25.1 Introduction

Additives are crucial to the successful application and proliferation of plastics. Small amounts of the appropriate additive can make the difference between a useless material and one with excellent mechanical properties and durability. Antioxidants and other stabilizers are used in parts per million concentrations, and yet without them some of today’s most successful plastics such as polypropylene and PVC would not be commercially viable at all. Dispersants and coupling agents are also additives which, even when used in low concentrations, can have a profound effect on the performance and viability of plastic materials in diverse applications from packaging to consumer appliances, electronics, automotive, and aerospace.

Dispersants adhere to the particles but have no strong or specific interactions with the surrounding polymer. Coupling agents also adhere to the particulate matter but, in contrast to dispersants, they must also adhere to the polymer through chemical bonds or through chain entanglement (Figure 25.1). As we shall see, dispersants and coupling agents provide different advantages and are selected based upon the needs of the application in question. Contrary to popular belief, good coupling is not always the desired option.

25.2 Dispersants

25.2.1 Terminology

Dispersants are one of many types of surfactants and have the classic surfactant structure, being composed of two (or more) segments with distinctly different chemistries and, therefore, properties (Figure 25.2). The very name surfactant stems from the propensity of such molecules to accumulate at, and influence the properties of, surfaces. They are said to be surface active.

The general structure of a dispersants is

A — B

or

Anchor — Buffer

Examples would be block copolymers of the structure A-A-A-B-B-B-B or low molecular weight molecules such as CH₃-(CH₂)ₙ-CO₂H

25.2.2 Basic Principles

Several modes of dispersant actions are known, but the main ones are steric stabilization, charge stabilization, and a combination of the two, aptly named electrosteric stabilization. The latter two rely upon charges and are only practicable in polar media such as water. In polymer systems, steric stabilizers are the preferred type. Steric stabilization is contingent upon three factors:

1. Strong anchoring of the dispersant “head” to the particle/inclusion
2. Solubility/compatibility of the dispersant “tail” with the surrounding polymer matrix
3. Sufficient “tail” length to prevent particles from approaching closely enough for van der Waals forces to dominate and force particle agglomeration

Crudely speaking, the dispersant can be conceptualized as a molecular spring on the surface of the inclusion. As particles approach, the springs are compressed, and if bonded well enough that they are not dislodged from the filler surface, then they bounce back to their preferred conformation, thus preventing particles from becoming close enough to fall into a deep potential energy minimum. Each of the three aspects listed above will be covered individually.

25.2.3 Coupling to the Filler/Inclusion

As mentioned, the dispersant must be well anchored. The strength of bond needed depends upon the circumstances. For
example at room temperature a weak, van der Waals interaction between dispersant and inclusion may be enough to prevent the dispersant from becoming displaced from the surface. In thermoplastics and thermosets, where high temperatures and/or high shear rates are the norm, there is a far greater tendency for the extreme conditions to challenge the dispersant–inclusion bond. The so-called weak bonds such as van der Waals forces are not enough to ensure adequate bonding, and the strong bond types such as ionic and covalent bonding are employed instead.

### 25.2.4 Bond Strengths

- **van der Waals**: $<5 \text{ kJmol}^{-1}$
- **Ionic**: $\sim20 \text{ kJmol}^{-1}$
- **Covalent**: $\sim300 \text{ kJmol}^{-1}$

 Whereas van der Waals interactions are non-specific and exist between all substances, both ionic and covalent bonding require specific chemistry to take place between the dispersant “head” and the inclusion surface. In consequence, such bonding can only occur if there are appropriate sites on the filler surface for such chemistry to take place. Thus, it is observed that the dispersant anchor group must be chosen such that it matches the available sites (if any) on the surface.

As an example, stearic acid forms stable, ionic bonds with the surface of calcium carbonate and is the preferred dispersant for that filler in most commercial applications due to a combination of good performance and low cost. However, that dispersant in not efficacious on silica because it cannot bind to the surface groups, which are predominantly silanols.

Trialkoxy alkyl silanes are effective dispersants for silica because they can bond to the surface silanols. However, that type of dispersant has inappropriate chemistry to bond to calcium carbonate and is therefore ineffective on that type of filler (Figure 25.3).

It has been said that fillers are either basic or acidic and furthermore that acidic dispersants should be used on basic fillers and that conversely, basic dispersants should be used on acidic fillers. However, this simplistic approach is fallacious. Firstly, a large study showed that all mineral fillers are in fact amphoteric (Table 25.1). That is, they possess surfaces that are both acidic and basic. Furthermore, even a cursory glance at known dispersant – filler pairs will refute the above simplification. As one example, trialkoxy silanes are known to be excellent dispersants for silica but both the dispersant and the filler are known to be acidic in character. A further consideration is the definition of acid and base to be employed in the case of fillers and dispersants. The most usual meaning of those terms is that of Brønsted-Lowry Acids and Bases but that terminology applies to ionic systems, for example aqueous solutions and thus is not applicable to filler-polymer systems which are of much lower polarity. For polymer-filler systems, the type of interaction to consider is that of Lewis Acids and Bases whereby Lewis Bases are able to donate a pair of electrons and Lewis Acids are able to accept a lone pair of electrons. Several studies have shown that Lewis Acid–Base interactions are responsible for adhesion and so it should come as no surprise that they are a factor in the adhesion of dispersant molecules to fillers.

A study was conducted to find the optimal dispersant chemistry for a wide range of fillers. The dispersant tail group was a twelve carbon linear hydrocarbon chain and was kept constant. The dispersant head group chemistry was changed in order to discover which chemistries were able to bond to each type of filler surface. Head groups that bonded were found to be effective dispersants whereas head groups that could not find sites to bond to remained in solution and could

![Figure 25.2](image-url) Surfactant structure showing the “tail” and “head” groups.

