

EFFECT OF FILLERS ON EXPOSURE TO DIFFERENT ENVIRONMENTS

11.1 IRRADIATION

Many filled systems are exposed to irradiation during processing or use. Such processes include radiation crosslinking and vulcanization, development of antistatic properties, production of γ -radiation shields, and sterilization.¹⁻¹¹ The effect of fillers in these applications is studied.

Several studies look at the crosslinking of PVC compounds containing CaCO_3 .¹⁻³ Exposure of a PVC compound to γ -radiation will change its properties. Properties affected include tensile strength and Young modulus which are increased and elongation which is decreased. Figure 11.1 shows that the presence of calcium carbonate had minimal influence on crosslink density. Similarly, calcium carbonate did not influence the performance of the crosslinker (trimethylol propane trimethacrylate).

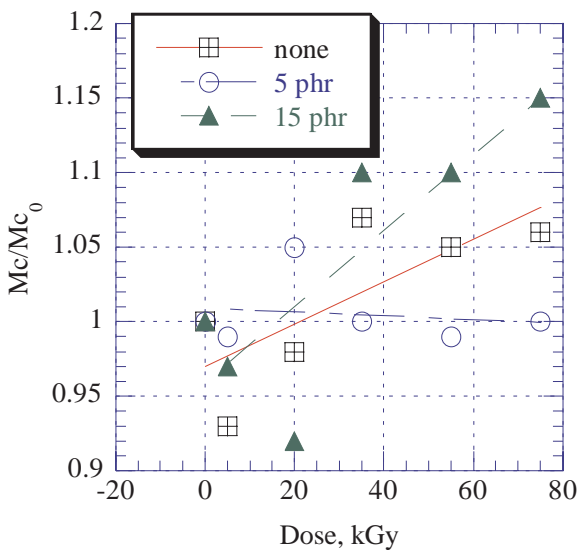


Figure 11.1. Molecular weight between crosslinks vs. dose of γ -radiation at different levels of calcium carbonate. [Adapted, by permission, from Bataille P, Mahlous M, Schreiber H P, *Polym. Engng. Sci.*, **34**, No. 12, 1994, 981-5.]

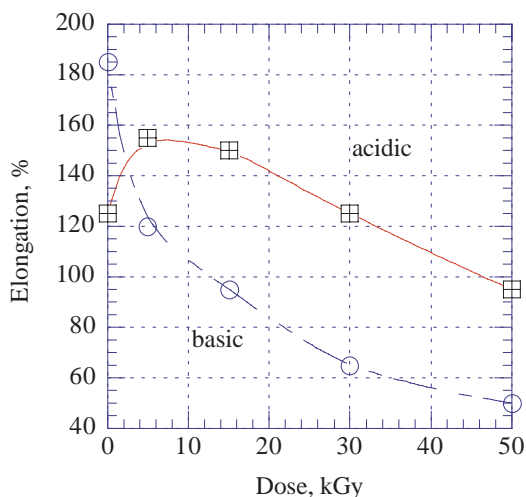


Figure 11.2. Elongation vs. γ -rays dose for PVC filled with 15 phr CaCO_3 . [Adapted, by permission, from Ulkem I, Bataille P, Schreiber H P, *J. Macromol. Sci. A*, **31**, No.3, 1994, 291-303.]

Figure 11.2 shows that the use of acidic filler helps to preserve elongation when the filled material is exposed to γ -radiation.³ Both acidic and basic calcium carbonate were evaluated. The acidic version was obtained through surface treatment of normally basic calcium carbonate. Due to lower acid/base interaction, Young modulus and yield stress of the compounds containing the acidic filler were lower but elongation was less affected.

Elongation was better retained also by the addition of 5% soot to LDPE. The material underwent a rapid crosslinking at 50-60 kGy which improved its elongation by a factor of 4. At the same time, its tensile strength was decreased by 30%.⁴ Polyethylene containing carbon black was found to be resistant to ionizing radiation.⁵⁻⁶ The impact strength of carbon black filled HDPE and HDPE/EPDM was improved after exposure to γ -radiation.⁶

Figure 11.3 gives data on the radical decay in PE filled with silica. The increased addition of filler gradually decreases radical decay. This data has significance in two areas. The data shows first that polymer chains are gradually immobilized as the amount of filler is increased. Second, a lower rate of radical decay signifies an increasing probability that chemical conversions and localized reactions are occurring.⁷

Radiation vulcanization of carbon fiber reinforced styrene-butadiene rubber causes a substantial increase in crosslink density (Figure 11.4) and tensile strength (Figure 11.5).⁸ This magnitude of change is possible only when the interaction between the filler and the matrix is improved. When irradiated in the presence of air, carbon fibers gain functionality which substantially increases their adhesion resulting in a spectacular improvement in properties. SEM studies show that as the dose of radiation increases, the adhesion of the

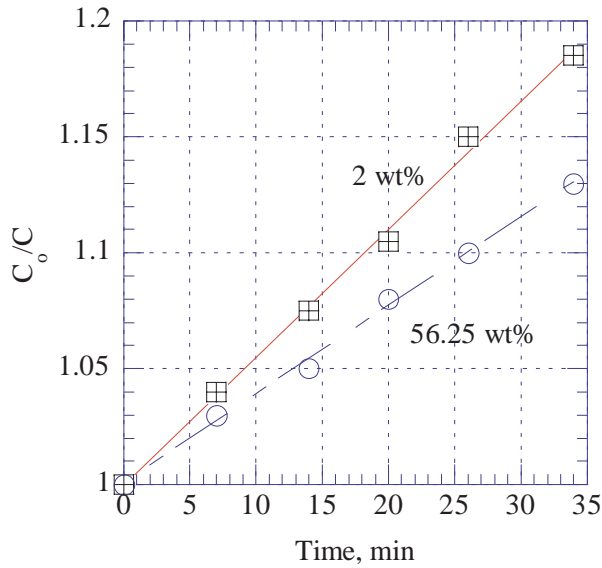


Figure 11.3. Free radical decay in silica filled PE. [Adapted, by permission, from Szocs F, Klimova M, Chodak I, Chorvath I, *Eur. Polym. J.*, **32**, No.3, 1996, 401-2.]

