

INFLUENCE OF FILLERS ON PERFORMANCE OF OTHER ADDITIVES AND VICE VERSA

Product formulations are complex, consisting of numerous additives designed to perform certain functions. The performance of these additives depends on other components of a mixture. Similarly, fillers are added to perform certain tasks, and their performance might be enhanced or retarded by other components of the mixture. This chapter reviews the current understanding of these interactions, in order to highlight potential improvements or potential risks related to the application of fillers in complex formulations, which contain components that may interact due to physical or chemical forces.

13.1 ADHESION PROMOTERS

There are two groups of chemical materials which have similar chemical composition. These are adhesion promoters and coupling agents. In this section, the main object of the discussion is the performance of the entire system (product) in the relationship to the surrounding materials (frequently called substrates) with which the material must form durable bonding. Other aspects of physical and chemical interaction are discussed in one of the following sections entitled "Coupling Agents".

Adhesion promoters are most frequently used in coatings, adhesives, and sealants, but they also find application in other processes where adhesion between two layers of materials is of importance, namely in coated fabric, pultrusion, and lamination of several layers (e.g., calendering). It is surprising to find that in spite of so many applications, the literature on the subject almost does not exist.¹⁻⁴ Interfacial adhesion between layers of bromobutyl-based tire inner liner was found to be a problem.¹ Adhesion increased when 3.75 phr MgO and 3 phr 3-aminopropyltriethoxysilane was used. It should be noted that very large amount of silane had to be used to promote adhesion. In another study,² the effect of drying temperature on the penetration of silane into polymer (PVC) layer was investigated. At lower drying temperatures silane was able to diffuse more effectively into the polymer layer. Sulfur containing silanes were found to promote adhesion of organic

materials to metals and inorganic substrates.³ Salt spray resistance and adhesion of epoxy coatings were improved by the addition of silanes.⁴

It is noticeable from the above short review of publications that the effect of fillers is not evaluated. It is therefore necessary to use a fundamental approach to assess the problem. Three groups of chemical materials are mainly used to enhance adhesion of organic material to various substrates. These include silanes, polyurethanes, and tackifying resins. In most cases of the above mentioned products, adhesion promoters will work in formulations containing various fillers. Considering that fillers contain similar reactive groups to many substrates which are joined together, it is quite easy to anticipate that there must be a competition between functional groups on the filler surface and similar groups on the substrate surface for reaction with an adhesion promoter.

In the case of silanes, hydroxyl groups are found on both filler and substrate, and these groups compete for reaction with silane. It is well-known in the practice of adhesives that primer gives superior adhesion to the same silane added into the mass of adhesive. The reason is related to the mechanism of cure of silanes which occurs in the presence of moisture. Silane must migrate to the substrate surface, and react with moisture, and then free hydroxyl groups on the substrate surface in order to form bonding, affecting overall adhesion. If hydrolysis of methoxy or ethoxy groups (the first step of silane reactions) occurs in the bulk of adhesive, it is very likely that the next step of reaction (reaction between two hydroxyl groups) also occurs in the bulk, producing a small molecular weight oligomer or bonding with filler, which will further immobilize the silane molecule. It is thus simple to understand that silane added to the adhesive bulk cannot be as effective as when applied as a primer because it is partially used for ineffective reactions. Extending this explanation to answer our question regarding the effect of fillers on silanes, it is easy to predict that fillers and water present in the formulation will retard the performance of adhesion promoter. This phenomenon was confirmed in many technological attempts. For example, fumed silica is an excellent rheological additive, but it cannot be effectively used in some polyurethane coatings or adhesives because it contains both reactive hydroxyl groups and water which react with adhesion promoter (silane), and such materials do not have adhesion to substrates. Silanized fumed silica does not consume adhesion promoter but has a much lower efficiency in changing the rheology of these systems.

A similar mechanism acts in the case of reactive adhesion promoters such as polyurethanes. Here water is a factor, as well as surface functional groups of fillers. The adhesion promoter is exhausted within the bulk of organic material (coating, adhesive, etc.) and unable to perform the task.

Tackifying materials are solutions of resins having high green strength. These, in turn, are easily absorbed by some fillers, and thus fillers may affect adhesion.

It is thus always important to evaluate fillers from the point of view of their effect on adhesion of the final product. On the other hand, fillers may also improve mechanical adhesion due to the fact that they increase surface roughness.

13.2 ANTISTATICS

Conductive fillers, intrinsically conductive polymers, and organic additives are used as antistatics. There is no common product available which has a combination of the above. The only known combinations are particulate and fibrous conductive fillers, which are claimed to produce a better effect.

There is a potential interference between fillers and organic antistatics. It should be mentioned that there are no general rules here, as there is no universal antistatic agent. Antistatic agents may affect the dispersion of fillers and their interaction with the matrix. The dispersion of fillers can be affected in both directions – it can be improved (some antistatics are titanates and zirconates which are also known to be dispersing agents) and it can be more difficult (surface charges on filler particles aid the mixing process, which antistatics eliminate, making dispersion of carbon black or graphite very difficult). Interaction between filler and matrix depends on adjacent functional groups on the surfaces of both interacting materials. Organic antistatics form a layer on the surface of fillers by which they change the character of its surface as well as isolate filler from the matrix polymer. The order of addition of both antistatic agent and filler should always be considered as an important factor.

Also, fillers may affect the performance of antistatic agents. Organic antistatic agents work well when they are on the surface and when the surface has a certain level of adsorbed moisture. Since antistatic agents are cationic, anionic, and nonionic surface active agents, they absorb very well on most fillers, which has to be compensated by larger additions in formulations containing fillers. When antistatics are mixed with fillers, they should be first predispersed in other organic materials in order to minimize the effect of their absorption on filler particles. Some fillers have a tendency to absorb water, which is another factor which may reduce the effectiveness of antistatic agents.

