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Polyurethane Nanocomposite Coatings for Aeronautical Applications

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8.1 Introduction

There is evidence that lacquer technology was developed in China many thousands of years ago, and these lacquers produced very hard, durable finishes that are both beautiful and very resistant to damage by water, acid, alkali, or abrasion. According to archaeological digs, ancient applications included coffins, plates, musical instruments, and furniture. In the lacquering of the Chinese musical instrument gu-qin, the lacquer was mixed with deer horn powder or ceramic powder to give it more strength as protection against scratches. The varnish resin used was derived from the varnish tree, unlike the modern chemical resins used nowadays.

Modern paint systems have been undergoing continual change with the fast development of modern industries. After the first powered wood-and-cloth plane flight in 1903, the aerospace industry has grown to be one of the most exciting, diverse, and fast-paced fields [1]. Especially in the last few decades, the aerospace industry is moving in a major way toward advanced composite materials [2,3] (see Figure 8.1). Composite structures have found commercial applications where high performance is required since the early 1970s, as an alternative to traditional metal-based aircraft components and structures [4]. Composite materials offer a wide range of benefits over traditional materials commonly used in aircraft, including improved chemical stability and good fire resistance, as well as their obvious weight and cost savings not only during manufacture but also during the lifetime of the aircraft [5].

There are disadvantages in composite materials, however. An obvious one is their considerably higher electrical resistance compared with aluminum, with limited applications such as electromagnetic shielding, circuits, antennas, and lightning strike protection [6]. Similarly, the lower thermal conductivity of composites poses a threat to composite fuel tanks and affects de-icing. Composite materials are also less resistant to impact, which is a major issue for aircraft manufacturers [7]. Another problem regarding composites is moisture absorption and aging over time [8–10].

FIGURE 8.1
An estimate of the composites ratios in structural aircraft. (From Bamford, F. GKN Aerospace—A Vision of the Future. April 2007.)

Typically, the protective painting systems for aerospace include a primer and topcoat (see Figure 8.2). The primer coat is porous and brittle, with no durability but providing corrosion protection and adhesion of the coating to the pretreated substrate surface. The topcoat is supposed to be flexible, have a matte finish, and be washable and chemically resistant with optimum exterior durability [11]. Because of high-performance requirements in terms of durability, flexibility, and corrosion protection, aerospace and military camouflage coatings have traditionally used two-component polyurethane systems [12–15]. However, many of the materials that are most critical

FIGURE 8.2
Typical aerospace coating system.

to the function of current aircraft coating systems are limited in that they are either not maintained for the life of the coating system (e.g., cladding), or have limited mission function [16]. Nanocomposites obtained by dispersing nano-scaled fillers of various functionalities within polymeric matrices are of particular importance because they offer a great opportunity to improve and tailor the properties of the polymer [17], which allows the adjustment of mechanical (wear, friction), chemical (corrosion, permeation, temperature insulation, biocompatibility, wettability), transport (electrical and thermal conductivity), and optical (transmission, reflection, absorption, color) properties of surfaces [18].

8.2 Background: In-Flight Environments and Damage Modes—Challenges and Opportunities in Aeronautical Engineering

Commercial and military aircraft operate in diverse worldwide environments. Composite structures for these aircrafts must be designed to withstand all these environments, including large variations in temperature and moisture, contact with aircraft liquids such as jet fuel and hydraulic fluid, and lightning strikes. The coatings that are applied to airplanes represent a highly technical challenge for paint makers as they are the most demanding of all paint systems (Figure 8.3). They need to be able to withstand temperatures ranging from -48°F in the air to 120°F on the ground, as well as strong UV exposure at 30,000 ft. In addition to coping with extreme temperature fluctuations, they need to resist cracking due to rapid changes in air pressure. They also need to resist erosion from air drag and deflect the impact of dust traveling at 500 mph, which has an effect similar to sandpaper. On the ground, aircraft coatings also have to withstand contact with aggressive fluids such as fuel, de-icing fluids, and hydraulic liquids. Additionally, the appearance of airplanes is important. Attractive colors and unique paint schemes are desirable for identifying and distinguishing one airline from another [19,20].

Thus, the design of modern aircraft paint to withstand these demands is reflected in its detailed specification. This includes requirements for temperature, UV, flexibility, adhesion, water resistance, and fluid and corrosion resistance, which can be systematically classified by

- Mechanical properties: increased modulus, strength, impact toughness
- Barrier properties: reduced moisture absorption, increased chemical resistance, reduced gaseous diffusion
- Fire retardant properties: reduced burn-through, enhanced FST properties, increased charring

FIGURE 8.3

Classification of environments encountered by aircraft coatings.

- Thermal properties: increased HDT and stability, enhanced conductivity, controlled coefficient of thermal expansion (CTE)
- Tribological properties: increased surface hardness, reduced wear rate, scratch resistance
- Electrical properties: conductivity, electrostatics, EMI shielding, EMH protection

The necessity to meet the requirements of such specifications has a strong influence on the paint formulation [21].

8.2.1 Interaction between Lightning and Aircraft

The effects of lightning strikes on aircraft can be divided into two types, direct and indirect effects. The direct effects refer to causes of damage, including heat, acoustic shockwave, and electricity. These can affect different components or areas of the aircraft with varying degrees of severity. The figures associated with a typical lightning strike are quoted by Reference 22 as ~30,000°C temperature generation, ~500 psi impact force from the acoustic

TABLE 8.1
Typical Lightning Strike Levels and Airframe Requirements

Threat	Criteria	Requirement
High-energy strike	Rare lightning strike 50–200 kA	Striking level in accordance with zoning diagram Continued safe flight (70% DLL) Ready detectable damage
Intermediate-energy strike	Medium lightning strike 30–50 kA	Repair needed (100% DLL) Visible damage
Low-energy strike	Nominal lightning strike 10–30 kA	No repair needed (150% DLL) No or barely visible damage

DLL = design limit load.
Source: Feraboli, P. and M. Miller, *Composites Part A*, 2009. 40 (6–7): p. 954–967.

shock, and ~200,000 amp of electric current [23] (see Table 8.1). The indirect effects refer to damage or interruption of electrical equipment onboard the aircraft by induced voltages. Unlike the direct effects, indirect effects can occur even if the lightning strike doesn’t make contact with the aircraft.

Aircraft can be divided into zones that define their susceptibility to lightning arc attachment. Figure 8.4 highlights the distribution of these zones across the aircraft [24]. There are three main zones, which are then subdivided into subzones. Typically the areas illustrated as zone 1 are the most likely locations for initial lightning strike attachments. Zone 2 locations are susceptible to subsequent swept stroke attachments after the initial attachment, and, finally, zone 3 locations are where arc attachments are unlikely. The zones are summarized as follows:

- Zone 1—Initial attachment point with probability of flash hang-on
- Zone 2—High probability of swept stroke reattachment from zone 1
- Zone 3—Low probability of lightning arc attachment

8.2.1.1 Damage Mechanism

As already mentioned, the direct effects of a lightning strike involve causes of damage, including the heat generated by the resistance of the paint. This resistive or Joule heating originally caused most damage. More recently, however, with the achievement of reduced dwell times in lightning strike testing, the question has been raised as to whether the acoustic shockwave that occurs in the first few microseconds of a lightning strike causes more damage than originally suspected. Lastly, the electrical charge that has already been found responsible for resistive heating may also causes a breakdown of the matrix because of the dielectric properties of the paint.

Zone 1 Initial attachment point with probability of flash hang-on,
Zone 2 High probability of swept stroke reattachment from zone 1.
Zone 3 Low probability of lightning arc attachment.

FIGURE 8.4

Lightning zone diagram for a typical large commercial transport per SAE 5414. (From Feraboli, P. and M. Miller, *Composites Part A*, 2009. 40(6–7): p. 954–967.)

Puncture is more likely to occur with a composite material than with a homogeneous plastic such as a polycarbonate because composites have microscopic holes (porosity) and material interfaces through which or along which an electric discharge can propagate, as shown in Figure 8.5, where projected damage area was obtained via C-scan for filled-hole specimens [24]. The field required for punching a given thickness of glass fiber or aramid fiber composite is, in fact, only slightly greater than that required to ionize a similar thickness of air. A measure of the ability of a nonconductive material to resist puncture is its dielectric strength. Homogeneous materials, such as acrylic and polycarbonate sheets, have very high dielectric strengths and are more resistant to puncture.