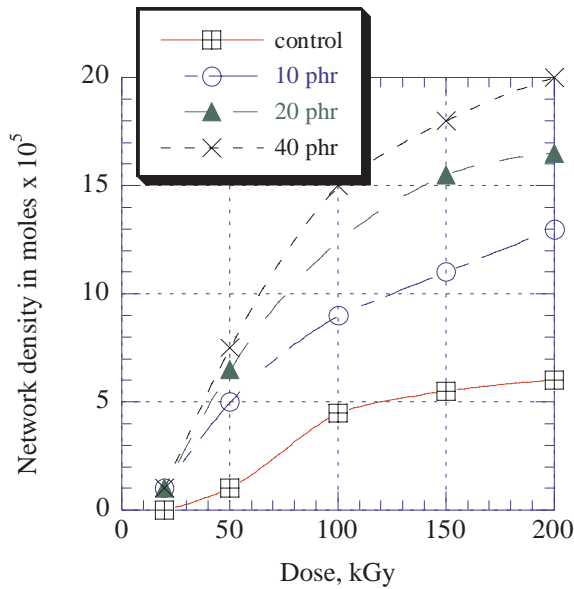


Figure 11.4. Effect of irradiation on crosslink density of SBR filled with carbon fiber. [Adapted, by permission, from Abdel-Aziz M M, Youssef H A, El Miligy A A, Yoshii F, Makuuchi K, *Polym. & Polym. Composites*, **4**, No.4, 1996, 259-68.]

matrix to the fiber increases. Here, a study of the morphology of the fracture surface of the fibers shows they have a matrix deposit on their surface.

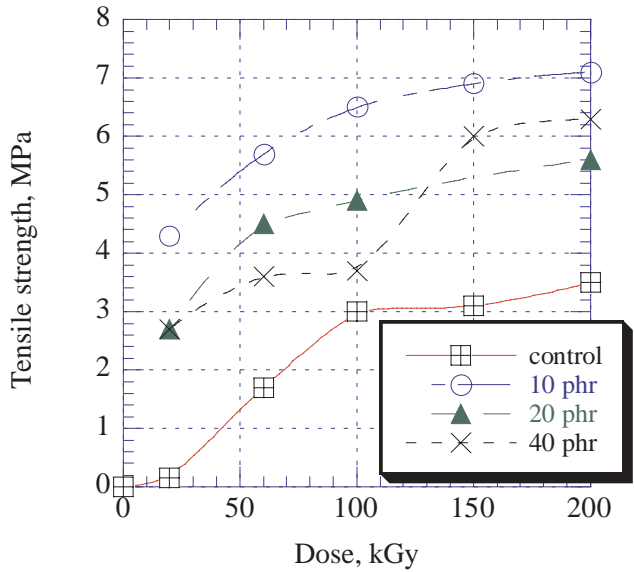


Figure 11.5. Effect of irradiation on tensile strength of SBR filled with carbon fibers. [Adapted, by permission, from Abdel-Aziz M M, Youssef H A, El Miligy A A, Yoshii F, Makuuchi K, *Polym. & Polym. Composites*, **4**, No.4, 1996, 259-68.]

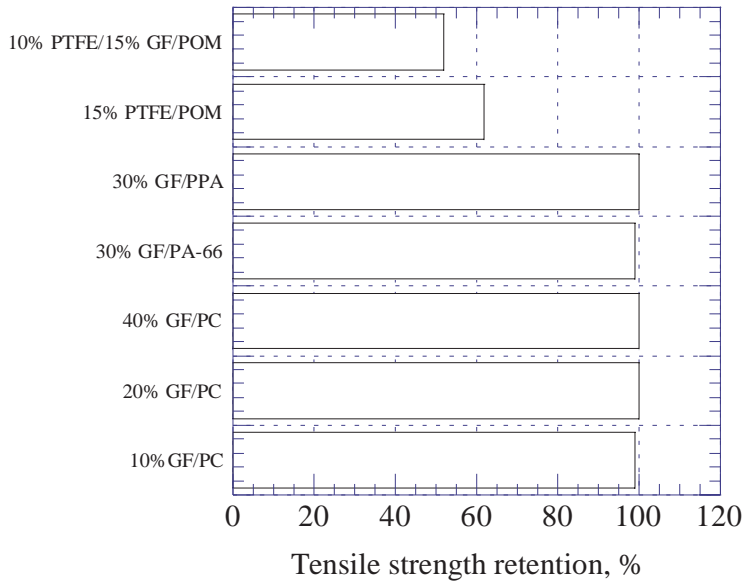


Figure 11.6. Tensile strength retention after exposure to γ -radiation at 3.5 MRad. [Adapted, by permission, from McIlvaine J, Antec 95. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 3346-9.]

Styrene-butadiene rubber loaded with lead oxide was studied to determine its effectiveness as shield for γ -radiation. The material did have the required performance but it gradually hardened on exposure to radiation.⁹

The effect of radiation sterilization on several plastics was studied (Figure 11.6). With exception of acetal, none were affected by radiation. Six month after exposure, no effect of radiation sterilization was found on impact and tensile strength.¹⁰

11.2 UV RADIATION

Fillers commonly constitute more than 50% of the total composition of processed polymers. Although their effect on weathering resistance has either been demonstrated in service or predicted based on theoretical assumptions, the number of weathering studies is rather small.¹²⁻⁴² This is perhaps because of the more pressing need to study polymers, which are the components most responsible for the physical properties and durability the composite materials.

Titanium dioxide, the white pigment used in many products, is probably the most extensively studied filler. When titanium dioxide is irradiated with a radiation wavelength of less than 405 nm, the absorbed energy is sufficient to promote electrons from the valence band to the conduction band. Positive holes are formed in the valence band with both holes and electrons able to move within the crystal lattice. During such movement, some holes and electrons will recombine, but these available on the crystal surface can initiate chemical reactions. Electrons may combine with oxygen forming radicals, whereas positive holes combine with hydroxyl groups, forming hydroxyl radicals. These radicals may then react with organic matter or water, initiating a radical reaction chain. In order to limit such reactions, producers of titanium dioxide pigments have developed methods to promote the recombination reactions. This is done either by using admixtures of transition metals (zinc or aluminum) or by coating the TiO_2 particles with alumina or silica. Transition metals act as a recombination center for both electrons and holes. Coating helps to destroy the hydroxyl radicals by facilitating their recombination to water and oxygen. Such measures improve the quality of titanium dioxide but they do not completely eliminate radical formation.