13.3 BLOWING AGENTS

Fillers may affect foaming in many ways.⁵⁻⁸ The addition of filler increases the viscosity of the system and may affect cure rate of reactive systems. Considering that bubble size depends on the balance of internal pressure of gas inside the bubble and viscosity of the material in the surroundings, size of the bubble depends on both curing rate and viscosity of the system. With viscosity increasing, the same pressure of gas results in lower expansion of the bubble. At lower viscosity, bubbles may coalesce, forming larger bubbles that are less uniformly distributed throughout the material. Balancing viscosity and the rate of gas formation is an important task

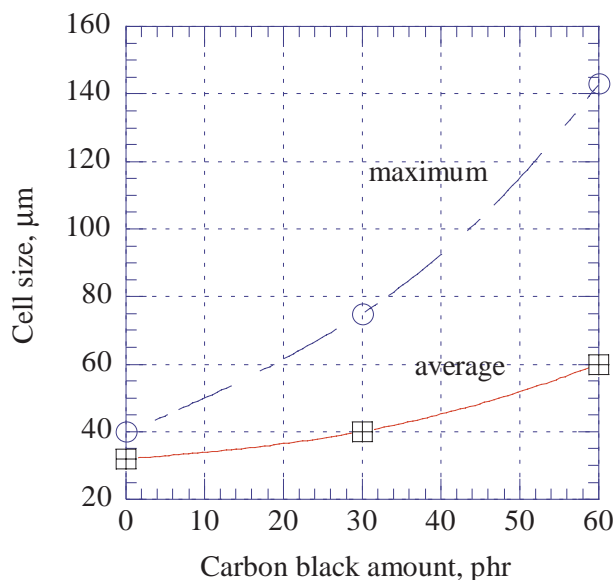


Figure 13.1. Cell size of vulcanized EPDM vs. concentration of carbon black. [Data from Guriya K C, Tripathy D K, *J. Appl. Polym. Sci.*, **62**, No.1, 1996, 117-27.]

of foaming. In addition, fillers have substantially higher density than the matrix, which makes systems containing fillers more difficult to foam.

The density of foam and its mechanical and thermal performances depend on the cell size and distribution. Fillers may affect cell sizes and distribution in several ways. On one hand, fillers have a nucleating effect, and they will participate in nucleation together with nucleating agents added to a formulation. Also, fillers are known to induce air pockets into the body of material, especially if they are not properly wetted. These air pockets will then be enlarged by a gas diffusing from the surroundings. The formation of foam depends on the properties of the matrix polymer, and fillers are known to change properties of the polymer due to interaction and adsorption.

From the above list of influences, it is pertinent that many properties of filler affect the foaming process and thus the performance of foaming agent. These properties include particle size and size distribution, surface area, shape, concentration, formation of agglomerates, distribution in the matrix, surface properties, and functional groups. It can also be predicted that these numerous parameters affect foaming in a complex way. This complexity eliminated fillers from foams in 1960s and 1970s; later, many regulations (fire protection, toxicity), cost, and increasing performance expectations brought fillers back to foams. Figure 13.1 shows the effect of filler on cell size. Increased concentration of carbon black contributes to the increase of average cell size and maximum cell size.⁸

13.4 CATALYSTS

The effect of fillers on the performance of catalysts attracted attention in current works.⁹⁻¹³ Fillers are used as active supports of catalysts in the molecular design of polymers. The works on metallocene catalysts are far beyond the scope of this publication, and their review can be found in a specialized publication.¹³ Several fillers are used for catalyst support. The most prominent members of this group include kaolin, tufa, dolomite, perlite, Al_2O_3 , SiO_2 , CaSO_4 , and wollastonite.^{11,12} These fillers participate in single-site catalytic systems but they can also be used for other purposes and should be considered in applications when catalyst is used in filled systems. One common application of a filler/catalyst system is in filler elastomer technology where monomers are polymerized in the presence of catalyst absorbed on filler, resulting in reactor-grade filled elastomers. These elastomers have properties which cannot be achieved by simple mixing. Typically, 25-50% active groups on the filler surface are utilized to attach catalyst, and these catalysts have efficiency increased by a factor of 10 to 1000. In addition to changes in catalytic activity, such reactive systems change polymer morphology, forming very regular polymers, designed for the structure needed. Although the above processes are highly specialized technologies applied on the industrial scale to produce special grades of polymers, the general principles are also applied in simple filled systems, which are the subject of our discussion. Therefore, the observations gathered from the synthesis of metallocene catalyzed polymers have relevance to these simple systems.

The role of filler in catalyst-containing systems is not restricted to morphological changes and reaction rate increases. Fillers may also retard the chemical processes of catalyzed reactions. One example is given in Figure 13.2. The silica surface contains reactive hydroxyl groups which contribute to the absorption of common accelerators used in rubber processing. Compounds containing silica cure with reduced rate, since accelerator is depleted. Typical methods used to overcome this problem include either increased addition of accelerator or, more efficiently, the process of filler surface precoat with, for example, polyethylene glycol.⁹ Surface groups are neutralized by the coating and cannot further absorb accelerator. Such a precoat uses a controlled order of addition, based on the physical principle that substances adsorbed first on the surface are very difficult to replace.

The other interesting case of interaction between filler and catalyst was reported in the literature.¹² A new filler was developed for automotive bulk molding and sheet molding compounds. This filler is composed of calcium carbonate coated on the surface by a thermoplastic polymer. Because of the presence of coating, catalyst cannot combine with the surface groups of filler which results in a higher degree of styrene-based polymer crosslinking.