8.2.1.2 Protection Methodology

There are two basic ways of providing protection to nonconductive composites. One method employs diverter strips or bars on the exterior surface to serve as preferred streamer initiation points and to intercept lightning flashes,

FIGURE 8.5

Projected damage area obtained via C-scan for filled-hole specimens. (From Feraboli, P. and M. Miller, *Composites Part A*, 2009, 40(6–7): p. 954–967.)

while allowing the skin to be transparent to electromagnetic waves. This is the approach used for protection of radomes and some antenna fairings. The other method is to apply an electrically conductive material over the exterior of the structure. This latter method provides the most effective lightning protection and should be employed whenever possible. It also provides improved protection of enclosed systems against the indirect effects of lightning.

Where radio frequency transparency is not required, or conductive structural materials are utilized, a conductive coating can be applied to the exterior surfaces of composites to prevent electric field penetration and puncture, and to conduct lightning currents. Protective materials include arc- or flame-sprayed metals, woven wire fabrics, expanded metal foils, aluminized fiberglass, nickel-plated aramid fiber, and metal-loaded paints.

The initial lightning strike must be dispersed quickly around the airframe to prevent concentrated damage. Also, the airplane's electronic flight instruments must be shielded from disruption by the intense electromagnetic field. To accomplish this, a thin metal mesh or foil is embedded in the outer layers of the composite fuselage and wing [25]. A thin metal mesh embedded in the outer layer of the composites also shields the electrical systems [26].

But the metal mesh or foil increases the weight of the plane. If highly conductive composites were available to replace metal meshes or foils, the weight would be sharply reduced. Carbon nanotubes hold the potential for conducting composite structures, with good surface finish, to deliver an overall weight savings. Also, conducting resin systems have been investigated for

lightning strike protection [27]. Ben Wang's group [27] developed a unique technical approach to incorporate SWNT buckypaper materials into conventional fiber-reinforced and foam composite structures for improving EMI and lightning strike protection. The results show that foam structures with buckypaper of 700 mg surface can achieve as much as 26 dB of EMI shielding over the test range from 455 to 500 MHz, compared with a control panel made from a pure foam structure. Also, the results showed that random buckypaper samples exhibited better EMI shielding properties. For lightning strike resistance, no visible improvement or further improvement in electrical conductivity of buckypaper composites is needed in order to utilize SWNTs for the purpose of improving the EMI and lightning strike resistance properties of composite structures.

8.2.2 Rain, Sand, and Ice Particle Erosion

An aircraft is most likely to encounter dust and sand during take-off and landing, and rain during ascent and descent, as cruising altitudes are generally above cloud levels. However, military aircraft and missiles may experience all types of conditions [28,29].

Figure 8.6 shows the synergistic effects of liquid and sand erosion on a laboratory scale. When sand particles impact on a preexisting crack caused by liquid impact, the damage site is enhanced, since the crack is easily opened further by sand particle impact. These cracks are further exploited after prolonged exposure. If not caught in a timely manner, the sand may erode into the fiberglass blade skin, degrading its structural integrity. Additionally, since an expanded copper mesh is often embedded on the surface of the composite skin for lightning strike protection, the erosion damage may locally degrade the protection of the blade. Since lightning strikes tend to be concentrated at the outboard section of the blade, erosion damage may degrade lightning strike protection in an area where it is most necessary [30]. Current blade protection against erosion is either a metallic shield, usually nickel or titanium, or a polymeric coating or tape, which is usually either pure polyurethane (PU) or a blend of polyurethane with other polymers such as polyethylene [31].

Recent efforts have been concentrating on the development of new advanced polymeric materials as they already offer greater protection than metallic systems, do not alter blade dynamics in the same way that a metallic or ceramic system would, allow metallic elements to be eliminated from blades, and have the potential for much easier and lower cost replacement. A particular area that attracts much interest in research is the development of nanocomposite coatings, to be outlined in later sections.

8.2.2.1 Classification of Erosion Behavior

The erosion classification of rubber-like elastomers is complex and shows brittle, ductile, or rubber-like erosion behavior, depending on temperature

FIGURE 8.6

FLIR ZnS previously liquid impacted by 0.8 mm jets at 185 m s^{-1} (100 impact random array over 14 mm diameter circle) followed by sand erosion at $0.15 \text{ kg m}^{-2} \text{ s}^{-1}$ at 20 m s^{-1} by C25/52 sand. (From Jilbert, G.H. and J.E. Field, *Wear*, 2000. 243(1–2): p. 6–17)

and deformation time [31,32]. They react differently from brittle materials (ceramics and brittle polymers) [33,34] or ductile materials (metals and ductile plastics) [35]. Single impact seems to cause no visible damage at all, which is in agreement with the incubation time observed in the erosion process before a steady state is obtained [36]. During this incubation time, the substrate may even increase a little in weight as a result of particles embedded in the substrate surface. In the case of polyurethane elastomers, the incubation time is found to decrease with increasing brittleness and decreasing angle of attack [37]. At oblique impact, maximum erosion is found at glancing impact, as with ductile materials. The erosion rate of PUs, for example, is found to differ by an order of magnitude between normal impact and 30° angle of incidence [38]. The difficulty of erosion classification is fundamental to polymeric materials. Depending on the temperature and rate of deformation, the same material may behave in a dominantly ductile, rubber-like, or brittle fashion.

A great difference in the classification of various materials in respect to their erosive wear exists when the variation in impact angle and time is

FIGURE 8.7

Schematic depiction of typical erosion behaviors. (From Barkoula, N.M. and J. Karger-Kocsis, *Journal of Materials Science*, 2002, 37(18): p. 3807–3820.)

considered. Figure 8.7 shows typical erosion diagrams as a function of impact time and angle, respectively. Taking impact time into account, an incubation period is involved in ductile erosion with the weight increases first followed by settling down to a steady state, as shown in Figure 8.7 (left). Normal impacts (the impact angle $\alpha \approx 90^\circ$) are due to the initial embedding of erosion sands in the target material surface. Figure 8.7 (right) demonstrates that the maximum material removal occurs at low impingement angles in ductile behavior, whereas at high impingement angles brittle erosion dominates. The differences in the erosion behavior can be traced to material removal mechanisms that can range from tearing and fatigue for rubbers, through cutting and chip formation for ductile metals and polymers, to crack formation and brittle fracture for ceramics, glasses, and brittle polymers [39].

8.2.2.2 Sand Abrasion Mechanism

The abrasive action of sand and dust is probably one of the simpler mechanisms to understand and explain. At low speeds, tangential abrasion is generally performed using a Taber abraser which is a rotary platform; other tests have been developed using sand fed onto rubber discs. At the high speeds encountered by propellers and rotor blades, we see damage also occurring at perpendicular impact. Perpendicular impact damage is generally in the form of micro-pitting of the surface, and embedding of sand into the pits is not uncommon on soft polymeric coatings. At oblique angles (typically tested at 30°), we see a combination of scrubbing abrasion and micro-cutting. This scrubbing action is generally resisted very well by resilient materials such as polyurethane, as is sand abrasion on the whole; however, when it does occur along with micro-cutting we see an effect called “comet tailing” where material is plastically deformed by micro-fatigue, forming ridges which are then more susceptible to removal due to the exposure of ridges and a structure

FIGURE 8.8

Possible mechanisms of solid particle erosion: (a) abrasion at low impact angles, (b) surface fatigue at low speed, high impingement angle, (c) brittle fracture or multiple plastic deformation at medium speed, large impingement angle, (d) surface melting at high impact speeds, (e) macroscopic erosion with secondary effects. (From Barkoula, N.M. and J. Karger-Kocsis, *Journal of Materials Science*, 2002. 37(18): p. 3807–3820; G.W. Stachowiak, A.W.B., *Engineering Tribology*, Amsterdam; New York: Elsevier, 1993 (Tribology series; 24).)

that is weakened by fatigue cracks [41]. Mechanisms of erosive wear were summarized schematically by Stachowiak and Batchelor [42], as shown in Figure 8.8. Details of the solid particle erosion behavior of polymers and polymeric composites were reviewed by Barkoula [40].