Considering the fact that titanium dioxide plays the dual role of stabilizer and sensitizer, one may anticipate that its effect depends not only on the type and quality of titanium dioxide but also on the properties of the binder (polymer). Figures 11.7 and 11.8 show the effect of titanium dioxide on mass loss during the weathering of a durable and a non-durable binder. The durable binder is sufficiently stable to withstand weathering without the need for UV stabilization. The addition of titanium dioxide causes formation of free radicals in the vicinity of its crystals in the binder, which triggers rapidly accelerating degradative changes leading to the decreased weather stability of the material. A non-durable binder (Figure 11.8) is also the subject of radical formation in the vicinity of titanium dioxide particles but the protective effect of the pigment is sufficient to offset the negative effect of radical process, resulting in a net improvement in weather stability of the material. Since most of the changes in the material occur around titanium dioxide particles, eventually the binder is sufficiently eroded that pigment and binder separation or chalking occur (Figure 11.9).

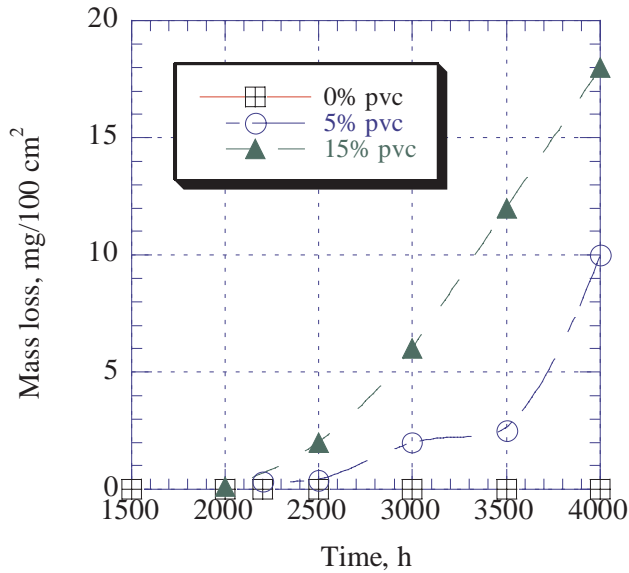


Figure 11.7. Mass loss of a durable binder vs. exposure time relative to pigment load. [Adapted, by permission, from Simpson L A, *Austral. OCCA Proc. News*, **20**, 1983, 6.]

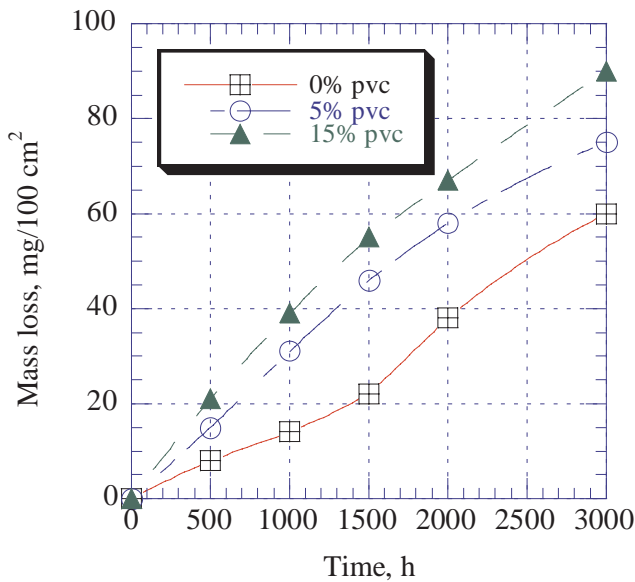


Figure 11.8. Mass loss of a non-durable binder vs. exposure time relative to pigment load. [Adapted, by permission, from Simpson L A, *Austral. OCCA Proc. News*, **20**, 1983, 6.]

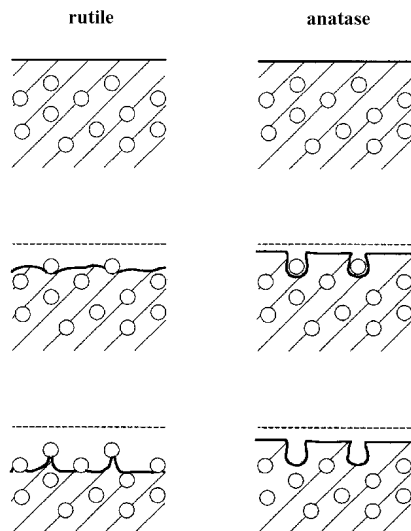


Figure 11.9. Model of binder degradation. [After Braun J H, *Prog. Org. Coat.*, **15**, 1987, 249.]

Different grades of titanium dioxide produce different effects. The mechanism of chalking described by Figure 11.9 results in changes in material gloss. Both durable and non-durable binder respond to an increasing concentration of titanium dioxide in similar ways, i.e., gloss decreases more rapidly with a higher concentration of TiO_2 .

Other parameters affect how titanium dioxide participates in degradative processes. In the non-durable binder, titanium dioxide acts to screen the binder from UV radiation. The efficiency of screening depends on the degree to which TiO_2 is dispersed. Flocculated pigment has a lower screening power. Less flocculated pigments inhibit both gloss deterioration and mass loss of the material.

The temperature at which degradation occurs is also an important factor. Gloss is better retained when samples are irradiated at lower temperatures. This suggests that the rate of formation of free radicals is controlled by two processes: one being photon absorption; the other being the reaction of the excited species followed by radical formation. The quantum efficiency of radical formation is reduced when radicals recombine. Because radicals are formed within a rigid matrix, it is difficult for them to escape (the cage escape efficiency is reduced). At low temperatures, the matrix is more rigid than at high temperatures and recombination is the more probable outcome. Around T_g , the cage escape efficiency is rapidly reduced.