It is thus pertinent from this short review that catalysts and fillers have a very high affinity, and their interaction may increase or decrease polymerization rate as well as change the molecular structure of the resultant polymer.

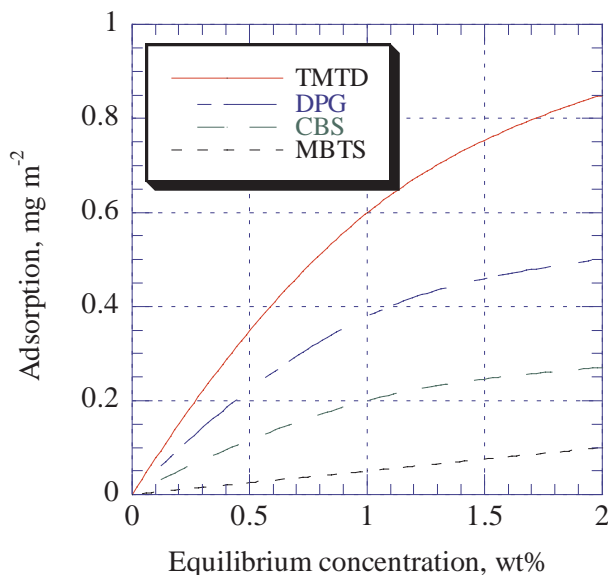


Figure 13.2. Adsorption of rubber accelerators on a silica surface. [Data from Bomo F, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper E.]

13.5 COMPATIBILIZERS

The most frequent compatibilizers of polymer blends are composed of block copolymers which have a chemical similarity to polymer components of the blend. Their role is to provide a vehicle for increasing the compatibility of normally incompatible polymers. It is usually quite a simple task if blend is only composed of polymers. In more complex systems, compatibilizer may more readily interact with other components (e.g., filler) than with the polymer which should be compatibilized. This is one example of the different effects of fillers found in studies of polymer blends.¹⁴⁻²⁰ A blend of PP/PA-6 was filled with glass beads.¹⁵ Ionomers and PP functionalized by reaction with maleic anhydride were used as compatibilizers. Addition of compatibilizer in the presence of filler may be used for encapsulation of filler – quite typical of studied systems. Filler encapsulation was a much more rapid process than blend compatibilization, which is typically a slow process. Thus, if compatibilizer was added in the presence of filler, filler was preferentially encapsulated. If the blend was compatibilized first and then filler added, best results were obtained. If high strength and high toughness are to be obtained simultaneously, it is beneficial to encapsulate filler in rubber toughened thermoplastic. Such a goal was set in studies of HDPE/EPDM/carbon black blends. Figure 13.3 shows the effect of interfacial modifier on the first normal stress difference, N_1 . The addition of rubber significantly increased melt elasticity due to dispersion of filler and formation of a core-shell dispersed phase. In addition, the viscosity and dynamic storage modulus increase, and dynamic loss modulus decreases.¹⁸

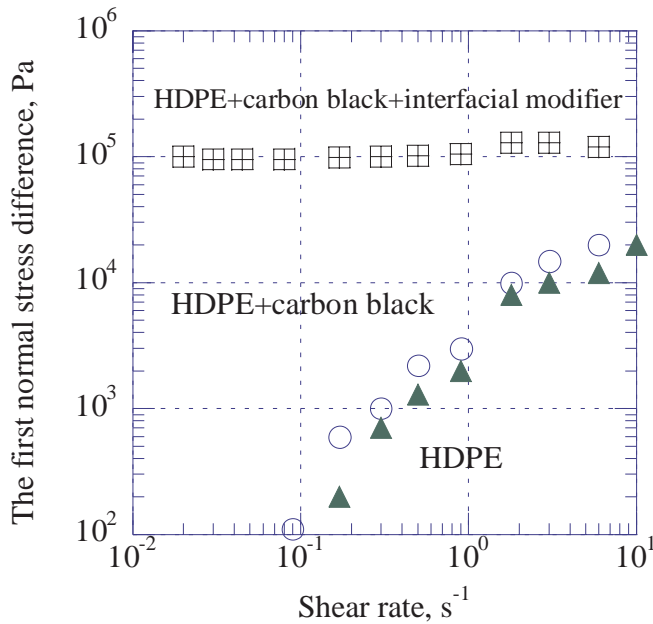


Figure 13.3. N_1 vs. $\dot{\gamma}$ for HDPE/carbon black composites. [Adapted, by permission, from Zhu J, Ou Y-C, Feng Y-P, *Polym. Int.*, **37**, No.2, 1995, 105-11.]

In another experiment,¹⁴ acrylic acid was absorbed on the surface of mica, forming an interlayer in a form of a coating, having thickness proportional to the amount of absorbed monomer. The rigidity of PP/mica composites is inversely proportional to the thickness of the interlayer. In PP filled with glass beads and compatibilized with EPM, the core-shell structure is less efficient in obtaining a strength/toughness balance than the presence of an EPM microphase.¹⁷

The incompatible system containing poly(vinylidene fluoride) and polystyrene was compatibilized by sepiolite addition. In this system, filler played the role of compatibilizer, giving the best performance at 10% concentration.

13.6 COUPLING AGENTS

One function of a coupling agent is to interact with filler. It is thus proven *a priori* that coupling agents affect filler properties, and modified fillers affect the system. Numerous works use this modification.²¹⁻⁵³ In this discussion, we summarize the effects obtained. Table 13.1 contains this summary.