8.2.2.3 Rain Erosion Mechanism

Liquid impact can damage materials since, during the very early stages of impact, compressible effects occur in the liquid. A basic theory for understanding the major features of high-speed liquid impact (impact speed $> 50 \text{ ms}^{-1}$) was the “water-hammer” pressure first analyzed by Joukowski in 1898 [43,44]. These high pressures are responsible for most of the damage resulting from liquid impact and are maintained while the edge of the contact area between the impacting liquid and the solid moves supersonically at the shock speed in

the liquid. However, the water-hammer pressure idea remained unchanged until the mid-1960s, when aircraft erosion became a big issue [45]. By using high-speed photography and clever experimental design, Bowden and Field were able to make visible a number of features associated with the initial stages of impact [46]. Thereafter, 30 years of research led to a reasonable understanding of the basic mechanics of the theory of guided acoustic waves [47]. One of the largest databases available for the erosion resistance of composite materials is based on rain erosion testing in the aerospace industry, performed by Hammond [48]. Existing polymeric coatings are elastomers and show rubber-like behavior under liquid impact. One critical aspect that seems to be a common cause for the failure of existing polymeric coatings is across-surface shearing as the water droplet is deflected outward across the surface following normal impact, causing a radial pattern of deformation. Another aspect is penetration of water into tiny surface defects. Of course, surface shearing could eventually cause surface defects due to tearing and fatigue cracking which can then be penetrated by the water, causing a rapid failure of the coating. At high speeds, water droplets have been shown to behave like hammers, which also opens the possibility of impact induced de-bonding of the coating from the substrate, increasing the likelihood of tearing and fatigue damage. The edges of polymeric tapes are also very vulnerable to water impact, and tests have revealed de-bonding of tapes due to water droplets striking the edges of tapes, causing them to lift (see Figure 8.9).

8.2.2.4 Protection Methodology

Prior to the 1970s, metal erosion strips were applied to protect blades; they performed excellently against rain erosion but suffered severely from sand,

FIGURE 8.9

(Left) Initial stage of impact between a water drop and a solid target with the contact edge moving faster than the shock velocity in the liquid (i.e., supersonically). The shock envelope is made up of many wavelets, which can be found from a Huygens-type construction. The liquid behind the envelope is compressed and the target beneath this area is subjected to high pressure. (Right) Broken edge of ZnS impacted 100 times in a random array over a 14 mm diameter circle by 0.8 mm jets after the hydraulic bursting disc test. (From Jilbert, G.H. and J.E. Field, *Wear*, 2000. 243(1–2): p. 6–17)

because titanium created a corona at night from the oxidation of particles chipped off by sand. Easy filled repair and no-corona Task L-100 paint and L-101 polyurethane paint were tested and were finally approved in 1991 to replace unstable estane and P0655 polyurethane elastomers, which were prone to hydrolysis. Hydrolysis in this case is a mechanism whereby an ester group in the primary backbone chain can be split into its two original organic acid and alcohol reactant groups [49]. The result is a broken bond in the molecular backbone, similar to a broken or missing link in a chain. In 1990, 3M 8663 and 8545 with a short shelf life and high recurring maintenance were developed; 3M 8663 was used extensively and proved to be efficient. Bayer 535330A has also been widely used in erosion protection. Since 1990, there have been two solutions for the harsh sandy environment common to rotor blades: existing metallic shields and resilient polyurethane coatings or tapes. Metallic shields are generally built into the structure of the blade to provide a near-seamless join and are usually produced from titanium or nickel. Nickel has been found to resist sand erosion more effectively than titanium. But compared with polymeric tapes, both materials are heavy. Commercial protective polyurethane topcoat is applied in an accurately controlled spray process to both civil and military aircraft. The spray ensures a controlled thin thickness coat can be applied, which allows the solvent to evaporate to produce a high quality coating. As a typical protection material for rotor blades, 3M polyurethane protective tape is made from an abrasion-resistant polyurethane elastomer that resists puncture, tearing, abrasion, and erosion [50]. It is formulated for resistance to ultraviolet light. When used in conjunction with an applied adhesive, 3M black tape provides protection of the surface from corrosion, abrasion, and minor impact damage. Tapes can easily be replaced as they are supplied in self-adhesive form. Hard ceramic materials are deemed unsuitable due to the processing conditions that could damage composite blades and to a lack of flexibility on blades that are designed to flex, causing both cracking of the coating and a change in dynamics of the blade.

8.2.2.5 Erosion-Testing Methods

The aim of solid particle impact testing is to investigate the resistance to erosion by solid particle impact of materials with a wide range of mechanical properties, and to explore the correlation between erosion rate and mechanical properties. Erosion testing has been carried out with different particle sizes, impact velocities, and impact angles in sand blast-type erosion test rigs [36,51,52]. There are four main types of erosion rigs: the sand or gas-blast rig, recirculating liquid slurry loop, centrifugal accelerator, and whirling-arm rig [53]. The whirling-arm rig has been used to simulate erosive wear conditions on a number of components, for example, helicopter rotor and gas turbine compressor blades, which are vulnerable to erosive wear from sand and dust particles, especially in desert terrain [54,55]. The main specification is to have a double-arm

rotating blade at a tip speed near sonic velocity (up to 550 m/s) and to simulate rainfall of 1 to 2 in./h with fine control. A schematic diagram of a rain erosion testing rig is given in Figure 8.10, which consists of the following subassemblies:

1. High speed motor and control: ~45 kW power, up to ~5000 rpm.
2. Container (concrete wall): ~3 m diameter and ~2 m high; the wall consists of ~5 in. thick oak timbers, 1~2 in. thick steel, and ~10 in. of double-reinforced concrete
3. Rotating arm and stands: The rotating arm apparatus consists of an ~2 m diameter, double-arm blade with sample holders; tip velocities between 0 and 600 mph.
4. Diagnostic and monitoring system: This includes digital recording system and synchronized strobe light system. Closed-circuit television cameras or displays provide a means to observe and record testing.
5. Feeding system and control (to simulate rainfall): A circular, overhead manifold with capillary tubes/needles produces artificial sand/rainfall; a central tank supplies temperature-controlled water/sand to manifold. Drop size and drop rate are controlled by manipulating the water temperature, capillary tube diameter, and storage tank pressure.
6. Control panel/room: Monitors and controls the tests remotely, with sound proofing (not shown in Figure 8.10).

FIGURE 8.10

Schematic illustration of the rotating-arm testing rig consisting of the subassemblies.

8.2.3 Ice Accretion

Ice accretion on aircraft surfaces is a serious hazard. Ice distorts the flow of air over the wing, diminishing the maximum lift, reducing the angle of attack for maximum lift, adversely affecting the aircraft handling qualities, and significantly increasing drag. Wind tunnel and flight tests have shown that frost, snow, and ice accumulations (on the leading edge or upper surface of the wing) no thicker or rougher than a piece of coarse sandpaper can reduce lift by 30% and increase drag by up to 40%. Larger accretions can reduce lift even further and increase drag by 80% or more. A NASA study [56] revealed close to 50% of the total drag associated with an ice encounter remained after all the protected surfaces were cleared. Also icing causes damage to external equipment such as antennae, can clog inlets, and causes impact damage to fuselage and engines [57].

8.2.3.1 Types of Ice

Ice forms on aircraft surfaces at 0° Celsius (0°C) or colder when liquid water is present. The following list illustrates the icing risk in terms of cloud type and ambient temperature. Structural ice adheres to the external surfaces of aircraft. It is described as rime, clear or glaze, or mixed [58]:

1. Rime ice has a rough, milky-white appearance resulting from air trapped when it strikes the leading edge of an airfoil and freezes. It typically occurs with temperatures between -15°C and -20°C . It is less dense, and can be easier to remove than clear ice.
2. Clear or glaze ice typically forms when temperatures are around -10°C to 2°C , with large water droplets, freezing drizzle, or freezing rain. It is the most dangerous type of structural ice not only because it is hard to see, but also because it can change the shape of the airfoil.
3. Mixed ice is a mixture of clear ice (from large drops) and rime (from small droplets) that has the worst characteristics of both, and can form rapidly when ice particles become embedded in clear ice and build a very rough accumulation. Mixed ice is most likely to form at temperatures between -15°C and -10°C .
4. Hoar frost occurs when moist air comes in contact with a surface at subzero temperatures. The water vapor, rather than condensing to form liquid water, changes directly to ice and is deposited in the form of frost.

