

Chapter 2

Additives, Nanocomposites, and Barrier Coatings

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Abstract Material use is often governed by the properties it brings to an application, but in some cases those desirable properties are rapidly degraded by their intended use environment. Heat, abrasion caused by part-on-part wear, and particulate impact can damage material properties, especially polymer–fiber-reinforced composites. To ensure that the benefits of polymer composites can be utilized in these extreme environments, protection is needed. The simplest form of protection is the use of additives to the polymer matrix, such as antioxidants, thermal stabilizers, and flame retardants. Of newer interest is the use of nanocomposite technology, which provides enhanced thermal and mechanical durability, which sometimes brings multifunctional performance to the composite. Barrier coatings represent an engineering solution to protect the composite part, but newer research focuses on incorporation of the barrier coating during composite fabrication so that the protection is engineered to be a covalently bound part of the polymer rather than a post-fabrication add-on coating produced via painting or adhesive bonding. This chapter provides a survey of the broad range of protection solutions available for composites, with an emphasis on approaches that yield thermal and/or abrasion protection in polymer composites.

2.1 Introduction

Synthetic polymers as a class of materials are relatively new (100+ years old) in comparison to metals, ceramics, and natural materials (1,000+ years old). Polymers in use with fiber reinforcement are even newer and, so not surprisingly, as these very new materials with attractive properties (ease of processing and forming, light

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weight, corrosion resistance) get more used, they eventually come into environments where they replace the older metals, ceramics, and natural materials. However, that replacement may not always be successful; sometimes the polymer composite may solve one problem, but have some other failing which prevents it from being completely successful in the final application. Specifically, a polymer composite may be superior in corrosion resistance, but not at all suitable to replace a metal in a very hot and wet environment. So, the materials scientist is left with a dilemma: Either go back to the original material and try to engineer a solution, or try to protect the polymer composite against the damage it is suffering in its end-use application. This is, unfortunately, easier said than done, due to growing trends pushing the further use of polymer composites, as well as a lack of solutions to protect the polymer composite against the many types of damage it may encounter. The lack of solutions is often due to the complexity of the material science problem in the first place, as both scientific issues and regulatory issues may predetermine what the material scientist can use. To better explain this point, some background on trends pushing for polymer composite use is needed, along with a general discussion of polymer composite protection design philosophy. Once these are defined, it becomes possible to understand and develop protection for these composites.

2.1.1 Polymer Composite Trends

Polymer composites as a class of materials continue to grow in use for a variety of reasons. Usually it is one particular property that drives their use, but in some cases it is multiple benefits that lead to their increasing use. In building construction, polymer composites have increased in use due to benefits in environmental resistance (no wood rot or termite damage), while in vehicles, composite growth is driven by light weight (fuel savings) and a resistance to environmental damage (no rust or corrosion). These factors leading to composite selection are usually driven by economics in that the composite is replacing something due to lower cost, or lower total maintenance costs, but more often in the case of vehicles and aerospace, the drive is almost strictly economics from fuel savings provided by the lightweight composites. At the time of this writing (June 2009), oil prices had dropped from their (2008) \$100 per barrel price to \$71–73 per barrel, but even at these lower prices, airlines, military air forces, and even mass ground transport (bus, truck) are still looking at unacceptable fuel efficiency. Plus, the cost of oil continues to be erratic, making it difficult to plan economically and budget for fuel costs. Thus, the drive to incorporate more polymer composites for fuel savings will continue, but the replacement of metal and ceramics is not so straightforward.

Metals and ceramics do have key advantages, which is why they have been in use for so long. Specifically, they tend to be very durable in most extreme environments (heat resistance and mechanical durability for metal; heat and corrosion for ceramics) where they are used as engine components, heat shields on aircraft, or external hulls exposed to the environment (UV, rain erosion, sand erosion).

But since these components are major parts of vehicles today, this is where all the weight savings are located, and so if you are to replace a metal or ceramic with a polymer composite, the composite must be suited to resist the environmental damage that metals and ceramics handle with ease. As will be explained later in this chapter (and has been explained in other chapters in this book), this is not an easy task due to the chemical structure of the polymers themselves. Carbon-based polymers are prone to oxidation and heat damage, tend not to do well against erosion due to their relative softness, and therefore require protection if they are to be used in extreme environments. So one must consider protection schemes in material and component design for polymer composites if they are to be used more to replace metals and ceramics, or find some way to incorporate the material properties of metals and ceramics directly into the composite structure. First we will discuss protection schemes, but later it will be clear that for practical protection to occur, we must look at the structure–property relationships of metals and ceramics and find a way to incorporate them into polymer + metal or polymer + ceramic hybrid composites that bring practical protection while not compromising the reasons for selecting the polymer composite in the first place. Before those protection schemes for polymer composites can be implemented, though, we first need to understand how polymer composites degrade.

2.2 Degradation of Polymer Composites: Reaction to Heat, Fire, Electrical, and Wear

2.2.1 Degradation vs. Decomposition

The terms “degradation” and “decomposition” are sometimes used interchangeably when discussing polymeric composites, but they should not be used this way, as they have distinctly separate mechanisms. While they are related in that decomposition can lead to degradation of properties, or degradation can precede decomposition, the two are quite different, and how one protects against them may involve different schemes.

Degradation is a loss of properties caused by a physical change in the polymer. The properties and physical changes that occur can be quite broad in behavior, so some specific examples are needed to describe this further. For a polymer exposed to heat which causes the polymer to melt, flow, or soften (but not break chemical bonds), the physical, mechanical, and electrical properties of that material may degrade [1]. Likewise, for a polymer exposed to great amounts of mechanical stress, the polymer may begin to buckle and crack, leading to a degradation in mechanical integrity.

Decomposition occurs when the chemical structure of the polymer itself is changed by a particular stimulus. Going back to heat damage, decomposition

would be caused by enough heat being put into the polymer such that the polymer bonds break and change, either lowering polymer molecular weight, which leads to irreversible property degradation, or worse, that leads to small molecule pyrolysis and polymer ignition.

To better explain these two terms and to understand how to protect a polymer composite against degradation and decomposition, three typical types of extreme environment damage are discussed below. Ultimately though, damage is caused by energy from external stimuli either causing a physical change in the matrix polymer, or the energy exciting the bonds of the polymer such that the bonds break, which results in chemically induced physical damage to the polymer composite. While the exact stimuli that induce this type of bond cleavage and loss of properties may differ, ultimately it can be said that any type of energy which can break chemical bonds will lead to polymer degradation and decomposition in a composite.

2.2.2 Heat and Fire Damage

Heat and fire damage to polymeric materials is probably the most well-understood of the polymer degradation/decomposition mechanisms, although there is still plenty that is not fully understood or elucidated yet, especially for specific polymer systems and complex systems such as polymer composites. Heat damage is a typical precursor to fire damage in that heat causes the polymer to melt and soften first, which causes degradation of mechanical properties. The heat source causing the damage to a composite may be a hot object (engine, radiant energy source), or it may be a fire which causes heat damage through convection and radiation, or through those means and direct thermo-oxidative decomposition of the polymer composite if it is in direct contact with the open flame.

In regards to heat damage, it is quite common for composites to begin to fail structurally once the matrix resin temperature goes above the glass transition temperature (T_g) of the polymer. T_g is the temperature at which the polymer chains slip past each other from a solid phase into a rubbery or semi-liquid phase, and the polymer can greatly lose stiffness and modulus above this temperature. T_g is often well below the decomposition temperature of the polymer, which is the temperature at which enough heat energy has entered into the polymer to cause bonds to begin to break and the polymer to fragment. If the fragments are of a low enough molecular weight, they can immediately begin to pyrolyze, which leads to rapid loss of mechanical properties as the matrix resin vaporizes; more often, if enough mass has been pyrolyzed, this decomposition of the polymer serves as the source for polymer ignition which leads to fire propagation. However, some polymers will cross-link and form a carbonaceous residue (char) rather than pyrolyzing small fragments; these materials will still lose mechanical integrity, but will not easily ignite as the polymer decomposes. The mechanisms and pathways from this type of heat damage are complex and often polymer-specific (see Chap. 1 for some details), but other references provide some general reaction schemes to consider [2–6].

The previous paragraph is a rather simplistic explanation of the phenomenon of heat damage on a polymer composite, but the reality is more complex. Depending upon how fast a polymer goes from solid to liquid to gas (or solid to char), the mechanical degradation of the composite can rapidly lead to mechanical failure, which can exacerbate the heat and fire damage to the composite. Specifically, fiber reinforcement can fail and delaminate, which in turn exposes more surface area to additional heat/fire damage, which further accelerates the rate of polymer decomposition and burn-through. In drastic cases, the burning polymer can lead to rapid structural failure so that fire spreads rapidly, yielding significant losses. One notable example is the Norwegian minesweeper Orkla, which was an all-composite vessel that caught fire and rapidly sank after the fire spread through the ship and parts of the composite structure began to fail [7]. Some polymers degrade in such a way that they drip and form pools of molten flaming materials which cause rapid growths in heat release. Chief among these polymers are polyolefins and polyurethanes; the latter is well-known to cause pool-fire-type conditions that can rapidly release large amounts of heat that in turn can cause other nearby objects to ignite, leading to flashover fire conditions [8, 9]. Figures 2.1–2.3 attempt to better illustrate some of these phenomena relating to polymer decomposition caused by heat damage and how different types of systems affect flammability or the ability to propagate further heat/fire damage.