Table 13.1. Effect of coupling agent/filler interaction

Filler	Polymer	Coupling	Effect	Refs
Al borate	PC/ABS	silane	improved adhesion and orientation change due to response to flow	43
Al(OH) ₃	HDPE	OMCTS	increased adhesion to matrix depends on concentration of modifier	29
	PVC	silane	crosslinking decreases thermal stability, elongation and tensile str.	46
	silicone	PDMS	surface hydrophobization; resistance to solvent extraction and water	37
CaCO ₃	EPR	maleates	decreased disperse component of the surface energy; filler surface energy approaches surface energy of matrix	21
	rubber	fatty acid	decreased tensile strength and flexural cracking	49
	rubber	silanes	increased green strength, Mooney viscosity, and tensile properties	49
	silicone	PDMS	surface hydrophobization; resistance to solvent extraction and water	37
Carbon black	rubber	ammonia	slightly reduced bound rubber (7%)	35
	rubber	APTS	crosslinking through reaction between -NH ₂ and COOH from rubber	36
Carbon fiber	PEEK	polyimide	no improvement of mechanical properties	52
Fe ₂ O ₃	silicone	PDMS	surface hydrophobization; resistance to solvent extraction and water	37
Fumed silica	PEG	silane	improved mechanical properties and electric conductivity	39
	silicone	silane	specific interactions decreased	40
Glass beads	PET	APES	increases interfacial adhesion but hinders crystallization of PET by reducing nucleating activity of filler	23
	Epoxy	silane	fracture resistance increased but no improvement of H ₂ O resistance	33
Glass fiber	PP	MA	flex strength increased, notch Izod decreased with MA increasing	26
	PP	MA	increased tensile and flexural properties	31
Gold - nanosize	PMMA	TOAB	nanoparticles obtained by polymerization in the presence of Au	30
Hydroxyapatite		silanes	stable to water coating; stability depends on silane functional group; coating is permeable to ionic transport in body fluids	24
Jute fibers	Epoxy	ES	increased ; increase tensile retention in H ₂ O presence	27
Kaolin	HDPE	silane	increased stiffness and fracture resistance	35
	PA-66	silanes	improved wet strength and mechanical properties	45
Mg(OH) ₂	PP	silane	slight increase in flexural and impact strength	32
	PP	titanate	slight increase in impact strength	32
	PP	fatty acids	the most effective surface treatment improving toughness	32
Mica	PP	MA	increased tensile and flexural properties	31
	PP	MA	all mechanical properties increased except impact strength	38
	PP	MA	all mechanical properties increased except impact strength	44
	PA-66	silanes	improved wet strength and mechanical properties	45
Quartz	Polyester	silane	increased mechanical and water resistance, filler particle splitting	50
Silica	EPM	alcohol	reduced interaction with polymer and itself	48
	SBR	TESPT	Mooney viscosity decreased; larger pore size the later silica is added	28
	SBR	TESPT	Mooney viscosity decreased; reduced cure rate	34
	rubber	ammonia	substantially reduced bound rubber (85%)	34
Talc	PP	MA	increased tensile and flexural properties	31
	PP	MA	properties of system can be tailored to application	54
	PA-66	silanes	improved wet strength and mechanical properties	45
Wollastonite	PA-66	silanes	improved wet strength and mechanical properties	45
Zirconium silicate	HDPE	silane	improved impact strength in comparison to untreated filler	41
ZnO	PC	PDMS	reduced catalytic activity of pigment in photodegradation	42
	PET	PDMS	reduced catalytic activity of pigment in photodegradation	42

APES - γ -aminopropyltriethoxysilane; APTS - 3-aminopropyltriethoxysilane; ES - epoxy silane; MA- maleic anhydride; OMCTS - octamethylcyclotriethoxysiloxane; PDMS - poly(dimethyl siloxane); TESPT - (bis)(triethoxysilylpropyl)- tetrasulfone; TOAB - tetraoctylammonium bromide with H₄AuCl₄

13.7 DISPERSING AGENTS AND SURFACE ACTIVE AGENTS

Filler dispersion is a mostly mechanical process which requires sufficient shear for dispersion but two stages of the dispersion process sometimes require the help of additives. These are the stages of surface wetting and stabilization of the dispersion. In both stages, dispersing agents and surface active agents are frequently involved. Their effect on pigment dispersion is discussed here.⁵⁵⁻⁶¹ The surface wetting of filler by the matrix is frequently difficult because of high viscosities of the matrix or the lack of compatibility between filler and matrix. Here, dispersing agents can be of help. In the case of systems of high viscosity such as melts or dispersion in high viscosity polymers, the dispersion obtained is usually stable; therefore, no further action is required. But this is not the case in dispersions of filler in low viscosity liquids, where a large difference in density and a tendency of some fillers to flocculate or aggregate causes a good dispersion to be reversed. In such cases, surface active agents help to stabilize the suspensions.

The mechanisms of both processes are essentially similar, even though they are employed in different cases. Both dispersing agents and surface active agents have polar molecules composed of groups which easily interact with filler and matrix. Between these groups there is frequently a chain which is used to create some space between filler and matrix. From this description, it is clear that a filler modified by a surface active agent has modified surface groups, which changes its behavior in the system.