8.2.3.2 Current Icing Solutions

Extensive research has been undertaken to identify and prevent icing, and the methods can be classified as de-icing and anti-icing. The former removes

TABLE 8.2

Comparison of Anti-icing and De-icing

	Anti-icing	De-icing
Features	Preemptive, turned on before the flight enters icing conditions	Reactive, used after significant ice build up
Methods	Thermal heat, prop heat, pitot heat, fuel vent heat, windshield heat, and fluid surface de-icers	Surface de-ice equipment such as boots, weeping wing systems and heated wings

the ice from the surface after its formation, while the latter prevents the initiation of icing [57] (see Table 8.2).

To prevent ice build-up on rotor blades under icing conditions, equipment for anti-icing consists of an electrical matrix which covers 20% of the leading edge chordwise, from the tip along the length of the blade. Heat is phased into this matrix in different sectors, timed to coincide with the natural shedding cycle, that is, when sufficient ice has built up. The power supply for the matrix equipment is a drain on the electrical resources and since the only satisfactory solution would be to heat the whole blade, a generator large enough to do this would impose weight problems. A CNT paper resist heater has been fabricated in TEG, Germany [59]. The added value is the combination of higher flexibility of design compared to a metal heater, and high uniformity of temperature. Also, Han et al. reported a rapid thermal response and stable reversibility of transparent SWNT films made by a vacuum filtering method [60].

Also, the addition of a thermally insulating coating to the blade surface raises several concerns. The primary concern is that the coating might hinder heat transfer to the surface, blocking the heating needed to drive ice melting and shedding. A secondary concern is that the insulating coating might retain the heat in the blade structure, potentially causing thermal degradation of the composite structure [30]. Thus, effort to enhance the thermal conductivity of coatings to enhance their de-icing performance may be fruitful [61]. Current research is heading toward nanocomposite coatings, which create very high contact angles with water and where the reinforced polymer acts to absorb and dissipate the higher impact energy caused by repeated impact of particulate matter. A mixture of Rain-X and MP55 PTFE (powder Teflon) has also been claimed to be an outstanding coating to reduce ice adhesion to the surface of the space shuttle [62]. An anti-icing coating has also been developed by Cape Cod Research, Inc. for marine applications and is called PCM-based ice-phobic coating [63].

8.2.4 Environmental Corrosion

Corrosion damage to aircraft fuselages is an example of atmospheric corrosion caused by ultraviolet radiation, heat, and moisture, as well as salt and gas

concentrations. Corrosion is manifested in many different forms. Concentration cell or crevice corrosion is the most common type found on airplanes, occurring whenever water is trapped between two surfaces, such as under loose paint, within a delaminated bond line or in an unsealed joint. It can quickly develop into pitting or exfoliation corrosion, depending on the alloy, form, and temper of the material under attack [64]. The Aloha Airlines incident in 1988 highlighted crevice corrosion damage as a major safety concern [65].

Among criteria for material properties, fatigue and corrosion are the primary failure modes of aircraft structural components and are therefore the most significant criteria in materials selection. To meet these key requirements, normally coatings are used to provide corrosion properties while the substrate gives fatigue resistance [15,66]. For naval aircraft, sea vapor poses a threat to the substrate. The introduction of de-icing chemicals brings corrosion to the aircraft surface [67]. Also composites eliminate a lot of corrosion problems, but introduce different galvanic corrosion: conducting carbon fibers can become exposed (anodic), and aluminum airframes and fasteners can become cathodic [68]. Coating systems exist to prevent galvanic corrosion at the composite/fastener/structural frame interface and provide sealing fastener coatings, coatings for interface regions, conductive gap fillers, and repair methods. In this case, the topcoat provides water resistance and barrier properties. The primer provides corrosion protection when the coating system is damaged as well as adhesion to the metal substrate.

There are three basic protective mechanisms of anticorrosion coatings: barrier protection, passivation of substrate surface (inhibitive effect), and sacrificial protection (galvanic effect) [69]. Barrier protection is obtained by impeding the transport of aggressive species into the surface of the substrate by application of a coating system with low permeability for liquids, gases, and ions. Passivation of the substrate surface can be obtained by a chemical conversion layer or by addition of inhibitive pigments to the coating. Metallic, organic, and inorganic coatings have all been widely applied for protection of metals against corrosion by means of sacrificial protection; that is, protection is obtained by sacrificial corrosion of an electrochemically more active metal, which is in electrical contact with the substrate. Recently, the introduction of acetate- and formate-based de-icing chemicals led to the discovery that corrosion damage on aircraft has become significantly more frequent [70].

In summary, the engineering challenges of lightning strike hazards, icing, fatigue, erosion, and corrosion environments warrant the need to develop novel coatings systems with multifunctional compensating properties. Nanotechnology-enabled composite systems offer optimal opportunities to achieve these requirements.

8.3 Coating Material Systems

A coating system usually consists of multiple layers of different coatings with different properties and purposes. Depending on the required properties of the coating system, the individual coats can be metallic, inorganic, or organic [71]. As described above, the topcoat is exposed to the external environment and must provide the surface with the required color and gloss. In addition to adequate resistance to alternating weathering conditions and impacts from objects, the topcoat should also have a high resistance to UV. Nanocomposites obtained by dispersing nano-scaled fillers of various functionalities within polymeric matrices are of particular importance because they offer a great opportunity to improve and tailor the multifunctional properties of the polymer.

8.3.1 Polyurethane Matrix

Film formation (i.e., the transition from a liquid product to a solid coating) can occur in three ways: either by evaporation of the solvent, by chemical reaction, or by a combination of both [72]. Chemically curing binders for coatings curing at room temperature may be divided into three subgroups, depending on the type of chemical process that forms the basis for the formation of a solid coating (Figure 8.11). Oxidatively cured coatings absorb and react with oxygen from the air in the presence of a catalyst. Similarly, moisture-curing coatings, such as zinc silicates, react with moisture from air during the curing process. Two-component systems rely on a reaction between a binder and curing agent (often in the presence of catalysts such as various types of solvents) that must be supplied in separate containers by the coating manufacturer.

FIGURE 8.11

Classification of binders according to curing mechanisms.

Polyurethane (PU) elastomers are largely applied to industry and consumer products, particularly in the fields of heavy pressure, load, impact, and wear because they possess excellent comprehensive properties such as high wear, oil and corrosion resistance, high elasticity and damping, good adhesion to other materials and so on [73–75]. Literally thousands of different polyurethanes can be made from the array of commercially available isocyanates and active hydrogen compounds, and can mainly be divided into two-component and one-component systems. Two-component systems can take two forms: one shot systems and a prepolymer route. In one shot systems [69], the polyol is first blended with catalysts and flame retardants, plasticizers, fillers, etc., as required to form the resin component, and then reacted with the iso component, which is made up of only diisocyanate. In the prepolymer route, the first step is to produce a prepolymer by reacting one equivalent of polyol with up to two equivalents of isocyanate. Polyurethanes are then produced by the reaction of prepolymers with a chain extender (also known as a curative), such as a short-chain polyol or diamine. Typically, additives such as catalysts, flame retardants, plasticizers, fillers, etc., are blended into the prepolymer prior to chain extension.

8.3.2 Nanoscale Fillers

There exists a wide variety of nano-scale fillers used in modern polymer composite materials, among which are very basic and common fillers like titania, alumina, and silica, clays [76–80], and then carbon nanotubes (CNTs) in single and multiwalled configurations [81–85], as seen in Figure 8.12 [86]. Here, we only discuss three typical types of geometry: clay, CNTs, diamond, and alumina, with particular focus on aeronautical coating applications. This is a convenient way of discussing polymer nanocomposites, because the processing methods used and the properties achieved depend strongly on the geometry of the fillers.

FIGURE 8.12

Typical morphologies of (a) particles, (b) tubes or rods—carbon nanotubes (CNTs), and (c) layered montmorillonite. (From Fornes, T.D. et al. *Polymer*, 2001. 42(25): p. 09929–09940.)