![Figure 25.3](image-url) CaCO₃ and silica with stearic acid and silane dispersants.
Table 25.1 Most effective dispersant head groups for different fillers

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Best Dispersant</th>
<th>Second Best</th>
<th>Third Best</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate</td>
<td>Succinic anhydride</td>
<td>Carboxylic acid</td>
<td>Primary amine</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Sulfonic acid</td>
<td>Carboxylic acid</td>
<td>Succinic anhydride</td>
</tr>
<tr>
<td>Magnesium hydroxide</td>
<td>Succinic anhydride</td>
<td>Trichlorosilane</td>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>Mica</td>
<td>Primary amine</td>
<td>Trichlorosilane</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>Talc</td>
<td>Trichlorosilane</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Silica</td>
<td>Trichlorosilane</td>
<td>Sulfonic acid</td>
<td>Succinic anhydride</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Primary amine</td>
<td>Succinic anhydride</td>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Succinic anhydride</td>
<td>Carboxylic acid</td>
<td>Trichlorosilane</td>
</tr>
</tbody>
</table>

not perform their function as dispersants at the filler surface. The methodology was to disperse each filler type in a hydrocarbon oil (squalane) which served as a model for the polymer phase, for example polyethylene or polypropylene. These filler dispersions tended to exhibit high viscosity as no dispersant had yet been added. An excess (more than the amount needed to make a monolayer) of each potential dispersant was added and the viscosity was seen to drop dramatically if the dispersant head group was able to bond to the filler surface in high concentrations. On the other hand, test dispersants that failed to bond, because of incorrect head group chemistry, resulted in no change in dispersion viscosity. In this way, the drop in viscosity was used to rank the dispersant head groups in terms of their propensity to bond to each filler type. Oscillating viscosity measurements were chosen because they are known to be very sensitive to particle dispersion (Figure 25.4).

For the case of the particular grade of titanium dioxide tested, a hydroxyl head group did not bond at all to the filler surface as no change in viscosity was noted compared to the case with no dispersant present (denoted “none”). In contrast, carboxylic acid and succinic anhydride head groups were very effective at bonding surfactant to the particles and resulting in 1000-fold drop in viscosity. The best three dispersant head groups are listed for each filler (Table 25.1).

Some interesting observations can be made. Firstly, as stated earlier, basic fillers like calcium carbonate adsorb both acids and bases such as the primary amine. Likewise, acidic particulates like silica adsorb acids. Dolomite, which is usually considered to be essentially the same as calcium carbonate, actually displays substantially different surface chemistry. The common anchoring groups for dispersants and coupling agents, such as carboxylic acids, anhydrides and organosilanes perform well as expected. However, sulfonic

Figure 25.4 Rheological evaluation 20 wt% dispersion of TiO₂ in squalane with 0.2 wt% added dispersant.
acids also perform well although they are not commonly used as dispersants or coupling agents commercially. Other head groups with potential include sarcosine, phosphonic acids, and the trisilanols of polyhedral oligomeric silsequioxanes.

The results show how sensitive the rheological test is for finding an optimal dispersant. However, the results shown may not be valid for every type of talc, silica, calcium carbonate, etc., because dispersant adsorption varies depending upon the surface chemistry of the fillers and that may change from deposit to deposit and may alter depending upon processing techniques and contamination picked up during handling. In particular, it should be noted that the results for titanium dioxide are in no way representative of titanium dioxide in general because TiO₂ is invariably coated with proprietary inorganics and organics, so its surface chemistry varies tremendously.

An effective surface treatment chemistry for talc has eluded scientists for decades because the talc platelet faces are inert and only the edges contain reactive sites. The rheological study confirmed that talc did not respond to any of the usual dispersant types, but, surprisingly, trichlorosilane was seen to be very efficacious. This could pave the way for effective dispersants and coupling agents for talc.

The dispersants found using the rheological test were used to surface treat fillers, and the properties of the resultant composites were measured. In many cases, the dispersants were found to be very effective. The limitation of the rheological dispersant optimization method is that it measures only the amount of additive adsorbed at room temperature and not the strength of the bond between dispersant and filler. Methods to measure the strength of adsorption are available and include inverse gas chromatography and flow microcalorimetry.

### 25.2.5 Compatibility with the Polymer

According to the criteria for steric stabilization, the dispersant “tail” must be soluble in, or at least compatible with, the polymer. Solubility is governed by the principle that like dissolves like. In more scientific terms, it means that the dispersant tail and the polymer must be of similar polarity, or more precisely of similar solubility parameter. Therefore a perfluoroalkyl tail would be well suited to PTFE, an alkyl dispersant tail would be ideal for polyethylene and polypropylene, and a high polarity polyethylene oxide type tail would work in polymers such as PVC, PET, andnylons.

The reason that solubility of the tail is important lies in the mechanism for steric stabilization whereby the tail acts as a molecular spring. Long-chain tails adopt a random coil configuration, where the size of that coil (radius of gyration) increases depending upon how well the chain and the surrounding polymer interact. Although the shape and size of the polymer coil are perturbed by the proximity of the filler surface, the same trend applies, namely that a good solvent for the polymer leads to a larger polymer coil.

A large, well-solvated chain covers a greater volume and stabilizes the particle better against agglomeration. When particles approach and the coil is compressed compared to its ideal, equilibrium conformation, it acts to regain that preferred configuration by springing back and repelling the incoming particle. So, at least for long-chain steric stabilizers, the ability of the polymer to solvate the tail is essential.