The materials used for modification can be of low molecular weight but can also be small molecular weight polymers such as polyethylene wax, which was used to improve the dispersion of carbon black in polyethylene.⁵⁶ This wax helps in breaking carbon black agglomerates, resulting in reduced viscosity and torque and substantially improved dispersion. Also, comb-like grafted block copolymers are used as dispersing aid for polyethylene, resulting in a more efficient use of pigments due to a better dispersion.⁵⁵

Figure 13.4 shows the effect of pH of carbon black on the amount of dispersing agent required.⁵⁷ The suspension of carbon black in water was made using the sodium salt of a polymeric carboxylic acid, which is an anionic surfactant. Depending on pH, substantially different amounts of dispersing agent were needed. It is noticeable that the relationship is very steep, which indicates a very small tolerance to the differences in pH. A small difference in pH may completely alter dispersion. Also, difference in the specific surface area and surface treatment of carbon black has a strong influence on the quality of dispersion.

Figure 13.5 is an example of a collaborate activity of surfactant and filler in obtaining small and uniform cell sizes. The control foam was obtained with surfactant alone. The addition of silica increases nucleation and results in a very uniform polyurethane foam. This foam was developed to increase the insulation rating of refrigerator foams.⁶¹

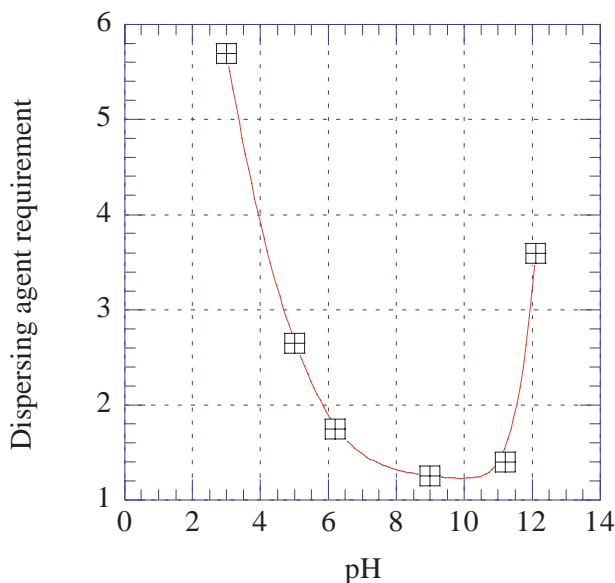


Figure 13.4. Dispersion agent requirement vs. pH in water dispersions of carbon black. [Adapted, by permission, from Foster J K, Sims, E S, *Polym. Paint Col. J.*, **184**, 1994, 312.]

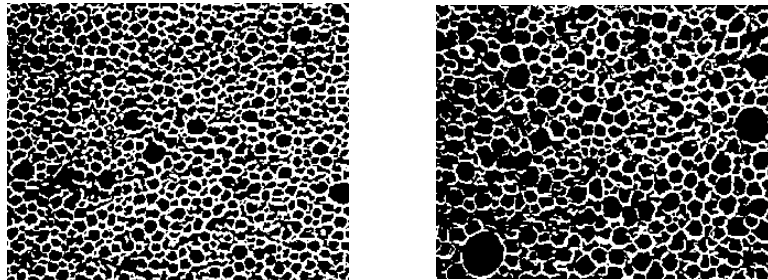


Figure 13.5. Micrographs of rigid polyurethane foams. left - surfactant/silica foam, right - control. Magnification 30x. [Adapted, by permission, from Okoroafor M O, Wang A, Bhattacharjee D, Cikut L, Haworth G J, *Polyurethanes '95. Conference Proceedings, Chicago, IL, 26th-29th Sept.1995*, 303-9.]

A surface active agent may also help in filler synthesis. Various surfactants can be used to aid the dispersion of precipitating filler. Addition of surfactant produces a more uniform particle size distribution. At the same time, the surface of filler is converted by reaction with surfactant. For example, alcohols and phenols may react with hydroxyl groups, changing surface properties and surface active groups.⁵⁹ In interpenetrating networks, such a surface change, caused by the interaction of Fe_2O_3 with surfactant, increased microphase separation in comparison with filler used without surfactant.⁶⁰

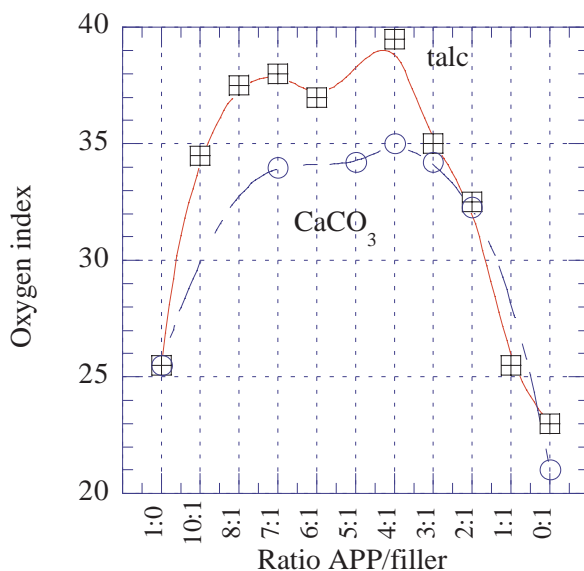


Figure 13.6. Oxygen index vs. ratio of ammonium polyphosphate/filler. [Data from Levchik G F, Levchik S V, Lesnikovich A I, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 361-3.]

Surface active agents were also employed in processes of filler recovery from waste paper.⁵⁸ An increased concentration of surfactant increased the recovery of kaolin and calcium carbonate from waste paper.

13.8 FLAME RETARDANTS

Combinations of inorganic and organic flame retardants are discussed here.⁶²⁻⁶⁸ Figure 13.6 shows that the addition of regular fillers, such as talc and CaCO_3 , to ammonium polyphosphate increased the fire resistance of PA-6.⁶² The function of filler in these combinations is to increase char yield and increase insulation properties of char. On the other hand, ammonium polyphosphate protects char from oxidation and hinders diffusion of combustible gases to the flame.