In Fig. 2.1, the typical burning behavior for a polymer is shown. As the material is heated, it begins to go from solid to liquid and can flow. As further heat is applied the material will decompose (thermal decomposition) (Fig. 2.1), and then materials will pyrolyze away from the surface, thus leaving the condensed phase (solid polymer/fuel) and entering into the gas phase where they can mix with oxygen and be combusted. Once ignition occurs, all oxygen is consumed at the flame front and pyrolysis products coming off from the condensed phase are continually carried to the flame front through convection and other fire-induced thermal flows. This process will continue until all of the polymer fuel that can be pyrolyzed is consumed, or the material is extinguished.

In Fig. 2.2, an example of how cross-linking and char formation to mitigate flame propagation for a polymer is shown. As the polymer is exposed to heat, it will begin to decompose, but instead of forming smaller fragments and flowing/melting under heat exposure, it will instead solidify further. The now highly cross-linked material can then turn to char which slows down the rate of fuel release/pyrolysis products into the gas phase for combustion. This phenomenon creates a low heat release material since more and more of the potential carbon fuel is bound up in a form that cannot be pyrolyzed further. In effect, char formation keeps the polymer in the condensed phase rather than allowing it to enter into the vapor phase (Fig. 2.2). The formation of this char can greatly lower heat release, as shown in Fig. 2.3.

In summary, heat damage to a polymer composite can at a minimum lead to a structural failure, but at its worst can lead to catastrophic fire loss, especially if the polymer composite is part of a major structure in a mass transport application or part of a building structure. Understanding all the possible fire-risk scenarios is beyond the scope of this chapter, but heat damage to a polymer composite is

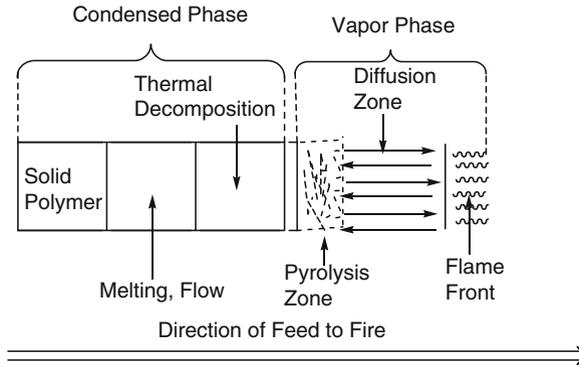


Fig. 2.1 Physical heat-induced decomposition behavior for non-charring polymers

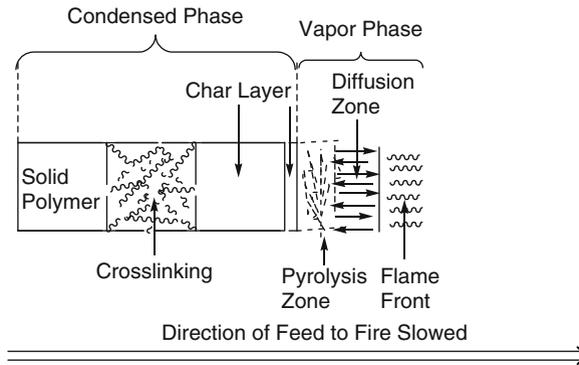


Fig. 2.2 Physical heat-induced decomposition behavior for charring polymers

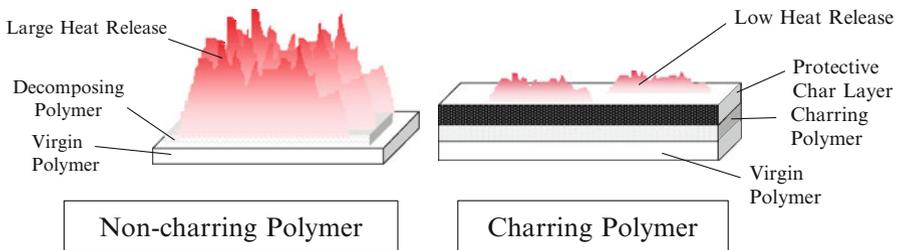


Fig. 2.3 Differences in heat release caused by non-charring and charring polymers [10]

something that the material scientist must pay attention to, as heat damage is probably the most likely type of damage that a polymer composite can encounter outside of its original design parameters. Knowing that the extent of heat damage is related to the composite matrix polymer chemical structure, we can focus on protecting that polymer from heat damage. Methods of heat protection will be

discussed in detail later in this chapter, but it should be made clear that if one can protect the polymer from getting too hot in the first place, all possible risks of structural failure and ignition are completely eliminated.

2.2.3 Electrical Damage

Electrical damage to composites primarily occurs when electrical arcing such as might be caused by circuit failure or lightning strike hits the composite and results in decomposition and degradation of the polymer. Electrical damage does not typically lead to just degradation of properties alone since most polymer composites are typically insulators, although if enough electrical current is dumped into a composite, it may heat to the point that it begins to soften. While the mechanism of damage is very similar to that of heat-induced damage, the timescale during which damage occurs is typically much shorter. The electrical arc rapidly decomposes the polymer by putting energy into the polymer bonds which then break via homolytic bond cleavage (single electron reactions), and then these unstable radicals react with other parts of the polymer to form char, or rapidly undergo depolymerization which results in localized matrix polymer vaporization. In some cases, the local electrical damage leads to rapid heating of the composite, which can lead to both electric and heat-induced damage to the composite. Worst-case scenarios will lead ignition of the composite, and this now-burning polymer will cause damage to nearby objects.

What makes electrical damage different from heat damage is that typically the electrical damage is localized, while most heat damage is spread over the entire composite or a large area of radiative/convective heat exposure. Specifically, damage occurs at the point of electrical impact. One example of electrical damage is lightning strike. Lightning strikes are very fast and very intense, and continue to be an area of concern for composite protection, especially with the increased use of composites for aircraft wings/fuselages and wind turbine blades. Damage from electrical failures (such as shorting electrical components in electronic enclosures) is much less intense, but is also localized and occurs very quickly. Since the damage occurs so quickly and will result in polymer decomposition, the best solution is similar to that of heat protection – make a change to the material so that the electrical damage never occurs. In this case, the best approach is to make the composite electrically conductive, or set up conductive pathways in the composite so the electrical charge goes through the composite, rather than being absorbed and causing damage.

2.2.4 Wear and Abrasion Damage

Mechanical wear or abrasion on a polymer composite typically causes degradation, not decomposition. However, if the motion causing the abrasion is fast enough and lasts long enough, the polymer can be heated to the point that decomposition will

occur. Indeed, sometimes the friction can be intense enough that mechanochemistry can occur which will result in chemical changes at the surface of the abrading materials [11]. Still, wear and abrasion typically cause a physical change to the composite, and not a chemical one. With wear and abrasion phenomena, either the polymer is worn away, leaving bare fiber reinforcement which loses mechanical integrity, or the fiber is worn away as well leading to structural weakness in the entire part. Like electrical damage, damage from abrasion and wear is localized; it occurs at the spot where the composite is in contact with another object. So with degradation being the main concern for this type of damage, the best ways to prevent damage are to prevent wear through engineering changes, or to modify the properties of the composite itself such that it can tolerate wear damage or has a harder surface to resist this type of damage. However, modification of the composite properties requires an understanding of the abrasion/wear on the composite surface, which can be complex, depending upon polymer structure and the media that is abrading/wearing out the composite surface. Some polymers are soft and rip away from abrasion while others are brittle and slowly chip away. With rain erosion, the mechanism of degradation begins with high-velocity water impacts first causing crack sites that the water seeps into and then parts of the composite spall (explosively pop off) as the water expands in the composite although the force from the water impact can lead to additional composite delamination [12]. So some understanding of what exactly is causing the damage is required before designing the protective system, but fundamentally this type of damage is due to physical changes at the macroscale and microscale for the polymer composite, not at the molecular scale.

2.2.5 Other Damage Types

For polymeric materials, degradation and decomposition can occur through other means besides the three discussed above. Ultraviolet (UV) radiation can result in severe polymer decomposition either by chemical bond cleavage or by creating free-radical sites along the polymer backbone. These sites lead to chemical changes in the polymer when this radical reacts with the rest of the polymer or with oxygen. These decompositions can in turn lead to degradation of properties for the composite. Oxidation of a polymer is discussed in other parts of this book (Chaps. 1, 5, and 13), and while this type of decomposition is often accelerated by heat, all polymeric materials suffer oxidation damage over time, even at room temperature or lower, although the kinetics of such oxidation are greatly reduced at lower temperatures. Such oxidation leads to significant chemical changes in the polymer structure, which in turn degrades the polymer properties in ways both minor (discoloration) and major (embrittlement and mechanical failure). UV and non-heat-induced oxidation damage is certainly something that the material science engineer needs to consider, but it is not the emphasis of this chapter. Additional review articles on this topic can be obtained elsewhere [13].