### 25.2.6 Tail Length

In reality, other factors become as, or more important, than selecting the dispersant with the ideal polarity. One essential observation is that long-chain dispersants are not needed to achieve many of the desirable effects associated with good dispersion, namely decreased viscosity (better processability), good gloss, raised impact resistance, and for pigments, higher tinting strength. Stearic acid has only an 18-carbon chain length, and yet it is a highly effective dispersant used in many situations. It was shown in the rheological study mentioned previously that a chain length of just 3-4 carbons is enough to reduce viscosity to a minimum.

Such short-chain dispersants cannot adopt a random coil configuration; they will be more or less linear molecules no matter the ability of the polymer to solvate the chains. In fact, molecules like stearic acid on calcium carbonate pack together so tightly that there is no possibility for the polymer to penetrate between the chains and interact with them anyway. Thus it is found that in reality, short-chain dispersants are often rather efficacious and need not be tuned to exactly match the polymer they are used in. The length of the chain can be tuned but in reality, stearate groups are so inexpensive that other types cannot compete in any but the most specialized applications. Similarly, in theory, the best dispersant tail is one with a polarity matched closely to that of the matrix polymer. However, in practice, hydrocarbon tail types predominate as they are available and at low cost.

### 25.3 Practical Use Considerations

These aspects are similar for coupling agents and are covered in more detail in that section.

#### 25.3.1 Pre-Coating

Dispersant may be added by the filler manufacturer. That entails additional cost but reduces water uptake during transportation and storage.

#### 25.3.2 In Situ Treatment

In situ coating is less expensive as the dispersant is added during extrusion. The dispersant melts and dissolves in the polymer melt which acts as a solvent to facilitate the surface treatment.
25.3.3 Amounts to Use and Surface Coverage

Optimal dispersion is normally found at a monolayer of dispersant. This can be detected by measuring viscosity. The viscosity of the filler dispersion in solvent or polymer will decrease as dispersant is added and then level off at monolayer coverage. Adding too much dispersant may cause problems in the composite as free dispersant molecules can interfere with antioxidants. It can also lead to problems with adhesion and printability as the excess dispersant blooms to the polymer surface forming a weak boundary layer (i.e., a waxy layer with low cohesive strength).

25.4 Types of Dispersants

The types of dispersants are similar to the types of coupling agents because in both cases, the chemistry needed to bond the additive to the filler surface is the same.

If the type of coupling agent is not chosen properly, then it will usually act as a dispersant instead. For example, if an organosilane is used that bonds to the filler but the chemistry or reaction conditions do not allow it to bond to the polymer, then it will disperse but not couple. Thus, additives that are labeled as coupling agents do not necessarily couple.

25.4.1 Organosilanes

Silanes with an unfunctionalized hydrocarbon tail will disperse but not couple. Functionalized organosilanes cannot react with polyethylene or polypropylene because those polymers are inert, and thus coupling does not take place with those polymers.

25.4.2 Titanates

Titanates are usually referred to as coupling agents. However, when one looks at the property benefits claimed, such as improved dispersion, better flow, and higher gloss, it becomes clear that these additives are, in fact, dispersants and not coupling agents.

25.4.3 Unsaturated Acids

Unsaturated acids, such as those based on polybutadiene, can be used as effective dispersants in situations where the double bonds are not able to react chemically with the polymer matrix.

25.4.4 Acid-Functionalized Polymers

These additives are normally used as coupling agents whereby the acid groups (e.g., acrylic or maleic) adhere to the filler, and the polymer chains entangle with the matrix polymer chains. If the coupling agent has polymer chains that are too low in molecular weight then they cannot entangle, and it will act as a dispersant rather than as a coupling agent.

Similarly, if the coupling agent polymer is not miscible with the matrix polymer then entanglement will not occur, but dispersion may be improved instead.

25.5 Property Effects

Many advantages result from the use of dispersants, and these will be covered separately.

25.5.1 Flow/Processability

The addition of any particulate matter to a fluid results in an increase in viscosity (although rare exceptions do exist). As progressively more filler is added, the viscosity rises until flow is so slow, and therefore extruder throughput is so poor as to be economically unviable as a commercial process. At still higher filler levels, viscosity approaches infinity, and the polymer melt cannot flow at all (Figure 25.5).

Using a dispersant allows reduced viscosity (improved productivity) at constant filler loading. A dispersant also enables the use of higher filler loading while maintaining constant viscosity.

25.5.2 Impact Resistance

Dispersants can raise impact resistance, especially unnotched impact resistance (see chapter on Functional Fillers for Plastics for a description of impact resistance measurement and trends). There are two effects responsible for it. Impact resistance is sensitive to any large particles as they concentrate stresses and thereby act as flaws (Figure 25.6). When impact takes place, cracks initiate from those larger filler particles or agglomerates of smaller particles. Addition of dispersant reduces or removes agglomerates that could otherwise have led to cracks.

The second mechanism by which dispersants improve impact resistance is by reducing bonding between filler and polymer. When impact occurs, the filler debonds from the polymer to create multiple microvoids as each filler particle debonds. These voids or crazes help to adsorb energy. It is well known that crazing is a mechanism to improve impact resistance.

![Figure 25.5 The effect of filler and dispersant on viscosity.](image-url)
resistance. Elastomeric impact modifiers also work through crazing. Hard fillers are not nearly as effective as elastomers at raising impact resistance. However, fillers can raise modulus and impact resistance together, something not possible with elastomeric impact modifiers.

Of these two mechanisms, namely dispersion and debonding, by which dispersants improve impact resistance, the relative importance of each is not known because both effects occur simultaneously, and the effects cannot be separated.