The effect of pigment properties on photochemical activity is shown in Figure 11.10. Surface passivated titanium dioxide (RL90) and CdS both decrease the amount of carbonyl group formation as the concentration of pigment increases. ZnO and untreated titanium dioxide also contribute to a decrease in carbonyl group formation but only at low concentrations. Above a certain level, each cause an increase in the formation of carbonyl groups. Treated TiO_2 and CdS have poor photocatalytic activity and they participate in

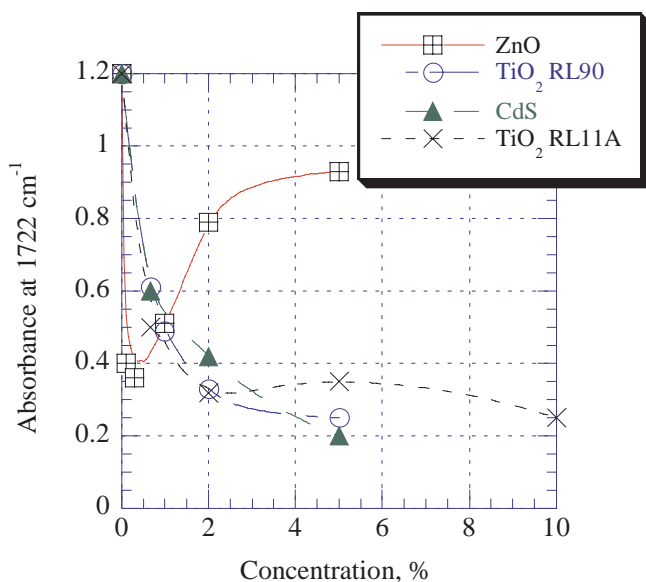


Figure 11.10. Carbonyl content in photooxidized EP copolymer film vs. filler concentration. [Adapted, by permission, from Lacoste J, Singh R P, Boussand J, Arnaud R, *J. Polym. Sci., Polym. Chem.*, **25**, 1987, 2799.]

photodegradative processes by actively screening radiation. In the first part of the curve (Figure 11.10), there is a very low quantum yield of photocatalysis due to electron-hole recombination. ZnO and untreated TiO₂ provide screening at low concentrations. At higher concentrations, their photocatalytic effect becomes predominant and carbonyl concentration increases. On the other hand, ZnO has long been known to stabilize some polymers. Formation of zinc carboxylates was found to contribute to the stabilizing efficiency of ZnO in HDPE.³⁹ From a comparison of the effect of several metal oxides including ZnO and TiO₂ on the stability of LDPE, it was postulated that the stabilizing activity of a filler depends on its ability to induce crystallinity to the matrix.⁴⁰

Small additions of fine particle TiO₂ are currently used to preserve the vitamin content of milk packaged in plastic films. As small as 0.5-1% concentrations of TiO₂ are sufficient to retain more than 90% of vitamin A in milk exposed to UV for 3 days.³⁶ This example shows that fillers may not only protect materials against degradation but they also protect the contents. A 2% addition of fine particle TiO₂ (spherical particles of 15-30 nm diameter) absorbs all UV light below 350 nm (the most degrading part of UV) at film thickness of 70 μm .

A recent study³⁵ shows another possible application of TiO₂. Combination of peroxides and TiO₂ or ZnO was used for controlled degradation of PVC on exposure to sun light. It is possible to degrade this PVC in only one month.

The tensile strength of the material and other mechanical properties were better preserved when pigment, regardless of the color, was added. Studies of fourteen iron oxide pigments in a PVC matrix showed that pigments with a large inherent ESR spectrum strength, have poor weatherability.¹⁶ PVC plates with an ESR spectrum strength lower than

1 exhibited very good weatherability, equivalent to five years of outdoor exposure. The type of pigment used in PVC greatly influenced the UV stability of the polymer.

An extensive studies²⁶ were conducted on the effect of pigments and TiO_2 on the degradation and stabilization properties of polymer matrices. These properties are important: dispersibility, light absorbing characteristics, semi-conductor properties, metal content, influence on polymer matrix, surface properties, composition of products of degradation. This list could be expanded to include: pigment surface area, absorption of components of matrix (e.g., stabilizers), wavelength of emitted radiation by pigment on energy absorption, generation of singlet oxygen, hydrogen abstraction, effect on polymer morphology (some pigments interfere in crystallization), interaction with polymer, etc. The way in which a pigment interacts with the polymer network is known to have an effect on the UV stability of the material but this effect can vary widely. For example, the stability of a composition to radiation at 375 nm can be increased by increasing pigment concentration. But there are also exceptions. Ultramarine blue increases durability of PP by 75% although it does not absorb UV. TiO_2 absorbs of UV as much as does channel black but has only a fraction of its stabilizing activity. Some types of dyes, such as, for example, azo condensation yellow, red and orange are known to decrease the stability of some polymers (e.g., PP fiber). In some polymers (e.g., PVC) most pigments (especially inorganic and carbon black) considerably increase durability. Phthalocyanine blue is a relatively good stabilizer for PP fiber but a poor pigment for PVC. Some dyes behave differently in low relative humidity than they do in moisture close to saturation. This shows that there is a substantial amount of work to be done to explore the very wide range of pigment, dye, and polymer combinations.

The addition of CaCO_3 to PP causes a slight reduction in carbonyl formation.²⁴ The efficiency of some antioxidants, such as Irganox 1010, was found to be reduced by the presence of CaCO_3 . In another study,³¹ PP stability was increased by the addition of CaCO_3 especially in combination with small addition of TiO_2 (0.5%) or HALS. In polyurethanes, CaCO_3 acts as a heat sink.³²

The addition of talc to PP increased the absorption of UV light somewhat due to the opacity of the filler but the absorption of UV was negligible compared to TiO_2 . This is related to the relatively large particle size of talc. No substantial difference was detected in stability of filled and unfilled PP exposed to UV radiation.³⁸

Silica, in the concentrations in which it is typically used, does not affect radical decay during the degradation of PMMA by UV, nor is the radical composition affected.²⁸ Large additions (above 50%) modify the material structure due to matrix absorption on the silica surface which also causes an increase in the radical decay rate. These data are contradictory to the data presented in Figure 11.3.⁷ Sand was added to PVC³⁴ and PE³³ and their photodegradation was monitored by molecular weight determination and measurements of changes in flexural strength and insoluble matter. Both sand containing polymers were more stable.