8.3.2.1 Nanoclay

The era of polymer nanocomposites received an impetus from Toyota in 1987. Its nylon-6–organophilic montmorillonite (MMT) clay nanocomposite showed dramatic improvements in mechanical and physical properties and heat distortion temperature at very low content of layered silicate [87]. The excellent properties lie in the unique structure of MMT, where the platelet thickness is only 1 nm, while its dimension in length and width can be around hundreds of nanometers. The unique structure makes nanoclay a very promising filler for coating applications, which require higher water barrier properties as well as robust mechanical properties, thermal stability, and flame retardance [88–90]. The effect of lamellar MMT on the permeability of protective coatings is illustrated in Figure 8.13. In coatings with spherical fillers, the aggressive species may migrate almost straight through the coating, whereas coatings formulated with lamellar nanoclay impede the transport of aggressive species by providing a tortuous diffusion path [91]. Three major processing methods have been developed to produce polymer–layered silicate nanocomposites: in

FIGURE 8.13

Idealized sketch of the effect of (a) spherical filler and (b) lamellar fillers in coatings. (c) The reduction of the relative permeability coefficient is dependent on the clay platelet aspect ratio in the polyimide–clay hybrid system with water vapor as permeate. Each hybrid contains 2.0 wt% clay. The aspect ratios for hectorite, saponite, montmorillonite, and synthetic mica are 46, 165, 218, and 1230, respectively. (From LeBaron et al. *Applied Clay Science*, 1999. 15(1–2): p. 11–29; Yano et al. *Journal of Polymer Science Part A: Polymer Chemistry*, 1997. 35(11): p. 2289–2294.)

FIGURE 8.14

Schematic illustrations of (A) conventional; (B) intercalated; (C) ordered exfoliated; and (D) disordered exfoliated polymer-clay nanocomposite. (From Yano et al., *Journal of Polymer Science Part A: Polymer Chemistry*, 1997, 35(11): p. 2289–2294.)

situ polymerization, the solution-induced intercalation method, and the melt processing method. The resulting polymer-layered silicate composites are ideally divided into four general types: conventional composites, intercalated nanocomposites, and ordered exfoliated and exfoliated nanocomposites, as shown in Figure 8.14 [92].

8.3.2.2 Carbon Nanotubes

The outstanding mechanical, thermal, and electrical properties of carbon nanotubes (CNTs), and their huge aspect ratio, motivated sustained research into their physical properties and potential applications, and a vast literature exists on this topic. Here, only a brief mention is made of the use of CNTs in coating applications and the research carried out by the author's research group. As shown in Figure 8.15, single-walled carbon nanotubes have outstanding mechanical properties, excellent thermal conductivity, and exceptional electrical conductivity, which demonstrates the revolution achieved by replacing micron-sized carbon fibers with carbon nanotubes and reflects the reduction in physical properties as the size of the carbon structure is increased [93].

8.3.2.2.1 Treatment of Carbon Nanotubes The nanotubes are dispersed either by direct mixing of CNTs into epoxy using a disperser or by a sonication method. However, to achieve good dispersion in a polymer matrix and strong interface adhesion between the surrounding polymer chains,

FIGURE 8.15

Comparison of the performance of carbon nanotubes against conventional materials. (From Daniel, L. and M. Chipara. *Carbon Nanotubes and Their Polymer-Based Composites in Space Environment*. September 14–17, 2009.)

carbon nanotubes have to be chemically functionalized (including copolymerization). Defects in nanotubes are important in the covalent chemistry of the tubes, because they can serve as anchor groups for further functionalization or for the covalent attachment of other chemical moieties. Therefore, defects can be utilized as a starting point for the development of the covalent chemistry of nanotubes. An analysis demonstrates that about 5% of carbon atoms in a SWNT are localized at defects [94]. The defects in a tube can be divided into four categories; one growth defect encountered frequently is the Stone-Wales defect, comprised of two pairs of five-member and seven-member rings, referred to as a 7-5-5-7 defect [95]. A Stone-Wales defect leads to local deformation of the nanotube sidewall, thereby introducing extra curvature. The strongest curvature occurs at the interface between the two five-member rings; as a result, addition reactions are most favored at the carbon-carbon double bonds in this region [96]. Removal of the nanotube caps by strong acids—for example, HNO_3 —can result in decoration of the ends with carboxylate groups [94,97–99]. Also, the carboxylate groups can be bonded on defects along the nanotube sidewalls. Typically, around 1%–3% of the carbon atoms of a SWNT are functionalized as carboxylate groups after nitric acid treatment [100].

In addition to defect functionalization, other approaches have been developed to functionalize the CNTs in both molecular and supramolecular

FIGURE 8.16

Functionalization possibilities for SWNTs: (a) defect-group functionalization, (b) covalent sidewall functionalization, (c) noncovalent exohedral functionalization with surfactant, (d) noncovalent exohedral functionalization with polymers, and (e) endohedral functionalization with, for example, C60. For methods (B–E), the tubes are drawn in an idealized way, but defects are found in real situations. (From Hu, H. et al. *Chemical Physics Letters*, 2001. 345(1–2): p. 25–28.)

chemistry. As shown in Figure 8.16, these approaches include defect functionalization, covalent functionalization of sidewalls, noncovalent exohedral functionalization, for example, formation of superamolecular adducts with surfactants or polymers, and endohedral functionalization [100–102].

The covalent functionalization of a nanotube with polymer is considered to be an effective way of improving compatibility and achieving a homogeneous dispersion by direct chemical linkage between the nanotubes and PU [103]. This includes “grafting onto” (directly reacting existing polymers containing terminal functional groups with the anterior functional groups on carbon nanotubes) [104], “grafting from” (growing polymers from carbon nanotube surfaces by in situ polymerization) [105] and in situ polycondensation [106]. Typically, for a PU matrix, the as-treated carboxylic carbon nanotubes are refluxed with thionyl chloride (SOCl_2). After the residual thionyl chloride is removed by vacuum evaporation, the acyl chloride MWNTs (MWNT-COCl) are washed repeatedly with anhydrous THF and dried under vacuum. An amine, for example, *para*-phenylenediamine (PPD), together with pyridine in DMF is added to the flask that contains MWNT-COCl, and the reaction

SCHEME 8.1

Reaction scheme for the synthesis and preparation of PPD-grafted MWNTs. (From Zhao, W. et al. *Macromolecular Materials and Engineering*, 2010. DOI:10.1002/mame.201000080.)

product is stirred under a pure N_2 atmosphere. After the reaction is finished, the solvent is completely removed by vacuum evaporation. The nanotubes are washed with ethanol until the filtrate shows the absence of amine by the titration method [107], and then are dried in a vacuum oven (Scheme 8.1).

8.3.2.2.2 Metal–Nanotube Nanohybrids The interactions between nanotubes and various metals are important in the formation of low-resistance ohmic contacts to nanotubes and other issues such as forming metal or superconducting nanowires on nanotube templates [108–110]. Generally, there are three methods to deposit metal nanoparticles onto a nanotube surface, including electrochemical, chemical, and physical methods, and each offers varying degrees of control of particle size and distribution along the nanotubes [111] (see Figure 8.17).

FIGURE 8.17

SEM images of (a) pristine MWNTs and (b) Ag-doped MWNTs after immersion in an aqueous solution of $AgNO_3$.

FIGURE 8.18

Nanowire network (nanonet) architecture: (a) network above percolation threshold, with pale lines indicating conducting pathways and (b) network conductance versus coverage for a random network of wires and dots. (From Gruner, G. *Journal of Materials Chemistry*, 2006. 16(35): p. 3533–3539.)

8.3.2.2.3 CNT Nanonets, Films, and Sheets To utilize these nanostructured materials in engineering applications, it is crucial to develop processing techniques that are both scalable for producing macroscopic structures and capable of efficiently utilizing nanoscale reinforcement in the as-manufactured composite. Some promising techniques for processing precursors for macroscopic composites are briefly outlined in the following paragraphs.