2.3 Active and Passive Protection Schemes

So now that the various types of damage have been described, we can begin to discuss how a material scientist should provide protection against these types of damage. After considering the type of damage that will occur and whether one is protecting against degradation or decomposition, the scientist must then choose from one of two general protection schemes: active or passive.

2.3.1 *Active Protection*

This type of protection scheme primarily uses engineering solutions or active labor (regular inspection by maintenance personnel) either to prevent damage to a material or to monitor for damage and then replace/repair the damaged part as it occurs. It is typically used in a reactive mode when a polymer composite is put into an application and damage is expected. For engineering solutions with active protection, part of the apparatus in which the composite is located is used to protect the composite against damage. This can be as simple as a heat shield/plate which protects the composite against thermal and abrasion damage, or complex venting and moving parts which either keep the composite cool or move erosion surfaces away from the composite. Even with this approach, there is frequently a need to monitor the composite through nondestructive evaluation (NDE) testing to make sure that no significant damage has occurred. The constant NDE work can add a lot of cost to the part in terms of long-term maintenance and mapping out the limits of use on the composite before it has to be replaced. Still, despite the higher costs associated with an active protection approach, it can be very easy to implement during component design, or to monitor and mitigate damage after the composite part is in use. However, this approach, while easy to implement, can easily be defeated. Should an unforeseen scenario occur, damage to the composite may be caused when the damage stimuli (UV, heat, abrasion, etc.) bypass the engineering protection.

2.3.2 *Passive Protection*

This approach is similar to active protection in that engineering solutions can be used, but instead this approach utilizes specific material design and chemical modification to resist damage which might occur, rather than actively testing and trying to prevent damage with through constant composite repair and replacement. This is the approach used for most polymeric materials, especially for oxidation, UV-induced, and flammability-induced damage. This is typically achieved through the use of antioxidants, UV stabilizers, or flame-retardant additives, but other forms of passive protection can be employed. As mentioned in the description of active

protection, engineering solutions can sometimes be considered passive protection because the heat or abrasion shield provides protection for the composite, but again, engineering solutions can be defeated. For passive protection, the design philosophy is to set a particular damage level for the composite and then test (often destructively) its ability to resist damage up to the set level. If the test specimen passes, then it is assumed that the composite part will do fine in the application that correlates to that test, and no additional monitoring of the composite is needed. However, NDE is still sometimes needed to see whether damage has occurred, or to set a lifetime for the part, as even passive protection schemes will wear out. What makes passive protection so attractive for composite durability enhancement is that the protection is always available and can be tailored to provide durability to a polymer that normally could not be used for a particular application. Sometimes this approach is quite cost-effective, but admittedly, it can result in the materials scientist playing a “balance of properties” game for the material as the researcher makes a modification which enhances one property at the expense of another.

For polymer composites today, both active and passive protection schemes are used, but this chapter focuses on the fundamentals and philosophies of design for the passive approach. Active protection schemes are application-specific and are driven by engineering designs, which are too detailed to try to cover in this chapter. Passive protection, though, has some underlying universal fundamentals that can be used to develop a damage-resistant composite. For passive protection there are three universal approaches: additives, polymer nanocomposite technology, and integrated barrier coatings. These three approaches will be discussed in turn in the next three sections.

2.4 Additive Approaches

The number of additive solutions for composite protection is so extensive that it is impossible to cover all of them in this chapter, especially since some of the chemistries for protection are polymer-specific. Where appropriate, some specific chemistries will be described to illustrate how the additive provides protection in general to the polymer, but for more detailed discussions on these additives, the reader is encouraged to read the other more comprehensive books on the subject [14–16].

For polymer composite applications, choosing the right additive can be a daunting decision. Most types of additives in use today have been optimized for a particular polymer chemistry and end-use performance, so that what works for one polymer may not work at all for another. Luckily, most polymer manufacturers have technical service researchers who deliberately formulate their polymeric materials to have the optimal balance of protective additives in it for certain applications. So if a material scientist was interested in purchasing a polyolefin for outdoor applications, he or she can contact the polymer company and just buy a polyolefin already formulated for that end-use application: it already has the necessary antioxidants, UV stabilizers, and other additives needed for passive

protection. This is particularly true for thermoplastic materials: one cannot buy a pure polymer, but must specify what the polymer needs to do and then buy the thermoplastic polymer. For thermoset resins, though, preformulated systems with additives included are not as widespread, and they are almost nonexistent for high-temperature thermosets such as polyimides. The primary reason for this is economics, but also, no one has really developed (high-temperature) antioxidants or UV stabilizers for high-temperature aerospace polymers.

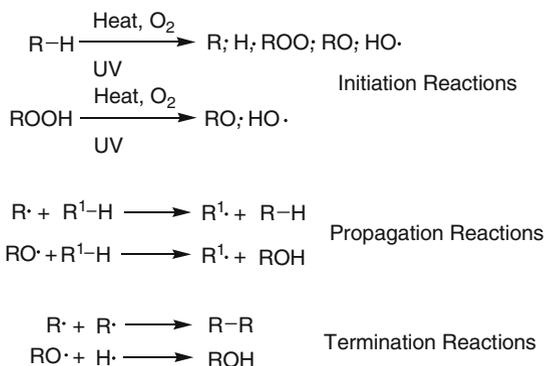
So in the end, material scientists manufacturing fiber-reinforced composite can save themselves a lot of time by just selecting the right additive-filled polymer. To select the right polymer, though, the material scientist will need to know the end-user requirements in detail and be willing to interact with the vendor selling the preformulated material. Should no suitable system be available to the material scientist, then the scientist can begin to consider formulating their own additive package to protect the composite, based upon the damage it needs to resist and the measurement metrics of damage resistance needed to commercialize/implement the composite successfully. For fiber-reinforced thermoplastics and some commodity thermoset resins, this approach will work very well, but for high-temperature thermoset resins and some high-melt-temperature thermoplastic polymers, the scientist will have to consider one of the other mechanisms of protection such as polymer nanocomposite technology or barrier coatings described later in this chapter.

2.4.1 UV Stabilizers and Antioxidants

Damage to a polymer initiated by UV or oxidation in general occurs through free-radical reactions. This begins with initiation reactions, followed by propagation reactions in which the radicals rearrange and form more stable radicals which in turn propagate additional initiation reactions. The process ends when the radicals terminate into a more stable product, or are stopped from further propagation by either the UV inhibitor or antioxidant. Some generic reaction schemes to illustrate this are shown in Fig. 2.4. In this figure the three main free-radical reaction types (initiation, propagation, termination) are shown, with two example chemical reactions representative for that reaction type given in the figure. Metals can also catalyze oxidation damage in a polymer, depending upon the polymer chemical structure and the propensity of the metal to undergo one-electron transfer reactions. Again, all of these reactions will be governed by the actual chemical structure and physical form (crystalline, amorphous) of the polymer, but the general scheme of reaction holds regardless of polymer chemistry and form.

There are three ways in which antioxidants and UV stabilizers work: by performing radical scavenging, decomposing peroxides that may form, or deactivating the metal that may be catalyzing the damage. Due to the variety of specific chemical reactions that may occur, antioxidant and UV stabilizer chemistry is tailored to specific polymer systems to address that system's decomposition mechanism and to be compatible with the polymer. Additives which are not fully compatible with

Fig. 2.4 Initiation, propagation, and termination reactions in UV/oxidation damage



the polymer matrix may work very well as an antioxidant/UV stabilizer, but will migrate out of the polymer over time (known as “blooming”), thus making the polymer vulnerable to damage.

Additives that are typically effective as antioxidants and UV stabilizers include hindered phenols, aromatic amines, hindered amines (only those which have a tendency to form N-oxides), hydroxylamines, benzofuranones, divalent sulfur compounds, phosphorus (III) compounds (phosphines and phosphites, with phosphites most common), and multi-dentate metal ligands (such as ethylenediaminetetracetic acid – EDTA). Just about every class of polymer in use today can be matched with a commercially available additive that has been optimized for that polymer. The exception to this would be high-temperature polymers (those processed above 300°C); no current commercial antioxidants or UV stabilizers are thermally stable enough to be processed at that temperature.

2.4.2 Flame-Retardant Additives

The chemistry of flame-retardant additives is highly varied and is optimized not only for specific polymer chemistries, but also to address flammability effects (flame spread, dripping, smoke release, etc.) that are required to be addressed in a specific regulatory fire test. The science of flame retardants as a class of additives is almost solely driven by fire-safety regulations, which address specific fire-risk scenarios. So while an antioxidant or UV inhibitor may be optimized for a particular polymer, and once in place can be used in all applications of that polymer, the same cannot be said of a flame-retardant additive. What helps one polymer pass one particular fire-safety test may not work for that same polymer (or a different polymer) in a different fire-safety test. Therefore, to select the proper flame-retardant additive, one must consider the polymer and the end-use application at the same time.

Flame-retardant chemistry includes such classes of compounds as halogenated organics, char formers, cross-linking compounds, mineral fillers, intumescent packages, phosphorus compounds, nitrogen-based compounds, and even certain metal and boron compounds. This chapter cannot cover all the flame-retardant chemistries available, but they are extensively covered elsewhere in review books and articles [17–29]. However, most flame-retardant additives achieve fire protection for a polymer through one or more of three broad mechanisms: vapor phase radical inhibition, endothermic cooling, or condensed phase char formation. Extensive details on these mechanisms can be found in the review papers cited for flame retardants in this chapter, but the general mechanisms will be described here. There will also be some discussion on vapor and condensed phase flame retardancy here, which can be seen in Figs. 2.1 and 2.2.