Smaller particles agglomerate more readily and require more mixing energy to separate. Nanofillers are worst of all and can be impossible to disperse properly. Researchers tend to plot properties versus the filler particle size as reported on the suppliers’ datasheet. This leads to problems in understanding and interpreting the experimental results. Firstly, the size distribution is important, not just the mean particle size (Figure 25.6). Secondly, it is the size of the filler particles in the final composite that counts, not the size printed in the datasheet. Experiments on stearic acid-coated calcium carbonate compounded into polymer using a twin screw extruder showed that larger particles (above about 1 micron) disperse perfectly, whereas particles smaller than that tended to agglomerate. Nano calcium carbonate with a datasheet particle size of 70 nm actually formed agglomerates larger than 100 microns in diameter (Figures 25.7–25.9). Not surprisingly, the impact resistance of that latter material was very low.

The ability to disperse the filler will depend upon its tendency to agglomerate, the screw design of the extruder, extrusion operating conditions, and whether dispersant or other additives that adsorb onto the filler are present (Figure 25.10).

**25.5.3 Gloss**

Gloss is higher for smaller, well-dispersed filler particles so dispersants are of value. Lower angles of gloss measurement are more sensitive to gloss reduction due to filler addition than are higher angles. Fillers can and are used to degloss surfaces, for example to prevent glare from reflected sunlight or to suit the preferences of a given market. Large filler particles are effective at reducing gloss levels.

**25.6 Coupling Agents**

**25.6.1 Introduction**

While very loosely used in the scientific and especially trade literature, the term coupling agent is interpreted here as meaning a class of adhesives used to firmly bond (couple) polymers to inclusions such as fibers and particulate fillers. This coupling has the effect of increasing the interfacial
stress required to debond the filler–polymer interface, which, in turn, results in higher tensile and flexural strength, increased stiffness at high strains, and sometimes improved toughness. The coupled interface also reduces water absorption giving improved property retention and often better electrical stability under humid and wet conditions.

As described earlier, dispersants can also improve polymer processing and some composite properties, but they do not give the strong interface that coupling agents do. Much of the confusion in the literature arises from failure to discriminate between the beneficial effects due to dispersion and to coupling and from the tendency to describe any additive that produces an improvement as a coupling agent. To further complicate matters, the best coupling agents are often also good dispersants and so bring about improvements by both dispersion and coupling mechanisms.

Coupling agents are a very important ingredient in many high performance polymer composites. A striking recent example of this is the green or energy tire technology in which carbon black had been replaced by precipitated silica. As shown in Figure 25.11, this technology, which is only made possible by the use of coupling agents now dominates the automotive tire market in Europe.

25.6.2 Terminology

The definition of the term coupling agent, as used in this article, has been described above. As the non-polymer component being coupled may be in fiber or particulate form and may or may not be a reinforcement in the traditional sense, the general term “inclusion” is used here for this component.

25.6.3 Differences Between Dispersion and Coupling

The differences in the effects due to dispersion and to coupling arise from the nature of the inclusion interphase that is present. In the case of dispersion, this interphase is relatively weak and easily destroyed by strain or by the ingress of water. In the case of coupling, the interphase is much more resistant.

These differences are well illustrated in Table 25.2, which compares the effect of a non-coupling and a coupling surface treatment on precipitated calcium carbonate in an EPDM elastomer. Both additives improve processing (minimum viscosity) by a similar amount. This is a dispersion effect and shows that the coupling agent used in this case also possesses this ability. The dispersant lowers tensile strength, high extension modulus, and tear strength while the coupling agent increases them compared to the untreated filler. This is due to the differences in interphase strength mentioned above. Detergent swell is a complex property; influenced by dispersion, coupling, and the hydration resistance of the interphase, and we see that both approaches bring about a significant improvement but that coupling is the better of the two.
25.6.4 History

Before discussing the main types of coupling agents in any detail, it is useful to look at the history of coupling agent technology:

Industrial use of coupling agents can be traced back to the early days of glass reinforced unsaturated polyesters. Such resin-based composites were introduced in the 1940s and were of great interest, as they had excellent stiffness to weight ratios and were potentially able to substitute for metal in many applications. Their strength was found to rapidly drop off under humid or wet conditions, however, with losses of about 60% being experienced. This loss in strength, which severely limited their commercial uptake, was found to be due to water degradation of the resin fiber interphase, and this led to a search for fiber treatments that could reduce or prevent such attack.

The first successful glass fiber treatment found was a chromium complex of methyl-methacrylate. The initial versions of this product were the first coupling agents and reduced the strength losses under humid conditions to about 40%. This chromium-based chemistry was improved and later commercialized by DuPont and is still in use with glass fiber to some extent today.

The US air force was very interested in using glass fiber reinforced unsaturated polyester resins, but required even better humidity resistance, and so they funded research into better coupling agents. This research was quickly successful and led to silicon-based products that reduced the losses to under 10% and resulted in the birth of the organosilane coupling agent family, which still dominates the market over 40 years from their first introduction.

While there have been many attempts to find alternatives to the organosilanes, these have had limited success. The main competitive products are based on organic derivatives of titanium, aluminum, or zirconium but have only achieved niche use.

One of the main limitations of the organosilanes is their lack of success on fillers with basic surfaces, notably calcium carbonate. This has driven the development of acid or acid precursor coupling agents such as carboxylic anhydride grafted polymers. After a long gestation period, these coupling agents are beginning to make a significant commercial impact. This has been accelerated by the growing use of wood reinforced polymer composites where they are more effective than the silanes.

As described above, coupling agents were initially developed for use on glass fibers, and this remained their main application area for several decades. As a consequence most of the developments were aimed at this market. Gradually applications were developed for particulate fillers, but this remained a relatively small market sector until the 1980s when “green” or energy tire technology started to emerge. This technology allows carbon black to be replaced by precipitated silica/organosilane combinations, with a significant reduction in fuel consumption. This application has mushroomed until it is now a major consumer of organosilane coupling agents and has led to a new focus in technical development and to new types of silane coupling agents.