Carbon black is the best UV screening compound and provides long-term protection. Carbon black not only screens out UV but also inhibits photooxidation through a complex series of autooxidative mechanisms. Not only is the particle size of carbon black important (the best performance is in the range of 15-25 nm), but also the chemical composition of its surface. It was proven experimentally that the best results were obtained when Channel Black was used. Channel Black is no longer manufactured by the channel process but by

Table 11.1 Effect of fillers on the thermal stability of polymers

Filler	Polymer	Testing Method	Findings	Refs.
Al(OH) ₃	EEA	TG, TVA, IR	Retards thermal degradation (endothermic decomposition)	61
	PVC	HCl absorption	Higher degradation rate for uncrosslinked	44
	PBMA	TG, GC-MS	Inhibits monomer evolution, promotes ester decomposition	65
	PVB	TG, GC-MS	Reduces degradation temperature	64
CaCO ₃	LPDE, EEA	TG, DSC, TVA	Reduces degradation rate measured by volatiles	63
Carbon black	PE, PB	Peroxides	Antioxidant, radical scavenger, peroxide decomposition	59
Carbon fiber	Phenoxy	XPS	Fiber protected against oxidation by coating	47
Chalk	PE	TG	No change in degradation rate	58
Glass fiber	PES, PEEK	Tensile strength	Improved retention of tensile strength	71
Graphite	Silicone	Young modulus	Increased Young modulus indicates degradation	51
Iron oxide	Silicone	Young modulus	Increased Young modulus indicates degradation	51
Mg(OH) ₂	PA	TGA	Chains scission due to hydrolysis	52
	PBB	Weight loss	Substantially lower weight loss up to 20% filler	66
	PA	TGA	Reduced thermal stability	70
	EEA	TG	Improved thermal stability	61
Marble	PE	TG	No change in degradation rate	58
Silica	PBMA	TG, GC-MS	Improved thermal stability	65
	PVB	TG, GC-MS	Decreased thermal stability	64.
	PP	Carbonyl	Stability reduced (absorption of thermal stabilizers)	62

more modern techniques which are able to simulate the channel process and produce a surface composition similar to the original. Carbon black is widely used for the production of weather-resistant materials. It effectively protects polymers used as durable binders. In polymers which are less UV stable, carbon black affects thermal stability more than UV stability.³⁷ The performance of carbon black filled materials is concentration dependent. At very low concentrations (below 1 %) carbon black may reduce the photolytic stability of a material. The photolytic stability is increased at higher loadings and at least 2.5% is needed for minimum protection.

This shows that there is still inadequate information to assess the effect of fillers on photodegradation of filled materials. The processes occurring during photodegradation are complex in nature and as such require extensive studies. Specialized methods and equipment are needed to investigate changes in materials.⁴³

11.3 TEMPERATURE

Many fillers were studied in relationship to their effect on the thermal stability of polymers.^{3,11,37,44-71} Table 11.1 gives a summary of the findings. It shows that the role of the filler ranges from causing a decrease in the degradation rate through no effect to causing an increase in the degradation rate. Its behavior in any system is influenced by the presence of impurities and the potential reactivity of all system components. The examples of the results of experimental studies characterize the range of effects.

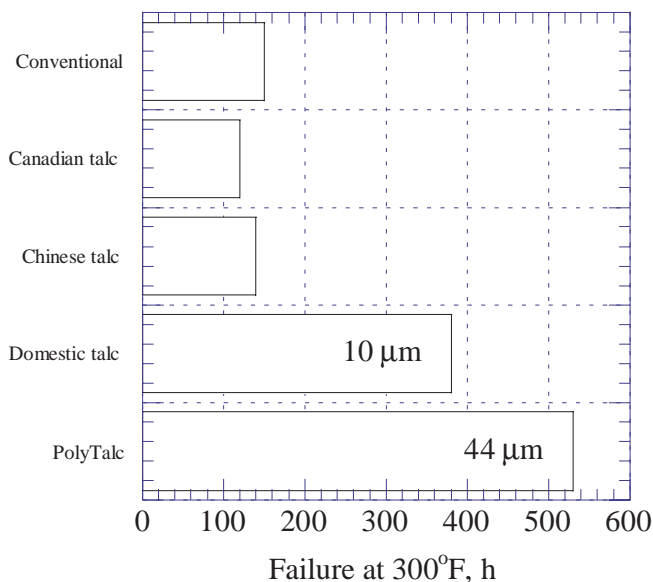


Figure 11.11. Heat aging of 40% talc in PP at 150°C. [Adapted, by permission, from Sherman L M, *Plast. Technol.*, **43**, No.4, 1997, 26-8.]

Figure 11.11 shows that talcs from different sources behave differently in polypropylene. The thermal stability of compounds depends on type and amount of impurities which are different depending on the origin of mineral and on the method of processing.

Calcium carbonate, especially the coated grades as well as some grades of silica are the most inert fillers and they do not much affect thermal degradation rates of many polymers. But, there are examples in which the thermal stability of some polymers can be improved. Figure 11.12 gives data on the dehydrochlorination rate of PVC with and without coated calcium carbonate.⁷² The compound containing filler has improved thermal stability. This is due to the participation of calcium carbonate and its stearate coating in a reaction with hydrogen chloride which is an autocatalyst for the thermal degradation of PVC.

Carbon black can increase the thermal stability of many polymers because of its properties. Phenoxyl and quinoid groups on the surface of carbon black function as antioxidants.⁵⁹ These groups also participate in the catalytic decomposition of peroxides which contributes to a reduction in degradation rate. Quinone, polynuclear structures, polyconjugated double bonds, and carbonyl groups all scavenge radicals. Many polymers and rubbers benefit from these properties of carbon black.