2.4.2.1 Vapor Phase Radical Inhibition

Flame retardants that act as vapor phase radical inhibitors begin by pyrolyzing with the polymer fuel and fragmenting into stable radicals, which help prevent free-radical propagation reactions in a flame front. They specifically form stable intermediates which give off less heat than the normal free-radical reactions that make up combustion, which helps pull heat out of the flame. Once enough radicals and heat have been removed, the free-radical cascade reaction that is combustion will cease. Examples of vapor phase radical inhibitors include organochlorine and organobromine compounds, as well as some phosphorus compounds. This principle of action is how Halon fire-extinguishing agents work, but for flame-retardant additives that work in this manner, the additive can only provide self-extinguishment behavior if there is enough free-radical scavenger to put out the flame. In large fires, these types of flame retardants can be completely overwhelmed. Finally, these types of flame retardants, especially halogenated ones, will cause more smoke to be formed during combustion due to the inhibition of clean combustion in the vapor phase. This is a design issue that material scientists will need to consider for composites used in mass human transport (bus, rail, ship, aircraft) applications.

2.4.2.2 Endothermic Cooling

This class of flame retardants is primarily condensed phase in its activity, but there is also some vapor phase action. When this flame retardant is heated, it decomposes endothermically to cool the condensed phase (thus preventing further heat-induced decomposition and pyrolysis) and typically releases a nonflammable gas. This nonflammable gas dilutes the total amount of fuel in the vapor phase which either prevents/delays ignition or keeps heat release low, allowing for self-extinguishment once the external flame is removed from the polymer. The types of additives that fall into this class are typically mineral fillers, including hydroxides such

as aluminum hydroxide (also known as alumina trihydrate) and magnesium hydroxide, as well as carbonates such as hydromagnesite. Organic carbonates can also be used as flame retardants, but they are not as effective as mineral filler systems. This is because the mineral filler flame retardants bring one additional benefit to the condensed phase: they dilute the total amount of fuel in the condensed phase, since after they release their nonflammable gas and cool the condensed phase, they are typically inorganic oxides, which cannot be burned further. Those oxides have not only replaced flammable polymer fuel, but sometimes will fuse together and form protective ceramic barriers as well.

2.4.2.3 Condensed Phase Char Formation

Materials that chemically react with a thermally decomposing polymer by forming newer, more stable bonds as old ones are broken by heat are referred to as char-forming flame retardants. Additives in this class typically include phosphorus flame retardants and intumescent fire-protection packages. Some metals can catalyze additional char formation, and sometimes additives which just slow down fuel pyrolysis rates through major increases in molten polymer viscosity (such as fumed silica and nanocomposites) can cause char to form. Specifically, the radicals in the condensed phase have more residence time in the condensed phase before volatilizing and therefore react with themselves rather than pyrolyzing and combusting. These polymers, by binding up polymeric fuel into highly cross-linked graphitic or glassy-carbon char, keep heat release rate low since there is very little mass being pyrolyzed for combustion (Fig. 2.3). Some flame-retardant additives (phosphorus in particular) can have some vapor phase activity while they promote char formation, but the dominance of condensed phase or vapor phase in the case of phosphorus is polymer dependent [17, 18, 24]. Finally, the polymer itself can include functional groups which activate under fire conditions to form char [30], but in some cases the cross-linking groups can release heat into the condensed phase, making flammability worse even though char yields are higher [31].

In a fire situation, polymer decomposition will occur. The flame retardant is only there to retard the growth of the fire, not to prevent it from occurring. In this aspect, flame-retardant additives are truly passive and only activate when enough heat is present to decompose the polymer. While the flame retardant may cause the polymer to self-extinguish quickly or char to the point that flames can no longer damage the composite, some damage will already have occurred during ignition and heat exposure. Therefore, with fire, one will always have polymer decomposition and degradation, but the question with the use of flame-retardant additives is how much damage has occurred. Did the flame retardant allow the structure to be saved so that it could be repaired? Did it just provide enough time for nearby people to evacuate the area and get to safety? How the flame retardant is used, and its ability to narrow the amount of damage that occurred or slow down the total destruction of the composite, depends upon the fire-safety regulation in use for that material. The use of flame retardants *does not* confer universal fire safety.

Just because something is flame retarded does not mean it is fire-safe. Certification of fire safety is the realm of fire-safety engineers who set the fire-safety codes which govern safe use of a polymeric composite material. Materials engineers seeking to understand and develop multifunctional polymeric composite materials where fire is a risk should take time to understand the regulations, and how those regulations affect flame-retardant choice and fire-safe material design. If the end use of the composite requires a high enough level of fire safety so that the composite can be repaired, multiple layers of defense may be needed to protect it. If the composite is sacrificial and must simply provide enough time for people to escape, then the use of additives may be enough. If one wants to save a structure, though, more robust flame-retardancy and fire-protection schemes will be needed. Flame-retardant additive use and fire safety of composites can be very tricky to implement into a composite on top of all the other product performance requirements. So if flame-retardant additives cannot be used due to strict product requirements, then the material scientist must consider using an inherently low heat release (low flammability) polymer or other approaches, such as polymer nanocomposites and integrated barrier systems.

2.5 Polymer Nanocomposites

In polymer nanocomposites, the minor (in concentration) reinforcing component is sub-micron in scale and is so evenly dispersed through the polymer that the major component of the final composite is not bulk polymer, but interfacial polymer. In effect, a polymer nanocomposite is a material in which interfacial polymer properties, not the bulk polymer + reinforcing article, dictate performance. Because of this distinction, and the fact that some nanoscale fillers can bring additional property enhancements (such as thermal, mechanical, and electrical), polymer nanocomposites are one of the fastest growing material science areas to date [32, 33]. However, polymer nanocomposites are not new technology as they have been around for quite a while hidden in common material forms. Only recent advances in polymer nanoscale science have revealed these materials to really be polymer nanocomposites (nanoscale fillers in a polymer matrix). Historical examples of polymer nanocomposites include rubber tires (carbon blacks), paints (organoclays as rheological modifiers), and the original technology which led to polymer nanocomposites as a field, polymer + clay hybrids produced by Toyota R&D 20 years ago [34, 35].

While there are numerous literature reviews on what a nanocomposite is, how it is prepared, and some of its uses [36–40], the technology is best described as a route to multifunctional materials. Specifically, through control of polymer structure (conversion of bulk polymer to interfacial polymer) and use of nanoscale filler structure–property relationships, it becomes possible to create a material that can serve more than one function and, in effect, replace several materials. For example, rather than using a conductive paint or embedded aluminum mesh to provide an

EMI shield on a composite part, one can use conductive nanofillers (such as carbon nanotubes and nanofibers) to provide an integrated EMI shield as well as enhanced mechanical properties in the final composite. Or, with the use of thermally conductive nanofillers, the polymer could replace a metal in a complex composite part assembly holding a heat-generating component, thus saving weight and possibly assembly costs while still allowing for heat dissipation.

2.5.1 Polymer Nanocomposite Protection Schemes

Despite the great promise and actual results achieved with polymer nanocomposite technology, preparing a successful polymer nanocomposite is not an easy task. One cannot simply drop nanofiller into a polymer and create a nanocomposite through simple mixing. Care must be taken to design the nanocomposite before synthesis so that the nanofiller will have the right interface with the polymer and will obtain uniform dispersion through processing. Only if good and uniform nanoparticle dispersion is achieved will one obtain enhanced properties [33–43]. Due to the all-interfacial nature of a polymer nanocomposite, the polymer degradation and decomposition mechanisms change in comparison to those of the bulk polymer. Because the polymer is all-interfacial, the nanofiller can have tremendous effects on the decomposition of the polymer under UV, abrasion, mechanical damage, or heat/fire damage scenarios, and the effects can be beneficial or detrimental.

Polymer nanocomposites greatly help the polymer resist heat and fire damage, from a typical delay in onset of depolymerization to large reductions in heat-release rate under fire [39, 40]. The mechanism for clay nanocomposite flammability reduction appears to be that the polymer pyrolysis rate is greatly slowed by the formation of a clay-rich layer, which increases molten resin viscosity and serves as a barrier against mass loss/fuel release [44]. For carbon nanotube and nanofiber nanocomposites, the mechanism of damage/heat release reduction is the formation of a nanoparticle network which also increases molten polymer viscosity, which in turn reduces mass loss/fuel release rates [45, 46]. These nanocomposites can also be combined with traditional flame-retardant additives to obtain synergistic flame-retardant effects, so that less additive is needed to obtain a regulatory passing flame performance [39, 40]. There are some cases of polymer nanocomposite + flame-retardant-additive antagonism, but these cases are very additive-specific, usually involving flame-retardant additives that help polymers pass tests by accelerating melt flow away from flames. Since polymer nanocomposites increase molten resin viscosity under fire conditions, the nanocomposites serve as “anti-drip” additives which leads to their antagonistic effect with melt-promoting flame-retardant additives.