A more complex fire retarding system was used in propylene-ethylene copolymer.⁶³ This system consists of huntite/hydromagnesite/antimony trioxide/decabromodiphenyl oxide. Fillers act as effective flame retardants and, in addition, reinforce the copolymer. At the same time, an agent acting in the gaseous phase was needed to reduce the height of flames. A combination of antimony trioxide and decabromodiphenyl oxide plays this role in the system.

Figure 13.7 shows the effect of two combinations on smoke release. Addition of zinc stannate or ammonium octamolybdate, AOM, gives better performance than antimony trioxide alone.⁶⁴ Antimony trioxide performance is also improved by brominated flame retardants.⁶⁵ Chlorinated hydrocarbons, antimony trioxide, and novel silicone powders form good combinations, reducing the heat release rate and smoke in thermoplastics.⁶⁶

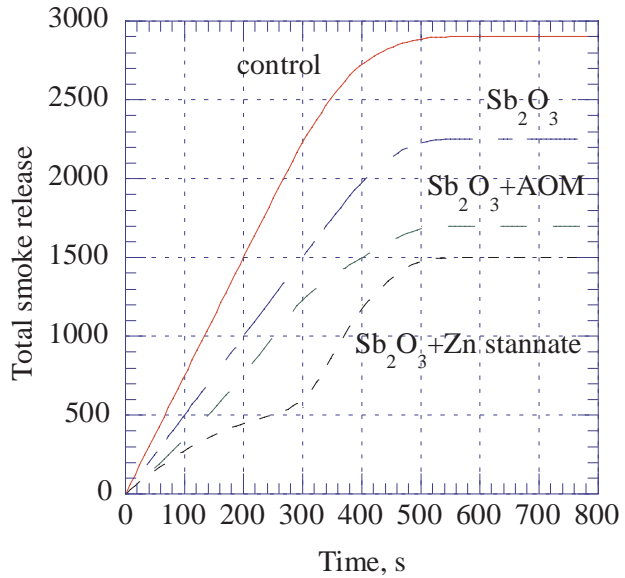


Figure 13.7. Total smoke release vs. time. [Data from Herbert M J, Flame Retardants '96. Conference proceedings, London, 17th-18th Jan.1996, 157-72.]

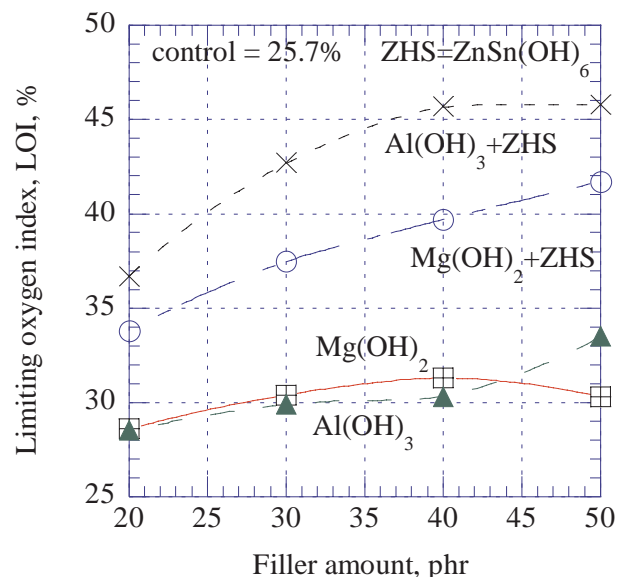


Figure 13.8. The effect of a zinc hydroxystannate coating on limiting oxygen index. [Data from Baggaley R G, Hornsby P R, Yahya R, Cussak P A, Monk A W, *Fire Mater.*, **21**, 1997, 179-85.]

Zinc hydroxystannate was found to enhance the performance of $Mg(OH)_2$ and $Al(OH)_3$. Figure 13.8 shows the effect of filler coated with zinc hydroxystannate on

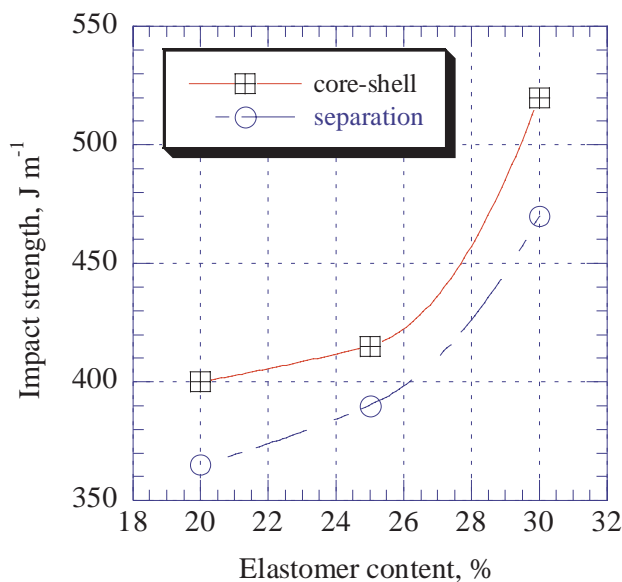


Figure 13.9. Elastomer content vs. impact strength of polypropylene containing 15% talc and maleic anhydride modified ethylene-propylene copolymer. [Data from Yu Long, Shanks R A, *J. Appl. Polym. Sci.*, **61**, No.11, 1996, 1877-85.]

the limiting oxygen index. Substantial improvements result.⁶⁸ Similar improvement of ignition time and heat release rate also occurs.