The most recent significant development in the market place has been the very strong growth in the use of cellulose fiber reinforced composites, especially those based on wood fiber and powder. Coupling agents are often used in these formulations, especially to reduce water absorption and accompanying loss of properties. Maleic anhydride grafted polyolefins have been found to be very suitable additives for this purpose, and this has led to a marked increase in their use.

25.6.5 Basic Principles

Coupling agents are essentially bifunctional molecules, where one functionality is able to react with the inclusion surface and the other with the polymer, thus coupling the two together. All coupling agents can therefore be regarded as having the simple structure:

\[ \text{Anchor} - \text{Buffer / Bridge} - \text{Couplant} \]

The challenge for the chemist is to find the functionalities A and C and to find a linking structure B that produces a molecule that is stable, non-hazardous, and easy to use. This may seem a simple task, but the author can verify that many of the potential structures result in products that are insoluble, high melting, compounds which are often impossible to use in any commercially useful way.

25.6.6 Anchoring the Inclusion

In practice, very few groups are utilized for bonding to the surface of the inclusion, the principal ones being certain metal hydroxides or derivatives of carboxylic acids and their

<table>
<thead>
<tr>
<th>Property</th>
<th>No Treatment</th>
<th>Dispersion</th>
<th>Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum viscosity at 160 °C (Monsanto Rheometer)</td>
<td>18.6</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>10.0</td>
<td>4.5</td>
<td>13.3</td>
</tr>
<tr>
<td>Modulus 300% (MPa)</td>
<td>2.3</td>
<td>1.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>16</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Detergent swell (%) (15 detergent 72 hours at 95 °C)</td>
<td>2.7</td>
<td>0.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>
precursors. Although the commercially used anchor groups are limited, all those shown effective for bonding dispersants to fillers, for example in the previously mentioned rheological study, should also be suitable anchor groups for coupling agents.

The origins of coupling agent technology being in glass fiber based composites meant that the main emphasis, at least until recently, has been on groups that can form strong, stable, bonds to glass surfaces. The principal potential anchoring site on glass and many silicas and silicates are the surface hydroxyls (silanols). The chemistry is discussed in more detail later, but certain metal hydroxides, notably those of chromium, titanium, aluminum, zirconium, and silicon are able to condense with these surface groups and potentially provide the desired bonding. This is the basis of the main coupling agent technologies in commercial use today. The biggest problem is that the coupling agent metal hydroxyls are also able to condense with themselves and can quickly lead to intractable solids, before any significant reaction with the inclusion has taken place, unless they have been stabilized in some way prior to use. In the case of some of the metals, this stabilization is achieved by converting the OH groups to alkoxy ones; with others this does not work, and the more extreme method of using low pH is employed.

While the metal hydroxide technology described above is suitable for glass and many siliceous fillers, it is not effective on other classes of important fillers such as carbonates, sulfates, and carbon blacks.

Carboxylic acids or their precursors, such as anhydrides, are successfully used for anchoring to basic inclusions. They also function well on amphoteric ones, and so their application spectrum overlaps to some degree with the metal hydroxides.

There is a small group of inclusions left which are not reactive with either type of functionality. The principal ones are carbon blacks, sulfates such as barium sulfate, and pure talcs. Of these, carbon blacks already possess a reactive surface which gives rise to similar effects that would be found by coupling and so do not really need treatments. The other inclusions mentioned, especially talc, remain a challenge and have provoked much research effort. Interestingly, trichlorosilanes were shown to be effective on talc although that technology is not yet commercialized. Carbon fibers are another type of filler that have no intrinsic bonding sites on the surface, instead they are post treated, for example using oxidation, to introduce reactive sites and enable coupling.

25.6.7 Coupling to the Polymer

Finding suitable groups for this are easy for some polymer types and very difficult for others. More polar polymers, for example nylons 6 and 6, 6 are able to interact well with fillers even in the absence of coupling agents. Their low polarity prevents them from bonding well to filler surfaces.

Polymers that are crosslinked by peroxide or other means are among the easiest, with unsaturated groups such as vinyl or methacrylic being adequate. There has been a lot of interest in unsaturated organic acids especially oleic and similar types, but, with the exception of acrylic and methacrylic acids, these have generally been found to be ineffective. While acrylic and methacrylic acids can achieve coupling, they are not easy to use.

Sulfur-cured elastomers are also relatively easy, using groups such as mercapto or polysulfide.

Condensation polymers such as polyamides and polyesters like PET are a little more difficult but are quite reactive at processing temperatures and can be reacted using groups such as amines and epoxides.

The most difficult polymers are thermoplastic polyolefins such as polypropylene and polyethylene. These have no obvious chemical handle. Some of the early work utilized the azide functionality, but this is a very hazardous group and no longer of commercial interest. More recent work uses unsaturation in combination with peroxide or possibly mechano-chemical grafting with the ultimate expression of this being to pre-graft the inclusion reactive functional group onto the polymer or to copolymerize with it.

Table 25.3 lists the principal polymer functionalities now used and the corresponding polymers.

**25.6.8 Bridging the Two Together**

This is the tricky bit and this is what really determines which structures are practical.

With carboxylic acid anchoring groups, it is not too difficult and they can be connected to a variety of functionalities through simple hydrocarbon chains. The principal limitation is with groups that would themselves react with the acid. The amino-functionality is a prime example of this.