Two-dimensional carbon nanotube macrostructures offer an opportunity to use carbon nanotubes with random networks of many carbon nanotubes, called *nanonets*, which enable numerous basic electronic functions at low cost [112]. Nanotube sheets (called “nanotube paper” or “buckypaper”) are normally obtained by filtering well dispersed SWNT suspensions, peeling the resulting sheet from the filter after washing and drying, and annealing the sheet at high temperatures to remove impurities [113]. So far, nanotube sheets, fibers, and composites can retain the properties of the individual nanotubes. Buckypaper can be impregnated with resin, including epoxy, bismaleimide, or cyanate ester, and can then be included as a ply or multiple plies within a laminate made up of traditional prepreps. In the resulting molded part, the prepreg acts as the structural component, while the buckypaper with its CNTs imparts thermal and electrical properties [114].

Various room temperature methods for making transparent nanotube films include drop-drying from solvent, airbrushing, and Langmuir–Blodgett deposition. These alternatives, however, present severe limitations in terms of film quality or production efficiency. Nanotube films made by the filtration method are homogeneous and controllable, and surfactants are easily removed. The architecture of a network of nanotubes is illustrated in Figure 8.18. With components that are conductors or semiconductors, a two-dimensional (2D) nanowire network (nanonet) is a conducting medium, with

several attractive attributes, such as electrical conductance, optical transparency, flexibility, and fault tolerance [115].

8.3.2.3 Alumina and Silica

Alumina and silica have been benchmark micron and nanoscale fillers in scratch- and abrasion-resistant nanocomposite polymers, as they are easy to obtain and the surfaces of both silica and alumina feature hydroxyl groups (OH) [116] that can be exploited with silane chemicals to add a reactive group to produce a good chemical interface with the resin [117–119]. According to Zhou et al. [85], the erosion wear mechanism of PUR composites reinforced by Al_2O_3 particles can be described as follows: the matrix is cut apart and torn by eroding particles at sharp angles and high velocity, but the Al_2O_3 particles are worn more slowly than the matrix due to their high hardness, so they protrude progressively more above the worn surface and protect the matrix underneath in the impact direction; meanwhile, cracks begin to initiate at the interface between the Al_2O_3 particles and the matrix, further propagate, and finally lead to removal of the Al_2O_3 particles. A schematic diagram of the entire erosion process is shown in Figure 8.19.

Even without surface treatment, silica and alumina are still demonstrated to improve sharply the hardness and elastic modulus of poly(-ether-ketone) (PEEK) matrices [120]. Figure 8.20 shows that for 10 wt% loading of fillers,

FIGURE 8.19

Schematic diagram of the erosion wear mechanism of composites: (a) beginning of erosion wear; (b) matrix has been ploughed, Al_2O_3 particles protrude, cracks born at the interface; (c) interfacial cracks become extended, and (d) Al_2O_3 particles are de-bonded and eroded away. (From Zhou, R. et al. *Wear*, 2005. 259(1–6F): p. 676–683.)

FIGURE 8.20

Variation of microhardness of nanocomposites as a function of the nanoparticle content in wt%. Variation of (a) Young's modulus E , (b) ultimate tensile stress (UTS), and (c) tensile failure elongation (e) of nanocomposites as a function of particle content in wt%. (From Kuo, M.C. et al. *Materials Chemistry and Physics*, 2005. 90(1): p. 185–195.)

the microhardness is seen to increase steadily from 21.7 Hv to > 30 Hv for silica (15 nm), to 30 Hv for silica (30 nm) and 28 Hv for alumina (30 nm), respectively. The elastic modulus also increases steadily from 3.9 GPa to > 5 GPa for silica (30 nm) and alumina (30 nm) and 4.5 GPa for silica (15 nm). Unavoidably, however, the tensile elongation decreases drastically from 12% for pure PEEK to just around 5% for alumina (30 nm) and silica (30 nm) at only 2 wt% loading. There was then a steady further decline in elongation down to ~4% for 10 wt% loading. At the same 10 wt% loading, the smaller silica particles (15 nm) had a more than linear drop from 12% PEEK to approximately 6%, which is still a dramatic reduction.

For polyurethane (PU)/alumina composites treated with silane coupling agents A-187 and A-1100, the results of erosion tests are shown in Figure 8.21. With increasing content of Al₂O₃ particles, the wear resistances of both composites rose gradually, reaching a maximum and then declined gradually. The peak wear resistance for the A-187-treated composites is 1.14 times that of pure PU when the Al₂O₃ particle content reaches 21 wt%. For the A-1100

FIGURE 8.21

Content of Al_2O_3 particles versus wear resistance in composites. (From Zhou, R. et al. *Wear*, 2005. 259(1–6F): p. 676–683.)

treated composites, the peak wear resistance is 1.25 times that of pure PU when the Al_2O_3 particle content reaches 34 wt%. Beside these results, there are several other good examples of interface works with alumina and polymers used in coatings. One particular work with acrylic-melamine automotive topcoats [121] examines the difference between various hydroxyl and amine functional group additions acting as chain extenders and further improving the mechanical performance. Figure 8.22 shows that the ultimate tensile strength decreases with increased loading of an alumina that had been given an apolar surface treatment (alkylbenzene sulfonic acid and toluene sulfonic acid). However, the introduction of polar and reactive tails on the alumina surface improves the mechanical performance up to levels of approximately 10% before falling off; the hydroxyl functional group (Lewis acid) gives better results than the amine group (Lewis basic) because of the acid–base interaction with acrylic-melamine polymer.

8.3.2.4 Nanodiamond

The use of chemical vapor deposition (CVD) diamond as a coating and diamond powder as a polishing and cutting medium is common; however, their use as a reinforcement is relatively new [122]. Nanodiamond (ND), also known as ultra-dispersed diamond [123], combines the unique properties of a diamond core such as superior hardness and thermal conductivity with a large readily modifiable surface, imparting enhanced mechanical strength, wear resistance, and thermal stability to composite materials even when pristine ND powders with a size of 2–10 nm are physically dispersed in the polymer matrix as reinforcement [123–125]. ND can be obtained in large quantities by detonation

FIGURE 8.22

Relative ultimate tensile strength of composites of alumina particles with different surface treatments and with varying particle volume concentration. (From Hosseinpour, D. et al. *Progress in Organic Coatings*, 2005. 54(3): p. 182–187.)

synthesis in a process that is relatively inexpensive and has broad applicability [126]. Evidence of functional groups such as hydroxyl (OH), amine (NH₂), and carboxyl (COOH) on the surface of detonation-produced diamond offer promise [127] for untreated ND, and the hydrogen functional groups on diamond can be utilized for bio-sensing applications [128]. Purification can be regarded as the first chemical treatment, where ND is heated with concentrated oxidizing acids or other compounds like KNO₃ to remove graphitic, amorphous sp² carbon materials, and metallic impurities [129]. Oxidation of the ND surface can be achieved by air oxidation or treatment with oxidizing mineral acids. Other reactions for the primary functionalization of ND include reaction with gaseous fluorine at elevated temperatures [130] and reaction with ammonia [131], chlorine [132], and hydrogen [133], yielding the functionalized diamond materials (see Figure 8.23). These materials can then be modified in a secondary step with more complex moieties [126]. Recently, Krueger reported a wet chemical method for hydroxylation of the ND surface, which allows for the subsequent grafting of different trialkoxysilanes and further functionalization by covalent bonding [134]. On the other hand, covalent grafting of alkyl and aryl moieties by radical reaction was reported by Nakamura and Tsubota [135,136].

The use of chlorine in this way was also demonstrated by Ando et al. by using the newly chlorinated surface as an intermediary for further functionalization to add both hydroxyl and amine groups which, as previously

FIGURE 8.23

Surface functionalization of nanodiamond yields various covalently modified derivatives with different terminal groups for further surface modification. (From Krueger, A. *Journal of Materials Chemistry*, 2008. 18(13): p. 1485–1492.)

discussed, are suitable for use with polyurethane [137,138]. The first example to integrate ND into polymer matrix has been reported by atom transfer radical polymerization (ATRP) using a “grafting-from” approach [139], which opened up a wide variety of ND–polymer brush materials with controlled dispersibility and functional group reactivity. It is evident that both the hardness and modulus of the polymer matrix (PVA) increase significantly upon the addition of ND [140]. The average value of hardness increases by ~80%; the modulus almost doubles with the addition of 0.6 wt% ND (see Figure 8.24), which suggests that excellent adhesion between the matrix and the functionalized ND particles is the main reason for this marked improvement in mechanical performance.