In intumescent fire retardant application, clay was combined with ammonium polyphosphate and pentaerythritol in the polypropylene matrix.⁶⁷ The fire retarding properties depended on the composition of clay. Ammonium polyphosphate played the role of carbonization catalyst and pentaerythritol the role of carbonization agent.

13.9 IMPACT MODIFIERS

Impact modifiers are frequently used in filled systems.⁶⁹⁻⁷⁸ The effect of the presence of both filler and impact modifier on mechanical properties depends on the microstructure. Figure 8.33 shows structure combinations.⁶⁹ If particles of filler and impact modifier occupy separate sites in the matrix, they form separated structures. If filler particles are embedded in the impact modifier resin, together they form a core-shell morphology. In a core-shell morphology, particles of filler become more elastic and may enhance adhesion to the matrix. These two structures have implications on mechanical properties. Typically, with a core-shell structure, the elastic modulus decreases, elongation increases, and impact strength increases. Figure 13.9 shows that some gains in impact strength were obtained due to a core-shell microstructure.

The above relationships between structure and basic mechanical properties are obtained from the analysis of experimental compounds as well as theoretical analy-

sis. In studies of PVC containing CaCO_3 and chlorinated polyethylene as impact modifier, impact strength increased on addition of filler, which formed core-shell structure with the filler.⁷⁸ Impact strength also increased with the amount of impact modifier (SEBS and SEBS modified with maleic anhydride) in glass spheres filled PP.⁷⁵ Both results are in agreement with the theoretical analysis.

In ultrafine talc-filled rigid PVC modified with acrylic modifier, impact strength consistently decreased with addition of filler regardless of the concentration of acrylic modifier.^{73,74} An increase in calcium carbonate caused a substantial increase in impact strength. Similar results were obtained for HDPE/EPDM/CB and HDPE/CB systems.⁷⁰ There were high increases in tensile strength due to increased addition of carbon black, but no substantial influence of impact modifier was noted. Impact strength always decreased with increasing carbon black concentration and only impact modifier was instrumental in increasing impact strength.

It can be thus summarized^{76,77} that a range of mechanical behavior can be generated by the appropriate choice of processing conditions, filler size, shape and concentration, and elastomer content and its distribution between the matrix and filler. These choices should lead to results predicted by theory.⁶⁹

13.10 UV STABILIZERS

There is a growing evidence that fillers may adversely affect the performance of UV stabilizers, including practical immobilization and loss of their effect on stabilized systems.⁷⁹⁻⁸³ These data coming from different sources indicate a growing

Table 13.2. Absorption of UV stabilizers on 30% Monarch 1300 suspended in xylene⁸³

UV stabilizer	Initial concentration, %	Absorption %
Tinuvin 384	3	27
Tinuvin 770	1.5/3	100
Tinuvin 292	1.5/3	83/100
Tinuvin 1130	3	81

concern that UV stabilizers, which are expensive additives, may not perform up to expectations. Table 13.2 shows the amounts of various stabilizers absorbed on carbon black. The absorbed quantities are substantial to raise further questions regarding the effect of this absorption on the performance of stabilizers, considering that carbon black is present in many formulations either as filler or pigment. Table 13.3 shows that carbon black is not the only filler which absorbs UV stabilizers.⁷⁹ Fillers used in this experiment, conducted in a cyclohexane suspension, were at low concentrations. The concentration of HALS was typical of many formulations. Results show that tertiary HALS is superior to secondary

Table 13.3. Absorption of secondary and tertiary HALS on different fillers⁷⁹

Filler	Concentration, %		HALS absorption, %	
	filler	HALS	secondary	tertiary
Talc	20	0.6	25	6
TiO ₂	4	0.6	17	7
CaCO ₃	4	0.6	75	40
Carbon black	8	0.6	20	7

HALS but that absorption on fillers occurs in both cases. Calcium carbonate is the most absorbing filler in this experiment.

The molecular mobility of various HALS was studied by the spin probe TEMPO, and ESR spectra were recorded.⁸⁰ In polyethylene filled with silica having a surface area of 139 m²/g, the concentration of silica was in the range from 0 to 25.9%. It was found that hydrogen bonds are formed between nitroxyl radicals and hydroxyl groups of filler. The formation of hydroxyl groups leads to changes in A_{ZZ} which is the peak-to-peak separation of the rigid limit spectrum. For isolated nitroxyl radicals (no hydrogen bonding) $A_{ZZ} = 3.33$ mT. For hydrogen bonded radicals this value changes to 3.83 mT. The measured values were from 3.4 to 4 mT depending on silica concentration. This suggests that addition of silica immobilizes HALS.

The above presented data may constitute evidence that under model conditions (without presence of polymer) UV stabilizers are adsorbed. It is conceivable that the absorption on filler may potentially play a positive role: it may slow down loss of stabilizers due to their migration and volatility. Figure 13.10 gives data on changes in carbonyl absorption during PP photooxidation. Both calcium carbonate and talc reduce the performance of HALS even though these fillers are only used in a very moderate concentration (10%), much lower than in typical products.

Table 13.4 shows the effect of the presence and absence of 1% silica on the performance of various UV stabilizers in stabilized polypropylene. The performance of all stabilizers was substantially

Table 13.4. Time to 0.06 carbonyl units for PP stabilized with various stabilizers in concentration of 0.1%⁸²

Stabilizer	Time, h	
	without silica	with silica
Control	384	432
Irganox 1010	1032	144
Cyanox LTDP	912	192
Irgafos 168	408	144
Chimassorb 944	1512	540
Cyasorb UV 3346	1512	720
Tinuvin 622	2004	456

retarded in the presence of silica.⁸² The addition of silica without the presence of UV stabilizer improves UV stability of the polymer. The data shows that the effect of filler is not restricted to HALS but extends to a broad spectrum of UV stabilizers.

