the chemistry is the lack of reaction homogeneity. Molecules which have interacted with surfaces preferentially undergo localized chemical conversions with their nearest neighbors. The reaction mechanisms of these adsorbed segments are different because their conformation and configuration are affected by this act of interaction which causes a shift in the preferred reaction in the unfilled systems. The largest influences of molecular mobility are on the organization of the interface, the effect on mechanical and rheological properties, and on morphology. These subjects are discussed in the following chapters.

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