8.3.3 Techniques for the Production of PU Nanocomposite Coatings

For manufacturing nanocomposites, the crucial step is achieving a well dispersed, largely homogenized mixture at the start. No matter how capable the

FIGURE 8.24

Variation of normalized hardness and modulus plotted as a function of ND content. (From Maitra, U. et al. *Solid State Communications*, 2009. 149(39–40): p. 1693–1697)

manufacturing technique, without this the quality of the resulting sample is likely to be poor. Major preparation methods for polymer nanocomposites include direct blending (including melt blending, solution blending, and emulsion blending), sol–gel, and in situ polymerizations [141,142]. While the majority of these techniques are not suitable for industrial application, the variations in resulting samples produced will help to build a better understanding of how the emergent properties change as a result of structural features. Films and coatings made of randomly distributed CNTs have been shown to possess excellent performance with low sheet resistance and high optical transparency as well as robust mechanical flexibility and thermal stability.

Cast molding is one of the simplest manufacturing processes for nanocomposite materials, whereby a well dispersed suspension is cast in a mould and left to cure and post cure to produce a film (Scheme 8.2). This is an effective method for producing tapes quickly. The disadvantages of this method, however, include nonuniform thickness and unsuitability for production scale-up.

Spray painting is the current method used for aircraft, and aircraft paints include additives that help to improve the viscosity, opacity, and color for spraying. By incorporating nanoparticles into the polymer solution, the viscosity of the solution will increase quickly, making the solution harder to spray. Depending on the weight percentage of nanoparticles added, there may not be adequate wetting of the nanoparticles or other additives by the

SCHEME 8.2

Schematic of the preparation of PU–MWNT nanocomposites. (From Zhao, W. et al. *Macromolecular Materials and Engineering*, 2010. DOI:10.1002/mame.201000080.)

resin, which can contribute to premature paint failure. These are all considerations that must be taken into account when attempting to disperse these particles into a paint matrix [143].

Electrospinning or electrostatic spin coating [144] is a method where a polymer solution or melt is electrically charged and fired as a jet or spray, through a capillary tube or Taylor cone. One of the main advantages of this method is continuous deposition of uniformly sized, homogeneous nanofibers. Nanofibers offer good mechanical properties, including improved surface area-to-volume ratio, increased flexibility and good tensile strength. This method is a possible solution for incorporating carbon nanotubes into nanofibers to improve the electrical properties of the fibers. In theory this could improve the dispersion and alignment of carbon nanotubes. There are inherent disadvantages, and the main issue revolves around how the resulting nanofibers should be used and encapsulated into a paint system. Other issues concern the process of nanofiber production. Typically, a large amount of solvent is required to obtain the correct viscosity for spraying. This can be expensive and potentially harmful if the solvent is toxic. While this method offers good dispersal in the nanofibers, it still requires the carbon nanotubes to be sufficiently dispersed in the original polymer solution.

8.3.4 The Need of a Roadmap

A clear roadmap for turning fundamental laboratory research in polymer nanocomposite and processes into successful innovations for coating applications is needed, such as the one illustrated in Figure 8.25. The development of nanoparticle-filled polymer systems is the core of the roadmap with the development of technology to tailor both nanoparticle–polymer interfaces and nanoparticle dispersions. The roadmap should be focused on existing polymeric systems that have been utilized by industry, but incorporating

FIGURE 8.25

A proposed nanocomposite coating technology roadmap.

diamond, alumina, silicon carbide, CNT, clay, and metallic nanoparticles (e.g., Cu, Ag).

8.3.4.1 Stage 1: Formulation of Coatings

Viable nanoparticle filled polymer systems should be formulated with tailored viscosity and particle distribution to enable the materials to be sprayed for coating and to be moulded or extruded for tape application as well as painting application.

8.3.4.2 Stage 2: Routes to Application

This step investigates materials suitable for spraying and tape-making processes, as well as the painting process.

8.3.4.3 Stage 3: Evaluation of Coatings

The performance of the coatings and tapes must be assessed against sand erosion, rain erosion, and sharp object cuts. The paints need to be assessed against lightning strikes. A suitable water erosion test rig is desperately needed.

8.3.4.4 Stage 4: Demonstration Tests on Articles

The industrial sectors have the responsibility for providing guidance and assessment of the technology for future implementation. The required series of short industrial applications include:

1. Erosion trial test on tapes and paints in rotorcraft environment
2. Erosion trial test on coatings in transport aircraft environment
3. Lightning strike test

The various particles need to be selected to target different applications. For example, while Al_2O_3 and SiC are primarily for sand erosion and sharp-object cutting resistance, diamond particles are chosen due to their high thermal conductivity and high electrical resistivity, which can be potentially used in coating layers that will aid heat conduction for de-icing. Metallic nanoparticles can be used for concocting paint formulations. It needs to be pointed out that a radical improvement in performance does not have to involve a significant increase in cost, for example, diamond particles start at £4 per gram, which equates to £1 to 2 per square meter of coating.

8.4 Recent Advances in Polymer Nanocomposite Coatings for Aerospace Composites

8.4.1 Lightning Strike Properties of Composite Structures

Since many aerospace applications require transparent, durable coatings that will be exposed to charged environments during flight, electrostatic dissipation (ESD) by intrinsic electrical conductivity is necessary. The potential of nanotubes as conducting fillers in multifunctional polymer composites has been successfully realized with a very small loading of 0.1 wt% or less. A variety of applications are being pursued using these conductive composites: electrostatic dissipation, electrostatic painting, electromagnetic interference (EMI) shielding, printable circuit wiring, and transparent conductive coating. The DC electrical resistivity of SWNT-PU composite films was measured by the four-probe method and the results are shown in Figure 8.26. Compared with pure PU film, the electrical resistivity decreased from $10^{13} \Omega \text{ cm}$ (pure PU) [145] to $10^8 \Omega \text{ cm}$ (0.5 wt% MWNTs) and $10^6 \Omega \text{ cm}$ (5.0 wt% MWNTs). Figure 8.26 also shows the required resistivity levels necessary for electrical applications such as electrostatic dissipation, and a 0.5 wt% MWNT loading would be sufficient for ESD applications [15,146–148]. Since such a very low MWNT loading will impart the composite with the required level of conductivity, the base polymer's other preferred physical properties and processability would not be compromised [147].

FIGURE 8.26

(a) Electrical conductivity of SWNT-polycarbonate nanocomposites as a function of nanotube loading, showing typical percolation behavior. Dashed lines represent the lower limits of electrical conductivity required for the specified applications. (b) Electrical conductivity as a function of reduced mass fraction of nanotubes, showing a threshold of 0.11 wt %. (From Ramasubramaniam, R. et al. *Applied Physics Letters*, 2003. 83: p. 2928.)

The new generation of civil aircraft depends heavily on electronic systems to implement safety-critical functions. Because these aircraft may be exposed to high intensity radiated fields (HIRFs) created by radio frequency (RF) emitters based on the ground, in the air, and at sea, civil aviation authorities have become increasingly concerned about the potential for electromagnetic interference (EMI) to these critical civilian aircraft electronic systems. Military aircraft and weapon systems must operate compatibly within an electromagnetic environment that can be even more severe than the civil HIRT environment. For example, aircraft that must take off from and land on naval ships can be exposed to a very intense electromagnetic environment

FIGURE 8.27

The relationship between thickness of carbon nanotube sheet and EMI shielding effectiveness. (From Zhao, W. et al. *International Journal of Smart and Nano Materials*, 2010, in press.)

with electric field strengths exceeding 1000 V/m [149]. There is a linear relationship between sample thickness and EMI SE value (see Figure 8.27); the EMI SE increases from 18.7 dB to 45.5 dB as the thickness of nanotube sheets increases from 68 to 339 μm . With one layer of CNT sheet of thickness 68 μm , the effectiveness of shielding increases dramatically and approaches the target value (20.3 dB) of EMI shielding materials needed for commercial applications [150].

Gou [151] developed specialty paper made of carbon nanofibers and nickel nanostrands as a surface layer on composite panels and explored the potential for replacing existing lightning strike protection materials. The lightning strike tests conducted on these composite panels showed that lightning strike tolerance is correlated with the surface conductivity of composite panels. Figure 8.28 shows the surface damage on these composite panels after a lightning strike. Clearly, the CP-CNFP-1 had the largest damaged area, where $\sim 5.9\%$ of the area of the paper was damaged. The carbon fibers underneath the paper were obviously damaged. However, only $\sim 3.3\%$ and $\sim 1\%$ of the area of the paper were damaged for CP-CNFP-2 and CP-CNFP-3, respectively.