With metal hydroxylic anchoring groups it is different. The polymer reactive groups are nearly always organic in nature, but with the exception of silicon, none of the metals that has suitable hydroxyls form stable metal carbon bonds. It is primarily this ability that makes silicon-based compounds the

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Main Polymers Used In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturation (e.g., vinyl or methacrylic)</td>
<td>Unsaturated polyesters, acrylics, peroxide cross-linked elastomers</td>
</tr>
<tr>
<td>Sulfidic (e.g., mercapto or polysulfide)</td>
<td>Sulfur-cured elastomers</td>
</tr>
<tr>
<td>Amino (e.g., primary, secondary, or a combination)</td>
<td>Polyamides, epoxies</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Epoxyies, polyesters (PET, PBT)</td>
</tr>
</tbody>
</table>
most widely used coupling agent type. With the other candidate metals, the polymer reactive group is attached through a relatively stable ester link (metal—oxygen—carbon) often with an adjacent carboxyl functionality to increase stability further.

25.6.9 Practical Use Considerations

The practical process of using coupling agents plays a big part in determining commercial acceptability. There are two main ways of utilizing them—pre-coated onto the inclusion or added during the composite preparation stage (in situ method). Both have advantages and limitations, and both are widely used. The pre-coating method can be broken down further into wet and dry coating.

25.6.10 Pre-Coating

This is generally significantly more costly than the in situ method, except where the inclusion is produced under conditions (such as a slurry) that allow the coating to be incorporated without extra processing. Glass fibers are a classic example, as they have to be coated with sizes, etc., immediately on production, in order to preserve their strength. Many coupling agents can then be incorporated into this coating process. The advantages of pre-coating include better control of the process, especially freedom from interference from other components in the composite formulation, and the ability to safely treat any evolved gases (significant quantities of alcohol can be released from the reaction of organosilanes with inclusion surfaces). On the down side, any fresh surface generated during composite production will remain untreated.

25.6.11 In Situ Treatment

The in situ method is usually significantly cheaper and can deal with the fresh surface question. It is less controlled than the pre-coating method, however, and prone to interference from other surface active species that may be in the formulation. Evolved gases from the coupling reaction can also be a significant problem.

The physical form of the coupling agent plays a very important role in determining its suitability for either method. Low volatility and high flash point are fairly obvious advantages.

With the in situ method it is essential that the coupling agent dissolves in the polymer (or in some cases monomer). In connection with this, the additive needs to be fluid at the processing temperature.

For pre-coating, the additive needs to be a liquid at the coating temperature, or to be readily soluble in a solvent that is of low hazard in the process (water being the most suitable).

For the best results a combination of pre-coating and in situ is sometimes employed.

25.6.12 Amounts to Use and Surface Coverage

One of the most common questions is how much coupling agent to use. There is no quick answer to this, but there are some simple guiding principles.

The most straightforward approach is to find the amount of additive that can just cover the surface of the inclusion, if it is spread one molecule thick. This gives rise to the monolayer concept.

While simple in principle, there are several factors that increase its complexity. At the simplest level, one just needs to know the specific surface area of the inclusion and the orientation of the coupling agent molecule at the surface (giving rise to a footprint area). The specific surface area is accessible by a number of methods, of which the BET nitrogen adsorption method is the most commonly used. The footprint area has been calculated by molecular modeling for a number of coupling agents and for different orientations (where this is relevant). From these two parameters, one can calculate the number of molecules required to give a monomolecular coverage of unit weight of the inclusion and using Avogadro’s number and molecular weight, this can be converted into a weight percent figure. A typical example follows for coverage of a particulate filler with a specific surface area of 10 m²/g by two different organosilanes of known coverage (Table 25.4).

Complexities arise from a number of sources. The nitrogen used to obtain the specific surface area is a very small molecule and may access surface that is not available to the coupling agent. Where this is a concern, one may use dye absorption to get a more meaningful specific surface area or even carry out an absorption isotherm using the coupling agent itself. In the rubber industry it is common to use cetyltrimethyl ammoniumbromide (CTAB) as a suitable large molecule for measuring the appropriate surface area of fillers such as carbon black and precipitated silicas. Methylene blue dye is also used.

The spacing of reactive groups in the inclusion surface is also an issue. The coupling agent molecules may be able to form a monolayer, but not all of them may be able to find surface groups to react with. This may not be a problem when, as is often the case, the coupling agent molecules can also react with each other, but can be an issue when they cannot.

While the monolayer concept is easily understood, its relevance to final properties is less clear. With some coupling agents, property changes can start with the first fraction of

Table 25.4 Calculated monolayer coverage levels for two different organosilanes on filler with a specific surface area of 10 m²/g

<table>
<thead>
<tr>
<th>Organosilane</th>
<th>Coverage (m²/g)</th>
<th>Monolayer (Weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma-aminopropyl trimethoxy silane</td>
<td>360</td>
<td>10/360 = 2.8%</td>
</tr>
<tr>
<td>Vinyl trimethoxy silane</td>
<td>525</td>
<td>10/525 = 1.9%</td>
</tr>
</tbody>
</table>
a monolayer and increase up to and past the monolayer level. With others there is a sharp optimum at or near the monolayer level and excess additive is very undesirable. Durability, especially under humid conditions, can follow a different pattern and generally requires at least monolayer coverage.

It has also been found that coupling agents often deposit non-uniformly with islands several molecules thick being present, together with uncoated surface. In this case, higher addition levels are required.

### 25.6.13 Types of Coupling Agents

The main types of coupling agents in commercial use are described below. Most, if not all of them, have other applications, mainly in the wider adhesive and dispersant markets. The discussions here are limited to their use as coupling agents. It is worth noting that there is little difference in the polymer reactive groupings; the main differences are in the inclusion reactive functionality and the way that the two functionalities are combined into a single molecule.