It can be postulated that three factors may play a role in stabilization in the presence of fillers. One factor is the discussed absorption which immobilizes stabilizer to the extent that it cannot perform its function. The second is its desorption capability, which, if it exists, may enhance the performance of stabilizer due to its better retention. However, it should be mentioned

that photochemical changes occur at very short time scales; therefore, there must always be a sufficient concentration of “free” (not absorbed) stabilizer to react with radicals. The third factor is the effect of filler on structure and related stability of stabilizer. The reduced stability of polypropylene in the presence of some stabilizers in Table 13.4 can be explained only by the formation of degradation products. It

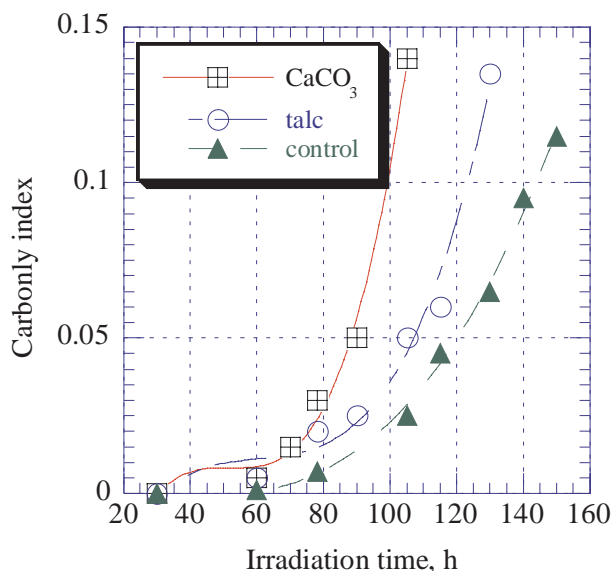


Figure 13.10. Carbonyl absorption during photooxidation of PP containing 0.3% HALS and fillers. [Adapted, by permission, from Hu X, Xu H, Zhang Z, *Polym. Degradat. Stabil.*, **43**, No.2, 1994, 225-8.]

is well established that adsorption of any chemical compound on filler may change its molecular structure, because the molecule must change its geometry to be adsorbed. Perhaps this change makes some products to degrade.

In summary, the data presented above show that there is a concern regarding performance of UV stabilizers in real systems, which typically include fillers. It is known from the automotive industry that the only method by which durability of automotive coatings could be increased was by the use of highly stabilized clear coat. It is also known from this field that a substantial amount of UV stabilizer from clear coat is absorbed on the pigmented coat, by which clear coat stability is reduced. There is also a growing tendency to protect materials with various surface coatings rather than adding UV stabilizers into the material bulk. This trend may reflect the reality of little progress made in stabilizing compounds during the last decade, which followed growing interest in stabilization due to arrival of HALS. The new developments in some pigments such as ultrafine TiO₂ should be closely monitored, since some pigments already offer better protection than organic stabilizers and at a fraction of the cost.

13.11 OTHER ADDITIVES

Many other additives affect performance of fillers, or their performance is affected by fillers. Some findings are discussed below.⁸⁴⁻⁹⁷

Combinations of particulate fillers and fibers give some unique properties. A combination of calcium carbonate and polyamide fibers gave the best dielectric

properties in natural rubber. This composition was also the most resistant to natural aging.⁸⁷ Addition of mica and zirconia to glass fiber reinforced composites reduces wear and the friction coefficient.⁸⁸ In sealants and adhesives, rheological properties depend on fillers. Good non-sag properties are the easiest to obtain by using combinations of spherical and elongated particles.

Properties of silica-filled LDPE depend on the crystallization rate, which depends on nucleation by filler particles. The crosslinking initiated by thermal decomposition of peroxide retards crystallization. The properties of the resultant product in the reactive system depend on the timing of both processes.^{89,90}

Friction and wear of metal oxide filled PTFE can be improved by liquid paraffin lubrication, and the friction coefficient decreases by one order of magnitude. On the other hand, the interaction between liquid paraffin oil and metal oxide filled PTFE reduces load-carrying capacity because of absorption on the surface layers of composite.⁹¹

Diamine salts of fatty acids are used as multifunctional additives in natural rubber compounds filled with carbon black.^{92,93} They affect the elastomer-carbon black interface. With an increased concentration of multifunctional additive, the concentration of bound rubber decreases but dispersion of carbon black is improved. In silica filled rubber, multifunctional additive also improves the dispersion of silica, but in addition, it decreases the negative influence of silica filler on vulcanization rate.

The rheological properties of suspensions of montmorillonite depend on the presence of electrolytes and polyelectrolytes.⁹⁴ The face-to-face interactions (coagulation) occur in the presence of polyvalent cations. The edge-to-face interactions are strongest at low pH and in the presence of high concentrations of electrolytes.

A combination of calcium hydroxide and vegetable oil in polyethylene gives a cost effective method of filling. Salts of fatty acids are formed during compounding, resulting in improved interaction between polymer and filler. In addition, there is a potential to use this system for waste recycling, where plastic waste is typically contaminated with vegetable oil.⁹⁶

Proprietary additives based on copolymers containing carboxyl groups are rheological modifiers used to lower the viscosity of systems filled with $\text{Al}(\text{OH})_3$.⁹⁷

The examples included in this chapter show that addition of filler to any composition must be evaluated for various interactions and interferences in properties other than the reasons for filler inclusion. Simple addition of filler without considering the possible effects may cause essential changes in the material.

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