Molybdenum disulfide is known to stabilize polyarylate. It was postulated that two mechanisms may be responsible for this process: the formation of coordination complexes between carboxyl groups and molybdenum disulfide and the reaction with oxygen (antioxidative effect).

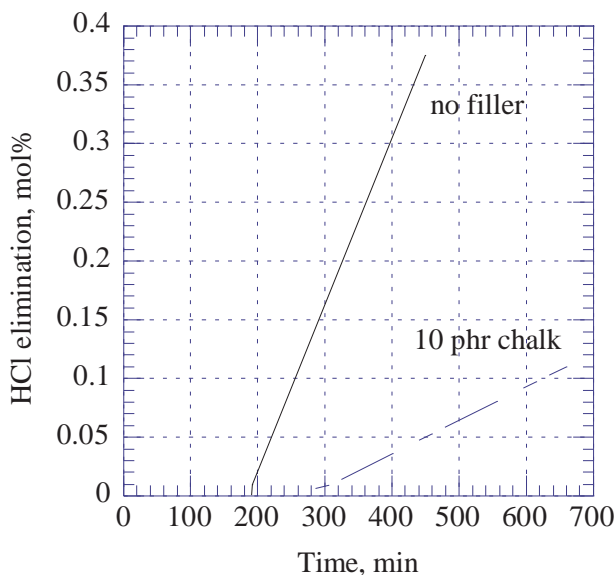


Figure 11.12. Dehydrochlorination rate of PVC with and without 10% calcium carbonate. [Adapted, by permission, from Braun D, Kraemer K, **Recycling of PVC & Mixed Plastic Waste**, La Manta F P, Ed., ChemTec Publishing, Toronto, 1996.]

The physical properties of some fillers play a role in their function as stabilizers. $\text{Al}(\text{OH})_3$ undergoes endothermic decomposition which lowers temperature of material. Loss of water from $\text{Mg}(\text{OH})_2$ may increase stability in some cases. In others, it may cause degradation. This is discussed below. The platelet structure of some fillers (e.g., talc or mica) contributes to an increased thermal stability because the degradation rate is increased as oxygen concentration increases. The structure formed by the platelets reduces the diffusion rate of oxygen.

There are many examples which show that a filler may reduce thermal stability of a polymer. Impurities in the form of metal salts such as formed by Co, Cd, Fe, Zn, etc. provide classic cases where, in their presence, thermal degradation is adversely affected. Water formed from the decomposition of fillers such as $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ can hydrolyze the backbone of polyamide and polyester which degrades the polymer.^{52,61}

Silica and other fillers affect thermal stability indirectly by adsorbing thermal stabilizers which prevents them from acting as stabilizers.⁶² Some zeolites were used to catalyze the degradation of polypropylene during waste processing. The type of cation was essential in decreasing the degradation temperature (e.g., Na^+).¹¹

11.4 LIQUIDS AND VAPORS

Resistance to water is the most important property of composites.⁷³⁻⁸¹

Figure 11.13 shows that in a jute filled epoxy resin, water intake increases with time of immersion and with the amount of fiber.⁷³ This jute fibers readily absorb water. A surface treatment of the jute with epoxy silane reduces the water intake. Tensile properties of a composite containing surface treated fiber remain constant up to a moisture content of 5%.

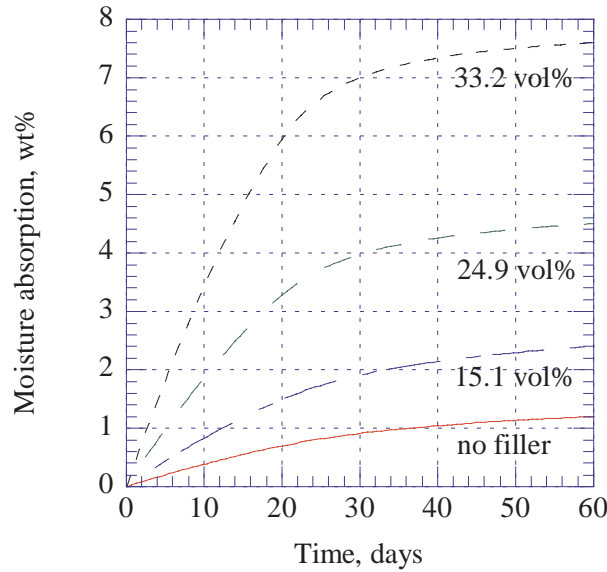


Figure 11. 13. Moisture absorption of epoxy containing jute fiber vs. exposure time. [Adapted, by permission, from Gassan J, Bledzki A K, *Polym. Composites*, **18**, No.2, 1997, 179-84.]

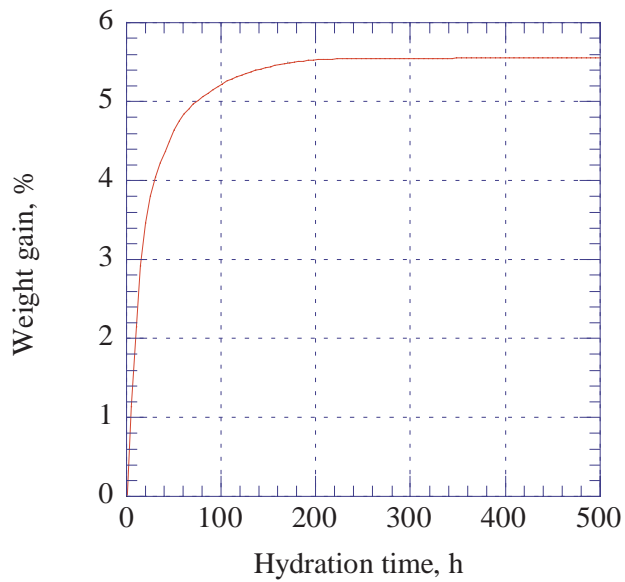


Figure 11.14. Weight increase vs. time of exposure of aramid fibers to 100% relative humidity at room temperature. [Adapted, by permission, from Connor C, Chadwick M M, *J. Mat. Sci.*, **31**, No. 14, 1996, 3871-7.]