For UV and oxidation damage, the results are mixed. There are reports that some nanocomposites accelerate UV degradation and UV-induced oxidation, but the cause is not clear. In some instances, metals in the nanofillers (such as the metals in the clay structure or absorbed onto the clay surface) accelerate the UV

degradation [47, 48]. In other cases, it may be that the large surface area of the clay nanofiller causes it to absorb the UV stabilizers from the matrix, thus removing that additive protection for the polymer from the system [49]. For carbon nanotube nanocomposites, however, there appear to be some enhancements in UV stability [50, 51]. Finally, it is possible to create titanium oxide (TiO_2)-rich nanocomposite films that are UV and X-ray opaque (but visibly transparent) and can provide protection to an underlying polymer substrate [52]. So for UV protection, more studies are needed, as well as careful selection of nanofiller to provide protection to the polymer. For oxidation damage protection there have not been as many studies, but in one extreme case the clay nanocomposite provided significant protection against an aggressive oxygen plasma by forming a clay-rich protective barrier on the surface of the polymer [53], much like the flame-retardancy mechanism for clays in the case of fire [44].

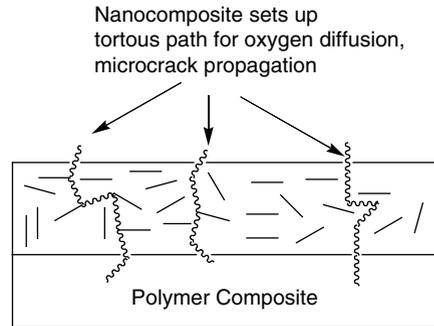
Other types of damage to polymer nanocomposites have not yet been well-studied. Abrasion damage presumably would be reduced with a nanocomposite, but this may be nanofiller-dependent, with graphene and graphite nanocomposites providing lower friction and less surface wear versus other fillers which toughen the surface and make it harder for the abrading object to wear away the polymer. Electrical damage presumably would be mitigated through the use of conductive nanofillers (such as carbon nanotubes and nanofibers), which create a conductive path through the composite, thus allowing high-intensity electricity to pass through the composite. While this mechanism of electrical protection has been proposed, the author could find no published papers proving this protective capability against lightning strike or electrical arcing.

While polymer nanocomposites have shown impressive ability to resist damage, they may not always be appropriate for polymer composite use. Cost of nanofillers is still relatively high compared to traditional fillers and additives, and nanofillers often cause viscosity changes in the polymer, which make processing and synthesis of the polymer difficult. Therefore, it may be more appropriate to utilize nanofiller technology in protection barrier approaches, thus putting the nanofiller where it is needed to protect the composite. This approach should reduce costs as well as solve some of the processing issues associated with polymer nanocomposite technology.

2.6 Barrier Coatings

One way to provide protection to many materials is to apply a protective coating, such as a paint or a plasma-deposited layer, after the part is manufactured. For fire protection, even very thin layers of silica deposited onto a polymer surface can lower heat release as well as delay ignition of the polymer [54, 55]. Intumescent barriers can provide superb fire and heat protection to a polymer composite or steel by creating oxidation-resistant/low thermal conductivity carbon foam [56–58]. There have even been recently published results regarding the use of carbon nanotubes to create “buckypapers” (a nonwoven fabric of nanotubes) which help

Fig. 2.5 Polymer nanocomposite top layer protecting underlying polymer protection to underlying polymer + fiber composite



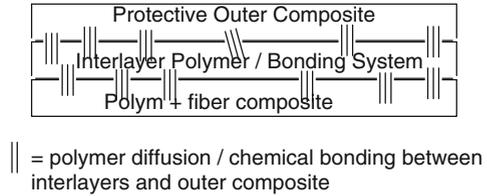
provide fire protection to composites [59]. Barrier-coating protection can also be more of a solid barrier than a true coating, such as ceramic tiles, insulation blankets, abrasion shields, and metal plates for electrical conduction/multi-threat protection. These protection systems, put in place after the part is made, are often referred to as “engineering solutions” in that one uses engineering to solve the problem rather than to address the flaw of the material itself. While all of these protection systems are effective and are in use today, they all have one key problem: because they are easily applied, they can be easily defeated. If the shield comes off, or the coating is broken or scratched, then protection is lost and the underlying polymer composite is subject to damage. Therefore, the use of an integrated protective coating to the polymer composite may be a superior approach.

2.6.1 *Integrated Protective Coatings for Composites*

When additive approaches are not acceptable and post-fabrication engineering solutions fail, it may be worthwhile to consider an integrated protective coating. This system borrows from additive, nanocomposite, and protective coating approaches, but puts the protection where it is needed in the final composite and makes sure that it is fully integrated into the part. In effect, the protective layer is designed to be fully compatible with the polymer composite and is created during the composite manufacture process. What follows in this section is an example of this type of protection conducted as a research project at UDRI, and so presents a particular case study on the integrated coating concept. More specifically, it represents an example of applying nanocomposite technology to provide protection for a composite. This example is not meant to be the definitive example of integrated coating technology, but instead a teaching example of how this problem can be looked at and potentially solved with polymer nanocomposites and the integrated coating approach.

In Figs. 2.5 and 2.6 are two generic examples of this approach. Figure 2.5 shows the nanocomposite approach applied as an outer barrier to the composite, while Fig. 2.6 shows a more complex protection scheme with multiple layers copolymerized.

Fig. 2.6 Protective outer composite with interlayer bonding system to provide composite from oxidation damage



In both cases, the protection system is copolymerized with the base composite. Potentially, this allows for the underlying composite to remain lower in cost and maintain maximum mechanical integrity while the protective layer provides a barrier against polymer decomposition and degradation. The approach should be optimal for polymeric systems that are created from monomer (such as thermoset resin systems or thermoplastics that can be polymerized from liquid monomers), but it could work for fully polymerized thermoplastics through melt bonding/specialized injection overmolding. For the purposes of this chapter, we will focus on the thermoset example and provide data for how this approach works in an aerospace grade polyimide. Note that the data provided in this chapter are meant to be as general as possible, while showing some actual results from fabricated composites utilizing the protective coating approach. We expect to publish the results in full in a peer-reviewed journal in the future.

The design approach to create a protective layer for composites follows three steps:

2.6.1.1 Step 1: Design Protective Coating System

In this step, we consider polymer chemistry (generally the bulk composite matrix polymer) and viscosity. We also consider what type of composite reinforcement, multifunctionality, service environment, and manufacturing process will be required. If we think about thermal protection for aerospace composites, we can focus on a polyimide with carbon fiber to be prepared by an autoclave process.

2.6.1.2 Step 2: Formulate Protective Coating System

In this step, we select the appropriate nanoparticles/surfactants which will yield thermal oxidative protection for dispersion into the polymer. The types of nanoparticles or fillers appropriate for this role are inorganic particles and fillers. The reason for this is that inorganic materials (typically metal and nonmetallic oxides) are already in their highest oxidation state and cannot be further damaged by high-temperature oxidation reactions. Through the use of ultrafine particle size alumina, fumed silica, carbon nanofibers, or exfoliated graphite, such layers can be prepared and co-cured with a polyimide + carbon fiber composite. However, one

would need to use high loadings of such fillers to make the top barrier more inorganic in character and more likely to provide thermal protection. At this point, one can develop multiple formulations with varied levels of inorganic content to create a graded structure, but for the purposes of the example in this chapter, we will start with a monolayer of highly filled polyimide to provide protection just at the surface of the composite.

2.6.1.3 Step 3: Fabricate Coating Film/Composite System

In this final step, a film of desired thickness (similar to a film adhesive) is applied either to the tool surface of the composite mold or to the composite preform. Nanoparticles + resin will diffuse into the fiber preform, forming a gradient structure, or at least ensuring that the polymer chains entangle sufficiently throughout the top layer and the underlying composite that when the polymers are fully cured, the top film and the composite are fully bonded at the molecular level. Diffusion of resin and nanofillers into the top ply of the composite will be determined by resin viscosity, and so if it is desired to minimize diffusion of nanoparticles into the composite, one can increase polymer viscosity to affect this change.

So we utilized an aromatic polyimide (RTM grade polyimide) typically used in aerospace applications along with

- Alumina (Al_2O_3 , median 1.5 μm particle size)
- Fumed silica (an organic treated grade)
- Vapor grown carbon nanofibers (high heat treated grade)
- Exfoliated graphite flake
- Multi-wall carbon nanotubes

These were all chosen as commercial off-the-shelf materials that can be provided in multi-kilogram to multiton amounts, so if they are successful, rapid scale-up and commercialization are possible.

First the materials were prepared into resin pellets for thermogravimetric analysis (TGA) screening. This was done by subjecting a fully cured resin pellet to TGA isothermal holds at 260°C (500°F) and 316°C (600°F) for 4 h under air. TGA results (Table 2.1) suggest that alumina alone reduces mass loss the most, but some of the other systems show good results at 260°C and so should be scaled up for additional testing. However, the reduction in mass loss provided by the alumina is not as impressive when one considers the fact that this particular sample is only 40 wt% polymer, and so other samples with significantly less inorganic content may provide more robust thermal protection. SEM analysis showed that in all cases, the dispersion of nanoparticles and alumina was uniform, so we can rule out nonuniform dispersion (nanoparticle agglomeration) as the reason for the discrepancies in results.