### 25.6.14 Organosilanes

These are the premier coupling agents in use today and so deserve pride of place in this section. Their success is largely due to the unique ability of silicon to stably connect polymer and inclusion functional groups and to do so in molecules that are low hazard liquids or low melting solids, soluble in most polymer types. An important, but often overlooked additional advantage is that precise coverage levels are not needed and excess coupling agent does not cause any problems. This is not true for many of the other organo-metallics, where a sharp peak in performance against loading is often reported and excess can be very detrimental. In these cases, precise control of addition level is essential.

As described earlier, the use of organosilanes grew from work sponsored by the US Air Force to find products that performed better than the original chrome complexes in glass fiber reinforced unsaturated polyester resin composites. The first success was achieved with vinyl trichlorosilane and its mixtures with allyl alcohol. The unsaturation provided the polymer reactive functionality while the chloro-groups provided the fiber reactive ones. The fiber reactivity comes about by hydrolysis of the chloro-groups to form silicon hydroxyls which are then able to condense with surface hydroxyls, as shown in the following simplified reaction sequence.

\[
\text{R—Si—Cl} + \text{H}_2\text{O} \rightarrow \text{R—Si—OH} + \text{HCl}
\]

\[
\text{Glass—OH} + \text{HO—Si—R} \rightarrow \text{Glass—Si—R} + \text{H}_2\text{O}
\]

While the chloro functionality is successful in achieving coupling to the inclusion, it has some limitations, notably the release of hydrogen chloride during the reaction. It was soon found that conversion of the chloro-groups to alkoxy ones (e.g., by reaction with a suitable alcohol, \(\text{R—OH}\)) produced more user friendly products of similar effectiveness. These liberate the corresponding alcohol rather than hydrogen chloride, when used. The first alkoxy-type silane coupling agent for commercial use was the vinyl trimethoxy one, still in significant use today. The surface coupling reaction still proceeds by hydrolysis to silanols and their subsequent condensation, as described above. The nature of the alkoxy group is important for a number of reasons. It determines the volatility and flash point of the molecule and also the rate of surface reaction. Potential toxicity issues related to alcohol also have to be considered. As an example, the use of methoxy-based organosilanes has been in decline due to the hazards associated with methanol release.

A frequently asked question is whether the silicon needs to have three surface reactive groups. The tri-functionality arose initially because the vinyl trichlorosilane (and hence the trialkoxy derivatives) was readily prepared. It is more difficult and expensive to make less functional molecules such as vinyl dimethyl mono-alkoxy silane. There is no definitive information on how such compounds might compare with the trialkoxy ones.

Once the vinyl functional product was established, attention moved to finding functionalities to suit other polymer systems. In quite a short period the following functionalities were developed.

- Primary amine
- Epoxy
- Methacryl
- Mercapto and polysulfide

The latter may seem rather exotic but are actually large tonnage products used in sulfur-cured elastomer systems. While many other functional types have been commercialized since, these five types still dominate the market and suit the majority of polymer systems.

For many years, product development and scientific research was focused on glass fiber applications, with particulate fillers being a relatively small segment. This changed significantly from the early 1980s when green (energy) tire technology began to appear. This technology is based on precipitated silica fillers and gives tires with lower rolling resistance and hence lower fuel consumption than the previous dominant carbon black technology. Despite the rolling resistance advantage, untreated silica gives very poor tread wear compared to carbon black, and it is the use of coupling agent technology that overcomes this and makes such tires a commercial reality. They have been so successful that virtually all new car tires in some parts of the world (notably Europe and Japan) are now silica based. The precipitated silicas have very high specific surface areas, which need virtually complete coverage if acceptable tread lives are to be achieved; this results in high silane addition.
levels (5–10 wt% on filler). As a result, the market is very significant and precipitated silica fillers, rather than glass fibers, have driven recent scientific understanding and commercial developments of coupling agent technologies.

One of the most important developments has been low volatile organic constituent (VOC) silanes. In the conventional trialkoxy products, about 50 wt% of the molecule is volatile alcohol which is released during reaction with the inclusion surface. The in situ addition method is widely used with particulates, especially in green tire technology and results in a very significant, uncontrolled, release of volatiles. Legislation is restricting such releases and has led to the commercialization of improved products. The reduction in volatiles is achieved by methods such as partially precondensing the silanes or by using alcohols which, while not volatile, still allow the surface reaction to take place and remain as inert materials in the final product.

25.6.15 Other Organo-Metallics

The main disadvantages of the organosilanes are their relatively high cost and their lack of activity on fillers such as calcium carbonate. Other organo-metallics have been extensively investigated in efforts to find alternative products. None has been wholly successful, although several have developed niche applications. The main types are briefly discussed below.

25.6.16 Chromium Salts

As mentioned earlier, these were the original coupling agents for use in polymer composites. Salts of trivalent chromium can be reacted with certain organic acids to produce cyclic complexes, such as shown in Figure 25.12. If the acid carries a polymer reactive functionality, this can be incorporated into the complex. The reaction between chromium chloride and methacrylic acid is particularly suitable, resulting in a complex with reactive unsaturation. This complex can react with inclusion surfaces through the chromium functionality and with suitable polymers through the unsaturation.

This technology has been developed by DuPont who market their Volan® products. It is technically very successful in its primary goal of producing strong, stable, interfaces, but there appear to be several limitations.

The first is that the only polymer reactive functionality available appears to be unsaturation, and this limits the types of polymer composites that they can be used with.

The second relates to the need to prevent the self-condensation referred to earlier. This reaction proceeds readily and results in intractable solids with no utility for coating inclusion surfaces. The self-condensation is prevented by providing the agents in solution stabilized by low pH and by the presence of chloride. The pH is raised just prior to use in order to start the polymerization with the inclusion surfaces. In many cases, the coated product has to be washed to remove chloride. Scope for in situ addition is also very limited.