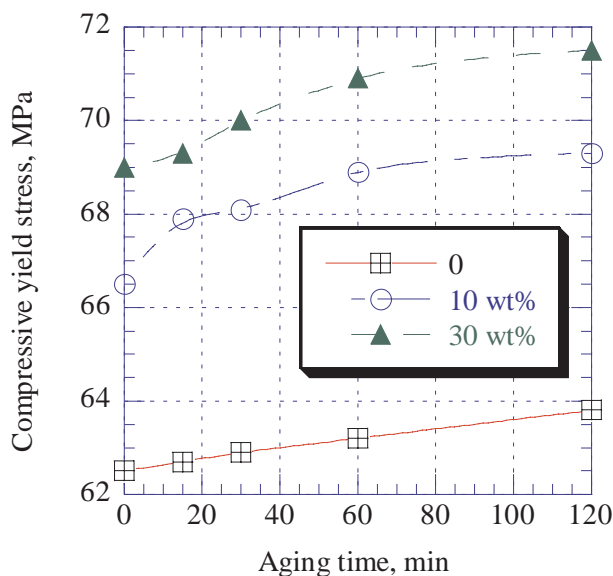


Figure 11.15. Yield stress of carbon fiber/polycarbonate composite vs. aging time in boiling water. [Adapted, by permission, from Nofal M M, Zihlif A M, Ragosta G, Martuscelli E, *Polym. Composites*, **17**, No.5, 1996, 705-9.]

Water absorption by natural fibers, such as cellulose causes the formation of internal forces capable of rotating fibers around their axis. This twisting motion introduces stress into the structure of composite.⁷⁹

Aramid fiber rapidly absorbs water on immersion (Figure 11.14). A NMR study of water absorption shows that water is absorbed into the voids of the fiber. These contain sodium salts (mostly sodium carbonate). This explains why water is so rapidly absorbed in the beginning of immersion.⁷⁸ Aramid fibers are resistant to bases and are fairly resistant to acids except for HNO_3 .⁷⁷ E-glass can withstand immersion in H_3PO_4 and acetic acid but it is not resistant to bases and strong acids. E-glass fiber is severely affected by oxalic acid which extracts about 25% of its weight.⁷⁵ Acid corrosion of E-glass fibers is attributed to calcium and aluminum depletion. The severity of this depletion depends on the acid type and on the method of fabrication of the fiber.

Carbon fiber in polycarbonate composites absorbs water.⁸⁰ Figure 11.15 shows compressive yield stress of composite vs. aging time in boiling water. Compressive yield stress increases with fiber addition as well as with the aging time. Aging in boiling water also enhances Young modulus of the composite.

Orientation of fiber is detrimental to performance of composites which contain carbon fibers (Figures 11.16 and 11.17).⁷⁴ Tensile strength of composites containing fibers oriented in a direction parallel to the surface is not affected by moisture content. Composites which have fibers oriented in a direction perpendicular to the surface, lose tensile strength as moisture increases (exception – carbon fiber/PEEK composite). Similar effects on tensile modulus, compression modulus and elongation have been observed.

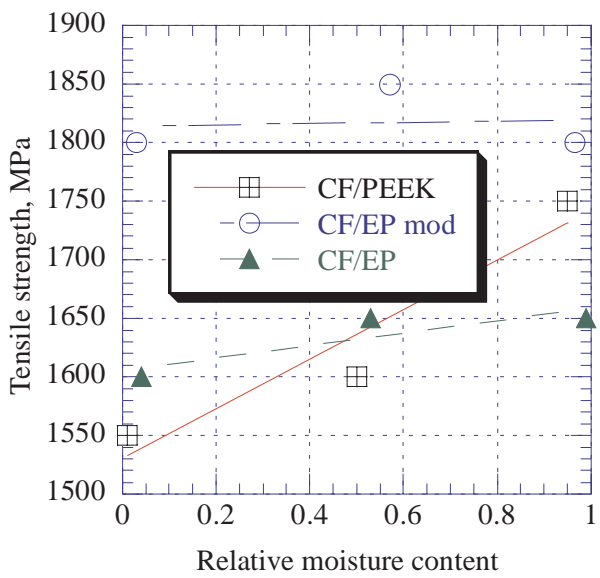


Figure 11.16. Tensile strength of laminates with fibers oriented parallel to the surface. [Adapted, by permission, from Selzer R, Friedrich K, *Composites, Part A*, **28A**, 1997, 595-604.]

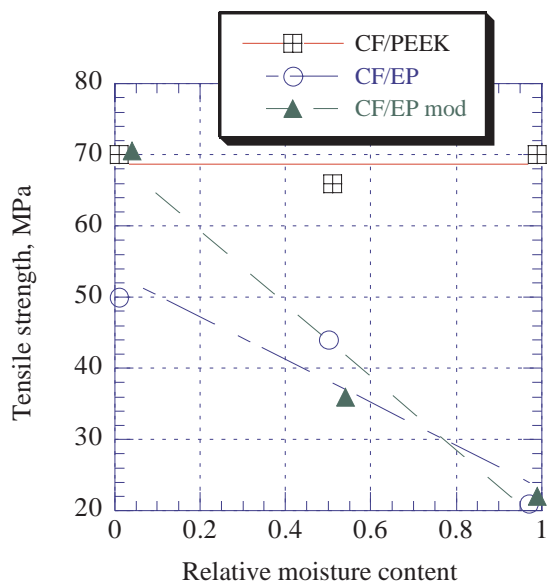


Figure 11.17. Tensile strength of laminates with fibers oriented perpendicular to the surface. [Adapted, by permission, from Selzer R, Friedrich K, *Composites, Part A*, **28A**, 1997, 595-604.]