With these data, the following polyimide + alumina and/or nanoparticles were scaled up and filmed for composite fabrication. Films were laid up with carbon fabric to make an 8 ply 6" square laminate, and the polyimide + alumina/

Table 2.1 TGA data for polyimide + inorganic systems

Sample	Weight loss after 4 h hold at 260°C (TGA)%	Weight loss after 4 h hold at 316°C (TGA)%
Polyimide (PI) control	0.22	0.76
PI + 60 wt% Al ₂ O ₃	0.14	0.39
PI + 50 wt% Al ₂ O ₃ + 10 wt% fumed silica	0.12	2.31
PI + 40 wt% Al ₂ O ₃ + 10 wt% fumed silica + 5 wt% carbon nanofiber	0.17	1.08
PI + 50 wt% Al ₂ O ₃ + 5 wt% exfoliated graphite	0.13	0.28
PI + 40 wt% Al ₂ O ₃ + 10 wt% fumed silica + 5 wt% exfoliated graphite	0.12	0.93
PI + 50 wt% Al ₂ O ₃ + 0.5 wt% carbon nanotubes	0.12	0.38
PI + 5 wt% carbon nanofiber	0.32	0.68

nanoparticle protective films consisted of 1 ply of the 8-ply stack applied on the tool side of the composite layup. All composites were then fully cured via autoclave processing, and the resulting panels were cut and machined for additional testing after autoclave cure.

- Polyimide + 60 wt% Al₂O₃
- Polyimide + 50 wt% Al₂O₃ + 10 wt% fumed silica
- Polyimide + 40 wt% Al₂O₃ + 10 wt% fumed silica + 5 wt% carbon nanofiber
- Polyimide + 50 wt% Al₂O₃ + 5 wt% exfoliated graphite
- Polyimide + 40 wt% Al₂O₃ + 10 wt% fumed silica + 5 wt% exfoliated graphite

Upon removal from the autoclave, it was observed that all the samples, with the exception of the polyimide + alumina sample, had some surface defects (not voids, but dents and very small cracks) on the protective ply/barrier layer. Optical microscopy revealed that all samples except the alumina-only sample had very thick top layers so that this resin area was not well-reinforced with carbon fiber. This makes sense in light of the known fact that fumed silica, carbon nanofibers, and exfoliated graphite are all known to increase polymer viscosity [60, 61]. Therefore, the increase in resin viscosity meant that during the autoclave processing, the resin in the top protective film did not fully migrate into the top layer of carbon fabric, thus resulting in a thicker outer layer on these composites. The alumina + polyimide sample did not show this effect, and indeed, during processing of the polyimide precursors with alumina, it was noted that the high levels of alumina did not affect the polymer viscosity much at all. With that in mind we can understand why the polyimide + alumina-only sample gave a good integrated top protective ply (Fig. 2.7) as compared to one of the polyimide + nanofiller systems (Fig. 2.8). When studying these figures, one needs to look closely at the top line of the panel (admittedly difficult to see in Fig. 2.7) and that thickness before it reaches the darker curve which is the top of the carbon fiber bundle. These pictures are micrographs taken edge-on in the composite so that one is looking at the top protective layer and how thick it is on top of the

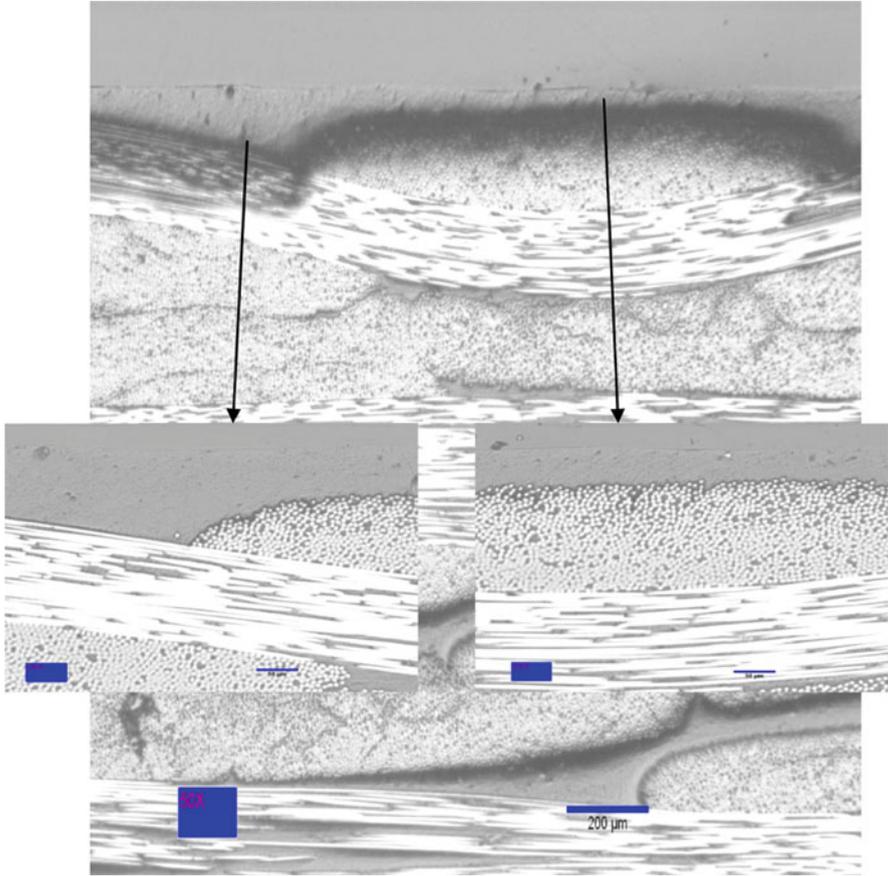


Fig. 2.7 Polyimide + 60 wt% Al_2O_3 micrographs

carbon fabric. In Fig. 2.7, the top layer is very thin, indicating that the resin-rich layer on this panel is very thin. For the other material (Fig. 2.8), the top layer is very thick, meaning that there is a large resin-rich layer which has no fiber reinforcement. This is important to keep in mind when looking at the thermal oxidative stability data and the panel skins after aging later in this section.

The panels with the protective plies were then subjected to thermal aging studies in calibrated ovens at 316°F for 200 h in air and then weighed for mass loss. The panels were all placed “protective laminate side up” in the ovens to minimize the effects of surface area, and the measured mass loss was normalized to surface area of the samples exposed to air to better understand the ability of the protective coatings to reduce the mass loss rate. The results from this study (Table 2.2) reflect the results in the TGA data (Table 2.1) in that the alumina sample gave the best performance. This makes sense in light of the fact that the top protective layer in

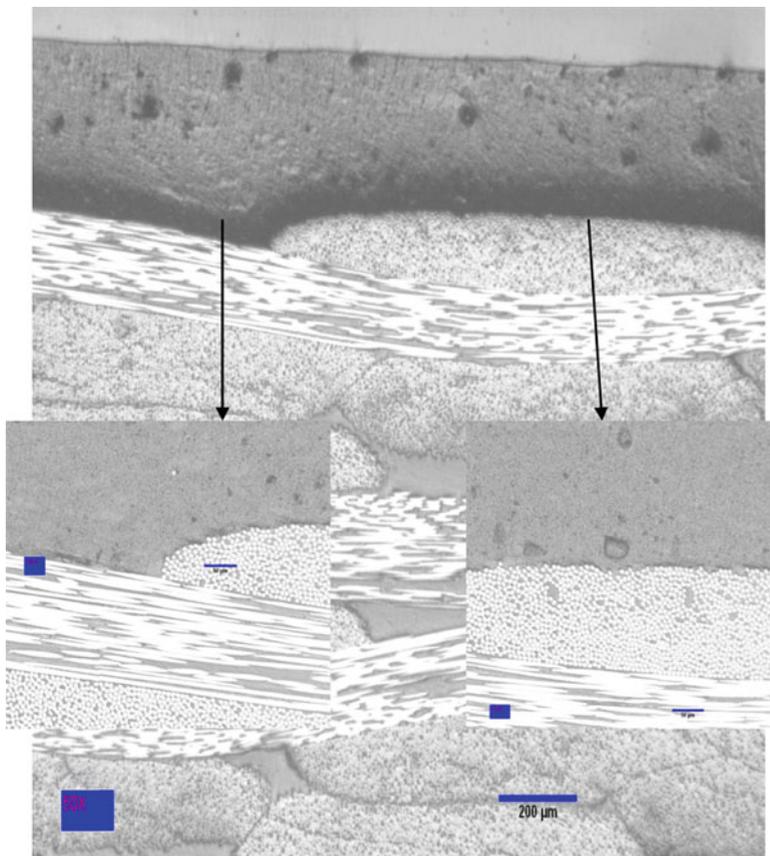


Fig. 2.8 Polyimide + 40 wt% Al_2O_3 + 10 wt% fumed silica + 5 wt% carbon nanofiber micrographs