Finally, the coating solutions are somewhat hazardous, being acidic and containing a toxic metal. This latter is especially important in considering process effluents.

The main application today appears to be with glass fibers in unsaturated polyester composites. There is little or no reported use with particulate fillers.

25.6.17 Aluminates

References to aluminate coupling agents can be found in the literature. There is little structural information, but they seem to be derivatives of aluminum tri-isopropoxide, with one or more of the alkoxide groups being replaced by long-chain hydrocarbons. While often referred to as coupling agents, they are more likely to be dispersants, and this is borne out by the performance data available. Interestingly, they are claimed to be effective on calcium carbonate. As surface reaction (needed for coupling) with this filler would not be expected from the chemistry, this supports the mode of action as being dispersion rather than coupling.

25.6.18 Zircoaluminates

These chemicals were introduced in the early 1980s. Careful control of the reaction conditions allows aluminum and zirconium salts to be reacted with organic acids to produce low molecular weight, cyclic complexes of the generic structure shown in Figure 25.13. The alkoxide groups on the metals allow reaction with inclusion surfaces, while the organic acid allows the introduction of polymer reactive

![Figure 25.12](image1.png) A chromium methacrylic acid complex.

![Figure 25.13](image2.png) A typical zircoaluminate structure.
functionalities. Quite a wide range of functionalities are possible and have been offered commercially at some stage. Today only primary amine, carboxy, oleophilic, and mercapto functionalities appear to be commercial.

There is very little published information, but the main applications would seem to be as adhesives in the broader sense, rather than as coupling agents. The main use in our narrower sphere appears to be with siliceous fillers in elastomer compounds.

The principal limitations are again based around the need to stabilize the structures and prevent self-condensation prior to use. This means that they are not isolated as neat compounds, but sold as solutions in a polar solvent. They can be diluted with water before use, provided the solution is kept acidic. These issues mean that they can be tricky to use. They are most suited to liquid systems and not suited to in situ addition in most other systems.

### 25.6.20 Titanates

This is the area where there is most confusion over the use of the term coupling agent and indeed there has been considerable controversy. Potentially, titanate coupling agents can be derived from tetra-alkoxy titanate \([\text{Ti(OR)}_4]\), where one or more of the alkoxides have been replaced by an organic moiety carrying a reactive functionality. The remaining alkoxides then provide the means of attachment to inclusion surfaces through hydrolysis and condensation reactions, as with the organosilanes.

Because of the instability of titanium to carbon bonds, any reactive functionality has to be attached through oxygen and even then, stability cannot be guaranteed. Many of the products available have long-chain hydrocarbon functionalities, and while they produce useful effects, these are more likely to arise from dispersion rather than coupling in the sense used in this chapter. The titanates appear to be effective with fillers such as calcium carbonate and carbon black, where it is difficult to envisage surface reaction mechanisms and weaker, dispersant-type interactions are more likely.

### 25.6.21 Unsaturated Acids

The success of organosilanes with unsaturation as the polymer reactive functionality suggests that unsaturated acids should be equally effective with fillers such as calcium carbonate. Despite a great deal of effort, there has been little commercial success with simple unsaturated acids. Long-chain ones, such as oleic, have not proved to have sufficient reactivity. Short-chain types such as maleic, acrylic, and methacrylic have been shown to be capable of producing coupling but are difficult to use on a commercial scale. A form of oligomerized unsaturated acid (Solplus™ C800) has recently been commercialized by Noveon with some success.

### 25.6.22 Acid-Functionalized Polymers

These are a growing class of coupling agents, their popularity being driven by the increasing use of cellulose-filled polymer composites, especially those based on wood flour. All the main types contain carboxylic acid or acid anhydride groups as the inclusion reactive species. This makes them very effective on basic fillers such as calcium carbonates and also on amphoteric ones like aluminum hydroxide. As mentioned above, they also function very well with cellulosic fillers such as wood flour.

The main polymer backbones in use are polyolefins such as polyethylene and polypropylene and the acid or anhydride is usually introduced by free radical grafting, although copolymerization is used in some instances. There are some special-ized products based on low molecular weight polybutadienes reacted with maleic anhydride through the “ene” reaction and which are used in elastomers. In most instances the products can be regarded as one in which the actual coupling agent (e.g., an unsaturated acid) has already been incorporated into the polymer, and interaction with the matrix is by mechanisms such as entanglement or co-crystallization. The polybutadienes are slightly different, in that the starting polymers have relatively low molecular weight, and the grafted products are more like true coupling agents, reacting with the host polymer by sulfur or free radical curing processes.

The acid functional polyolefins are not suited to pre-coating because they are solids and are therefore predominately used by the in situ process. The polybutadiene types can be used by either pre-coating or in situ methods and water dispersible forms are available.
25.7 Conclusions

We have seen that dispersants and coupling agents are powerful tools for tuning composites to give improved processability, and mechanical and aesthetic properties. The choice of either one or the other type of surface modifier will depend upon the type of enhancements sought (Table 25.5).

<table>
<thead>
<tr>
<th>Property</th>
<th>Dispersant</th>
<th>Coupling Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (MFI/MVR)</td>
<td>↑↑</td>
<td>↑↑ or ↓↓</td>
</tr>
<tr>
<td>Modulus</td>
<td>=</td>
<td>=</td>
</tr>
<tr>
<td>Yield strength</td>
<td>=</td>
<td>↑↑</td>
</tr>
<tr>
<td>HDT semi-crystalline</td>
<td>=</td>
<td>↑↑</td>
</tr>
<tr>
<td>polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impact resistance</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Elongation to break</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>

↑ Increase in property; ↓ decrease in property; = no appreciable change.

Table 25.5 Overview of dispersant versus coupling agent effects

References