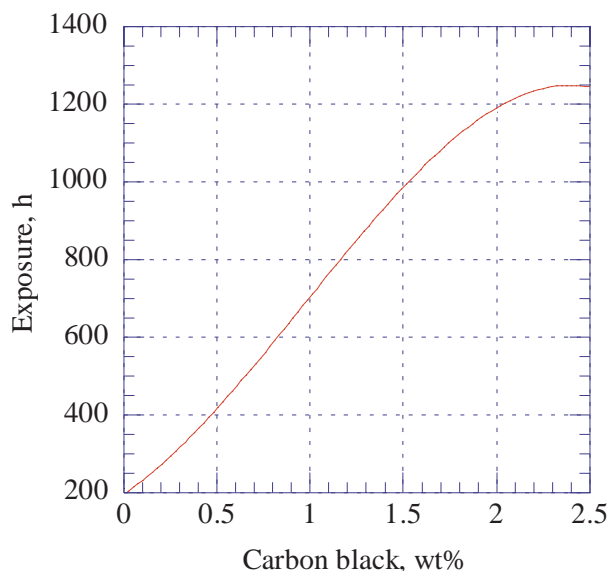


Figure 11.18. Exposure of PE stabilized by carbon black vs. concentration. [Adapted, by permission, from Turley R S, Strong A B, *J. Adv. Materials*, **25**, No.3, 1994, 53-9.]

11.5 STABILIZATION

Pigments and filler in combination with UV stabilizers may influence the stabilizing of the stabilizer.^{41,59,62,69,82-86} A typical stabilizing system used today consists of UV absorber and HALS. In most cases, formulation-specific solutions have been developed which give optimal performance. Still, these systems have many inherent deficiencies related to the properties of both types of stabilizers. UV absorbers perform only when an adequate surface concentration of stabilizer is available. Because of the nature of the mechanism of adsorption, UV absorbers cannot protect surface (to a depth of about 10 μm). In addition, UV stabilizers are not permanent and their concentration is gradually reduced during exposure to UV. This loss of stabilizer is enhanced when the surface layers are degraded. Here, fillers can help. Ultrafine grades of TiO_2 have improved absorption when their particle size is close to 20 nm. The pigment has a relatively low opacity (it does not absorb visible light) but it absorbs UV radiation very strongly.⁸⁵ Most TiO_2 is produced to achieve high opacity which is at a maximum when the particle size is in a range from 150 to 300 nm. New grades absorb UV light as well as UV stabilizers. The concentration of 0.2% ultrafine TiO_2 was found to give better performance in PP than 0.1 % UV absorber. Three advantages can be attributed to the use of pigment over an organic UV absorber: it is permanent, its performance is not lost when surface layers are degraded and it is less expensive. These attributes ensure a bright future for TiO_2 in this application.

HALS has also several limitations. Since it is volatile it evaporates slowly. Polymeric HALS are not volatile and will be retained much longer. But, they are less mobile and thus less reactive. HALS can react with radicals on the surface of the material which gives it advantage over UV absorber. But if the volatile HALS is used more of the surface material

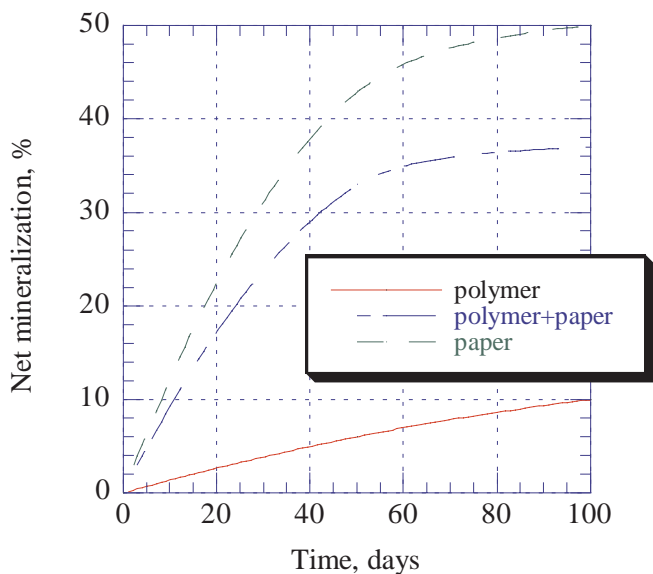


Figure 11.19. Kinetics of degradation in soil aerobic test. [Adapted, by permission, from Levit M R, Farrel R E, Gross R A, McCarthy S P, Antec'96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1387-91.]

will be lost to evaporation. Carbon black is able to perform some functions of HALS (see Section 11.3).⁵⁹ Figure 11.18 gives the concentration of carbon black required to obtain a predetermined length of service. Properties of the carbon black chosen are also important. The best results are obtained with carbon blacks which have the correct balance of particle size and backscattering efficiency.⁸⁶

The stabilizing effect of fillers extends to their interaction with UV stabilizers. HALS is readily adsorbed on the surface of fillers such as silica. The adsorption mechanism is by hydrogen bonding which immobilizes HALS.⁸² Selection of the appropriate HALS is important. Tertiary HALS is not as strongly adsorbed by fillers as secondary HALS.⁶⁹ The adsorption of HALS is frequently thought of to be a disadvantage but it can enhance the stabilizing activity of HALS when the filler acts as controlled release agent. Systems can be formulated which enhance HALS performance based on this principle.⁸³

11.6 DEGRADABLE MATERIALS

Starch and cellulosic materials are frequently used as fillers in degradable materials.^{76,87-93} The addition of starch to LDPE in combination with a pro-oxidant increases the photooxidation rate and the formation of hydroperoxides and carbonyl groups. Starch alone does not increase the photooxidation rate.⁹³ The addition of starch to LDPE increases its stability in 80°C water.⁷⁶ Slower degradation in water is due to leaching out of the pro-oxidant. The addition of starch causes biodegradation process under soil burial conditions.⁹² Further increase in the degradation rate can be achieved by preheating polyethylene filled with starch.⁹¹

Cellulosic materials such as wood flour, paper, and rayon improve biodegradation of poly(lactic acid) in aerobic soil (Figure 11.19). The polymer degrades at a rate similar to paper.⁹⁰

Hydroxyapatite and magnesium oxide improve biodegradation of polylactides.^{88,89} The degradation occurs in the bulk material whereas, in unfilled material, degradation occurs by surface erosion.

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