Table 2.2 Polyimide + protective coating weight loss data at 316°F aging

Formulation	Wt loss- 47 h (g/cm^2)	Wt loss- 100 h (g/cm^2)	Wt loss- 148 h (g/cm^2)	Wt loss- 200 h (g/cm^2)	Coated side calculated
Polyimide (PI) control	0.083	0.116	0.138	0.180	N/A
PI + 60 wt% Al_2O_3	0.055	0.083	0.102	0.133	0.086
PI + 50 wt% Al_2O_3 + 10 wt% fumed silica	0.061	0.102	0.129	0.184	0.188
PI + 40 wt% Al_2O_3 + 10 wt% fumed silica + 5 wt% carbon nanofibers	0.061	0.012	0.148	0.213	0.246
PI + 50 wt% Al_2O_3 + 5 wt% exfoliated graphite	0.069	0.099	0.124	0.174	0.168
PI + 40 wt% Al_2O_3 + 10 wt% fumed silica + 5 wt% exfoliated graphite	0.068	0.109	0.138	0.196	0.212

Fig. 2.9 Surface of PI + 40 wt% Al_2O_3 + 10 wt% fumed silica + 5 wt% carbon nanofiber after 200 h @ 316°C. Sample is a 1" square specimen



this sample is fully integrated into the composite structure (compare Fig. 2.7 to Fig. 2.8) and as polymer oxidizes away, it will leave an inorganic-rich top layer which can provide additional protection. Some of the other samples which were more effective in pellet form performed quite poorly in these tests, but post-aging analysis showed that the thick top layer was the reason for this. Specifically, the thicker top layers were more likely to crack open due to a lack of fiber reinforcement, and were also prone to polymer shrinkage during oxidation (which exacerbates the cracking), which fits with the known mechanism of polyimide oxidation, aging, and microcrack formation (Chaps. 9, 10 in this book). Examples of the extreme amounts of microcrack formation can be seen in Fig. 2.9, and the lack of microcracking can be seen in Fig. 2.10 for the polyimide + alumina sample.

With these preliminary results, we can state that the integrated protective coating concept works in principle, but more work is needed. Process work is needed to address resin viscosity increases created by the nanofibers, to see if it is possible to prevent the formation of thick top layers found in this study. Also, process work is needed to determine how much more alumina can be put into the top protective layer to further improve thermal oxidative protection. Fundamental research is also needed to see if it is possible to create fully inorganic top protective plies that

Fig. 2.10 Surface of PI + 60 wt% Al₂O₃ after 200 h @ 316°C. Sample is a 1" square specimen



copolymerize with polyimides without interfering with composite mechanical properties, so that mass loss under thermal aging will approach zero. The data set at this time is rather limited, but the proof-of-concept experiment strongly suggests that this approach has merit, and indeed, research programs are underway to push this concept further and to develop not only better systems than the ones displayed here, but also systems that can be commercialized and used for composite protection in 2–5 years.

2.7 Future Trends and Unsolved Problems for Composite Protection

Material durability is not a new problem, but since polymeric composites are a relatively new class of materials, there is still much to learn despite all we know today. This final section of the chapter shares some likely trends in research on these materials as they continue to replace metals and ceramics, as well as some other unsolved problems for composites that need to be addressed as research in the area progresses.

2.7.1 *Passive + Active Protection*

It is expected that the use of nanocomposites or additives alone will not be enough for composite durability as these materials go into extreme environments. Indeed, with flame-retardant polymer nanocomposites, it is the combination of flame-retardant additives and polymer nanocomposites that have led to better fire-safe materials with improved mechanical properties and cost performance profiles. So with polymer composites in need of protection from erosion, electrical, and heat damage, we will likely see traditional means of protection (passive protection) combined with additives and nanocomposite approaches. The approach described in this section is one of multiple lines of defense. No carbon-based material can withstand very high temperatures and oxidation for long, so while the approaches of nanofillers and protective barriers greatly improve the durability of polymer composites exposed to heat and air, heat shields may still be needed. With the combination of engineering solutions and enhanced composite durability through nanocomposites, the parts may increase their usable lifetime several times over, thus saving on maintenance costs, or allowing for lighter-weight engineering solutions to be used, which improves the entire system. As existing materials are improved through additive, nanocomposite, and protective barrier approaches, engineers will get more savvy about taking advantage of these property enhancements first to make step changes in performance, and later major redesigns of systems. Most materials are inserted into new applications this way, by step change improvement in existing applications, so this trend is likely to be observed in the next decade.

2.7.2 *Multifunctional Materials*

“Multifunctional materials” simply means that one material does the job of many. It resists heat, conducts electricity and heat, has all the right mechanical, weight, and color requirements, parks the car, slices bread, and is dirt cheap too! One gets the idea that a multifunctional material is something truly impressive and can be used in many different ways, but really there is much to be done in this field. This field of study is certainly ongoing, and polymer + carbon nanotube/nanofiber nanocomposites are likely to be the first real example of a multifunctional material. But still, these materials are not perfect. While they may be electrically and thermally conductive, they are not conductive *enough* to replace metals outright. Then there is the cost issue: nanotubes and nanofibers are expensive, and so while effective in low loadings, at \$100–200 per kg optimistically (sometimes \$1,000 s per kg), one has to decide if the improvements are really justified by the cost. One definite unsolved problem for nanotubes is how to functionalize them without compromising electrical conductivity or properties. Most side-wall functionalization of the nanotubes results in loss of electrical conductivity, or worse, shortening of the tubes and loss of mechanical reinforcement [62]. Another unsolved

issue is how to create an electrically and thermally conductive polymeric material that is transparent. The need for optical windows that can provide EMI shielding (or dissipate static discharge), energy for heads-up displays (computerized visual displays on transparent viewing surfaces), and the ability to resist erosion/wear/impact is still unsolved by any single material. Today it is accomplished with a multilayer system which adds cost and maintenance issues to the final system. For multifunctional materials to achieve actual success, one must first define an application that really can use such a material, and then design to that application. No one will say “Aha! I have the universal multifunctional material that everyone can use,” because it cannot be achieved. Actual applications and needs (technology pull), not just discoveries in the lab pushing the technology out, will drive this field.

2.7.3 Multicomponent Systems

As suggested earlier in this section, polymeric composites are likely to be used in concert with existing materials and solutions, but getting these materials to work well together is still unsolved. This is partly an engineering design issue (How can engineering keep the part out of harm’s way?) and partly a material selection issue (Which materials will minimize damage and work well with the polymer composite?). Most importantly, how each material influences the degradation and decomposition of the other has yet to be fully studied. If we are to go to metal + polymer, ceramic + polymer, or ceramic + metal + polymer hybrids, we need to understand at a macro, micro, and molecular scale how these materials interact in a range of environments. While there have been great strides in understanding the oxidation failure behavior of fiber-reinforced composites (see Chaps. 9,10), there is still much to learn, especially in regards to chemical decomposition pathways. Only by understanding the actual chemical species generated can the material scientist or polymer chemist develop a new means of defense. For truly complex structures, understanding how a metal catalyzes degradation (or char formation) in a polymer is important, as is understanding how changes in one structure lead to structural failure in another dissimilar material. In effect, it is an unknown problem which needs a multidisciplinary solution. It requires mechanical engineering, materials science, chemistry, and physics to come together on a problem of composite failure in an extreme environment and work in tandem toward a unifying understanding. Once that understanding is achieved, then one can design new materials or systems that survive the extreme environment. Much of this will have to rely upon experimental results and not just theory and modeling, although modeling is very important in understanding the behavior and in designing the right experiments to run. This unsolved problem is likely to continue to slow down composite insertion into many applications, but it is not insurmountable and can be addressed with careful study.

2.7.4 *Interfacial Fundamentals*

With both polymer nanocomposites and multi-material engineered structures, one of the great unknowns continues to be understanding the fundamental science (chemical, physical) at the interface between these dissimilar materials. The interfacial interactions can be complex, and without an understanding of these interactions, the material scientist has to think empirically at best, or outright guess at worst, to design a system that either takes advantage of these interactions or is not negatively affected by them. Since these interactions are complex, they will be explained in turn.

2.7.4.1 **Polymer Nanocomposite Interface Issues**

While polymer nanocomposites have been successfully commercialized, limitations on the interface between the nanoparticle and polymer have limited further commercialization of these materials. The interfacial issue is key to ensuring that a nanocomposite is formed in the first place, as without a well-designed interface to bridge the gap between nanoparticle and polymer, the two materials will typically separate, yielding expensive filled materials (microcomposites). The interfacial issues are nanoparticle-dependent; what works for a layered silicate is not always applicable to a carbon nanofiber/nanotube or colloidal inorganic particle.

For layered silicates and other layered inorganics, the main interfacial issue still to be addressed is the thermal stability of the organic treatment. Most inorganic layered materials are only miscible in polar polymer matrices, so organic treatments are needed to make the organophobic nanoparticle organophilic.

For layered silicates such as clays, the typical interface is an alkyl ammonium treatment put onto the clay surface through ion exchange. This treatment is chosen because of its low cost and well-established use to date in making organically treated clays. However, this treatment is thermally unstable above 180–200°C [63], and once the alkyl ammonium reaches this temperature it thermally decomposes to yield an amine and an alpha olefin via the Hoffman degradation reaction [64, 65]. The decomposition of this organic treatment causes the clay to return to organophobic status, which leads to polymer de-intercalation in the clay galleries (interlayer area) and subsequent phase separation. With sufficient thermal decomposition, the well-constructed nanocomposite will return to a microcomposite structure and all nanocomposite benefits will be lost [66–69]. With this in mind, one must consider the use of more thermally stable organic treatments for the layered silicate, such as imidazolium [70–73] or phosphonium compounds [74]. While these organic treatments are effective, they are not commercially available at this time, although more sources of imidazolium compounds are becoming available due to the increase in ionic liquid availability. However, not just any imidazolium or phosphonium compound can be used; one must ensure that long enough alkyl chains exist to enable intercalation of the polymer chains and miscibility with the polymer matrix as well

as any other interactions that may be needed to obtain a good nanocomposite structure [75–78]. Indeed, in some cases alkyl ammonium can do a better job than imidazolium in rapidly dispersing into the polymer matrix during processing [79–82]. However, even though alkyl ammonium dispersion can occur very quickly before the alkyl ammonium degrades sufficiently, if the polymer is kept at elevated temperatures for long periods of time (thermal aging), the alkyl ammonium will degrade and the clays will collapse, resulting in a microcomposite structure [83–86]. The thermal instability issues of alkyl ammoniums will need to be addressed for these materials to become more accepted and further commercialized.

On a final note, the alkyl ammonium discussion above is relevant to cation-exchangeable layered materials such as montmorillonite, laponite, hectorite, and similar layered silicates. For anionic-exchangeable layered materials (such as double-layered hydroxides), the organic group used to prepare the interface can vary greatly due to a wide range of commercially available anionic surfactants. The layered nanoparticles that fall into this category have only recently begun to be studied, but so far they do not appear to have the thermal instability issues that cationic-exchanged layered materials have [38, 87–91].

For carbon nanotubes and nanofibers, the interface is created in a very different way. An interface is often needed since the graphitic surface chemistry of these rod-like carbon nanoparticles does not lend itself to good interaction between the polymer and the nanoparticle. While dispersion of the nanoparticle can be achieved without additional interface, there are far fewer mechanical benefits, since as the polymer chains slip past each other, they have no good way to interact with the nanotube other than π – π bond interactions if aromatic groups are present, and even then these interactions are relatively weak compared to actual covalent bonds or polymer chain entanglements [37, 92]. What typically happens in the absence of an interface between polymer and nanotube/nanofiber is that the fibers “pull out” when the polymer breaks [93, 94], much like how fibers without good “sizings” pull out of composites when they break and fail. To achieve an interface between nanoparticle and polymer, in this case, one must covalently react a functional group onto the surface of the nanoparticle. For carbon nanotubes, this is done either at the end of the tube or on the wall of the tube itself, with reactions that either partially break open the graphitic structure of the wall or take advantage of defect sites on the nanotube surface [95–98].

For carbon nanofibers, a graphitic edge structure already exists and this is likely where reactions occur, although reactions on the wall of the nanofiber are also possible. The edge structure already exists due to the stacked “cup” (or coiled ribbon) structure of the nanofiber structure as opposed to the rolled sheet structure of the nanotube. These covalent reactions, once achieved, are permanent and tend to have very good stability; the treatment is unlikely to decompose during processing as sometimes happens with alkyl-ammonium-treated layered silicates. However, in so reacting with the wall of the nanotube, one weakens the properties of the nanotube. By disrupting the continuous sp^2 carbon network, electrical conductivity can be lost, and the tube itself can become mechanically weakened. This is a great problem for single-wall carbon nanotubes (SWNT) but less of a problem for multi-wall nanotubes (MWNT); only the outer wall of an MWNT is damaged during

functionalization, and the inner core maintains its properties. There have been some breakthroughs in creating interfaces for nanotubes which are not covalently bonded to the side wall of the tube [99, 100], but these technologies need to be studied further to ensure that they are stable to all processing conditions and really bring a benefit to nanocomposite properties. So for nanotubes and nanofibers, the interfacial issues remain without a satisfactory solution. Covalently functionalized MWNT or nanofibers can be used, but they do have high costs, which prevents their widespread use. The other issue, and the main one to address, is that the fundamentals of what type of interfacial chemistry structure and amount of interface on the nanotube/nanofiber surface are necessary to achieve good nanocomposite properties have not been fully elucidated, and so the material scientist trying to utilize these types of nanoparticles for protective schemes will have to spend more time doing basic research before implementing these materials into a solution.

There are plenty of chemical routes for functionalization of colloidal nanoparticles available, from direct covalent functionalization of the surface to encapsulation technology. What remains unknown is what exactly the interface should be and how much should be present. For example, if too much interface greatly clouds the surface of the nanoparticle, some nanoparticle benefits could be lost (especially important to conductive nanoparticles and nanoparticles with electro-optic effects). Likewise, if there is not enough interface, the nanoparticles will aggregate and form microcomposites and no benefits will be obtained. Perhaps it can best be said that at this time we do not know when an organic interface is needed, nor do we know when it is not needed, and we definitely do not know what the structure of that interface should be to maintain good dispersion and gain benefit of nanoparticle structure–property relationships. So much is still unknown because this class of nanofillers is still quite new in polymer nanocomposite research, and there is very little published work on the subject. Some materials, like polyhedral oligomeric silsesquioxanes (POSS) [101] are somewhat understood, but other systems, especially those in which nanoparticle shape and structure play a role in properties, remain elusive [102]. Finally, there is the uncertain issue of when it is better to mix in a nanoparticle to obtain properties, or to try to form the nanoparticle in situ during polymerization and obtain a true polymer + inorganic hybrid [103, 104]. It may be that the best properties can only be obtained through a hybrid structure rather than through a filled-system approach.

2.7.4.2 Engineered Structure Interfacial Issues

The interfacial issues with engineered structures are predominantly physical, since the interfacial area between dissimilar materials is typically macroscale, and as such, chemical effects are usually minimized. While engineers can look at material properties and try to match them based upon their physical properties, most of the database properties to choose from either are limited in temperature range, or are not well-described as regards all the properties over the lifetime of the part. As an

example, mismatch in coefficient of thermal expansion between a thermal ceramic shield and a polymer composite will cause the shield to come off during use, or worse, to break if constrained as one part presses against the other due to differences in thermal expansion. How does one engineer for this problem? Is it simply a case of putting an absorbing material (a negative CTE material) between the other two materials, or does the structure have to include engineered “air gaps” between parts to allow for expansion? The design principles to prevent damage to a composite are not always clear, but what is more, fundamental engineering rules to prevent negative interactions between materials do not appear to be very clear at this time. Some of the other chapters in this book suggest that “rules and tools” exist to help minimize these negative interactions and unforeseen failures in new applications for old materials, but much work needs to be done.

2.7.5 Life Cycle and Environmental Challenges

Because of recent interest in improving energy efficiency, polymer composites are making inroads into many applications where their light weight can result in energy savings (less fuel consumption) for conventional propulsion technology. However, as these materials are used more often, the questions of their life cycle and environmental impact come forward. More and more, materials used in part and vehicle construction need to be recycled at the end of their use. For thermoplastics, this is relatively easy; the materials can be reground and melted into new parts. If they cannot be reused in this manner, they can at least be incinerated easily for energy recovery. However, for thermosets, the material in most fiber-reinforced composite applications, recycling is not currently an option, at least not in commercially viable scales. Thermoset materials cannot be reground and reformed, and would need to be incinerated or sent to landfill. The incineration of commodity thermoset composites will yield energy generation, but high-performance composites (such as polyimides) present an incineration challenge in that they tend to be char formers, and so might absorb more energy than they would generate under incineration conditions. Plus, many of these composites have expensive fibers present as their reinforcement, so recovering the fiber while burning the resin is not something that can be easily done. Therefore, these materials present a real environmental and recycling challenge as they continue to grow in use. Recycling technology, either chemical (depolymerization and recapture of monomers) or physical (separation of polymer from fiber so fiber can be reused) is either in its infancy or nonexistent for thermoset polymer nanocomposites, and this presents a real unsolved problem for these materials. If the composites are damaged, replacement is easy, but what do you do with the damaged part? Along with preventing damage, figuring out what to do with the damaged composite at the end of its lifetime is of equal importance, and is something that researchers should begin considering when developing new materials.

2.7.6 *Final Thoughts and Conclusions*

As polymer composites continue to replace metals and ceramics, protection will be needed. As indicated throughout the chapter, there are many possible sources of protection to choose from. All the protection schemes available fall into active or passive schemes, but ultimately passive schemes are the ones most likely to succeed from a total cost and reliability perspective, although they will have a higher initial investment cost. Passive schemes of additives, polymer nanocomposites, and barrier coatings are available today, but each has its own limitations and appropriateness, depending upon the level of protection required. As long as one focuses utilizing on protection scheme/chemistry which addresses the mechanism of damage to the composite, it is very likely that the material scientist will enable the composite to replace a metal or ceramic successfully. Admittedly, there is still much work to do, but the goals are achievable, and it is highly probable that polymer composites designed to survive extreme environments will be discovered and commercialized.

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