8.4.2 Erosion-Resistance Coatings

Some tests have been performed to assess the effect of nanoparticles on the polymer matrix at an early stage, check equipment suitability, and provide damaged specimens to inspect and help with the determination of damage

FIGURE 8.28
(A) Surface damage of composite panels and (B) damage area and thickness of composite panels after lightning strike test: (a) CP-CNFP-1 ($\sigma = 222$ S/m); (b) CP-CNFP-2 ($\sigma = 31000$ S/m); and (c) CP-CNFP-3 ($\sigma = 34100$ S/m). (From Gou, J. et al. *Composites Part B: Engineering*. 41(2): p. 192–198.)

FIGURE 8.29

Surface damage pattern of (a) 3M 8663 tape, (b) 1% diamond nanocomposite, and (c) commercial defense polyurethane, under close range (25 mm) oscillation sand blasting test repeated for a total of 200 s. Dotted lines roughly indicate the range.

mechanisms. Samples of 1 wt% nanodiamond-reinforced polyurethane have been fabricated [155]. A basic comparison study was used to evaluate the rates and types of erosion that can be obtained with a sand blaster. Pieces of 3M 8663 tape measuring 30×30 , with 1% diamond nanocomposite and commercial defense polyurethane were attached to a section of rigid substrate with curvature to test for erosion at oblique angles.

To accelerate the damage, the nozzle was brought to a distance of 25 mm and the specimens were subjected to twelve 10-s periods in cycles. Figure 8.29(a) shows the 3M tape suffered substantial thinning across the damage area, with complete loss at edges and obvious signs of plastic deformation with comet tailing. The nanocomposite also suffered substantial thinning but only at the edges, that is, with more oblique impact angles and the center still appearing as it had after the early loss of initial materials (see Figure 8.29(b)). The commercial defense PU failed along the top edge; however, material loss was not as great in the center section as in the 3M tape (Figure 8.29(c)). Overall, this was an encouraging result for the nanocomposites as potential materials protecting against hard-particle erosion.

8.4.3 Anti-Icing and De-Icing Coatings

A conventional de-icing heater uses metal foil as the heating element. One of the disadvantages is that there is not a good, durable bond with the protecting layer. The other disadvantage is that heating may not be uniform, resulting in cold spots which retain ice on the airplane, and hot spots which cause the ice to melt and refreeze at different sites. The de-icer also needs to be applied to an irregularly shaped surface in order to heat the surface uniformly. The metal foil heating element in a conventional de-icer can either be flexible but fragile, or strong but inflexible.

FIGURE 8.30
Thermal cycle with different input voltages: stage I, ramp-up; stage II, stabilization; stage III, cool-down.

In this context, a composite heating element has been developed as described here that is both strong and, before curing, flexible. Therefore, it can follow an irregular shape on large surfaces and provide uniform heating on such surfaces. Due to the high electrical conductivity of carbon nanotube sheets, heating is achieved in the thin layer of the heating element (0.038 and 0.045 mm thick in the model heater) without using high voltage. Since the voltage drop across the heater is not high, the thin protection layer can be used without dielectric breakdown. Since the heater can be thin, it is applied directly to the region very close to the surface to be heated. Therefore, the amount of heat accumulated in the composite heater is minimized and the rate of heating can be high despite the low transverse thermal conductivity. Also, the electricity can penetrate through the heating element in the transverse direction despite the low transverse electrical conductivity.

The heater was used in a room environment at different input voltages. The temperature of the heater was monitored by a noncontact IR thermometer. The temperature as a function of heating time was recorded (Figure 8.30). The ramp-up, steady-state, and cool-down temperatures were recorded. If I is the current conducted through the heater, E is the voltage dropped across the heater, P is the power per unit area of the heater, ρ , L , W , and t are the

FIGURE 8.31

Brightness of an individual CNT-based specimen at different heating powers. The brightness of the sample increased exponentially with heating power. The maximum brightness was 110°C, at about 0.78 W.

resistivity, length, width, and thickness of the heater, then the equation relating the required power to heater resistivity and dimensions is

$$P_{LW} = IE = I^2 \rho L / Wt \quad (8.1)$$

Knowing that the heater in Kevlar was 0.038 mm thick and 2.10 cm wide, the distance between the foil in the middle section of the heater was 2.05 cm, and the voltmeter reading was 5 when the resistance was 62.7 Ω ; the conductivity of this particular composite was calculated to be 430 S/m. If a 45.7 μm thick heating element with a conductivity of 616.52 S/m is fabricated with dimensions of 2.46 $\times$ 2.07 cm, with 0.3 W/in² power density at an input voltage of 5 V, according to the above equation, it conducts a current, and voltage drop across the de-icer, as shown in Figure 8.31.

The heating capability of the MWNT films was verified in terms of response time and input power. The MWNT sheets showed a rapid thermal response and stable reversibility when heating the target substrate. Further tests are under development to demonstrate the potential of using MWNT sheets for de-icing applications.

8.4.4 Other Related Characteristic Properties

Various mechanical testing procedures are needed to help determine the effects of particles, their quantities, sizes, and any interface treatment on the final product compared to pure polyurethane. Certain tests are also useful to help elucidate the erosion mechanisms and determine suitable steps to improve performance, which may later involve using a more compliant polymer if increased hardness is detrimental to performance. Strain to failure

and elastic modulus are both properties that require evaluation to characterize the final materials, but they are also useful ways to gauge the quality of a material prior to submitting samples and should be classed as benchmark tests.

The base polymer material has a shore hardness of 90 A. Zoran et al. [152] performed shore hardness testing of a more compliant polyurethane with nano-sized and micro-scale silica and observed a 50% increase of shore hardness with nano-sized silica of up to 50% weight loading, but the micron-sized silica rose slightly to 30% weight loadings and then dropped sharply to almost half that of the pure resin at 50% weight. This corresponds to similar results mentioned earlier, with micro hardness testing of nano-sized silica and alumina PEEK [120].

Similar studies with clay in EPDM [78] saw an increase in hardness with nano-sized clay but an actual decrease of micron-sized clay platelets, but other studies have demonstrated no increase in hardness when modified clays have been added to polyurethane [153] despite an increase in breaking strain of 150%.

A hydrophobic nature of materials may be important both in resistance to climatic moisture and in prevention of ice build-up on blades; the contact angle measurement is a useful method for testing this. Chen et al. [154] looked into the effect of filler loading and surface finish of 12 nm silica on polyurethane using this method along with TEM, AFM, and peel testing. The substrate material that the polyurethane nanocomposite was prepared on had an effect on the density of silica at the surface with the silica seeming to prefer the glass substrate compared to the plastic and tin which resulted in less silica at the surface. They found that a higher loading of silica at the surface resulted in higher surface energy and thus lower bonding, and increased hydrophobic behavior to the water-glycol mixture that was chosen as it would not react with the polyurethane matrix. They also found that higher loadings had smoother surfaces when examined, which they felt was due to the fillers filling gaps; however, this could also be due to higher levels of branching from particles associated with the in situ polymerization method.

8.5 Concluding Remarks

Lightning strike, erosion, ice accretion, and environmental corrosion represent significant safety issues for aeronautical operation. The significance of these concerns is likely to increase as more and more composites are used in modern aircraft. It is important to understand the potentially damaging materials and situations that a coating system undergoes in order to identify those properties that are key to total system performance. New nanocomposites combined with nanoclay, carbon nanotube, nanodiamond, alumina, etc., have shed light on the multidisciplinary nature of protective coatings where major mechanical, physical, and chemical issues need to be addressed together. The developing ability to make uniform nanoscale components and

to integrate them in complex macromolecular structures will allow technologists to have a new level of control on the physical and chemical properties of components of macroscopic materials.

Novel coatings have also been widely developed for advanced polymer matrix systems. Notably, studies on self-healing polymers have demonstrated the repair of bulk mechanical damage as well as dramatic increases in fatigue life [155]. Also, the technology of self-cleaning coatings has developed rapidly over the years [156] and self-cleaning paint is currently available in Europe [157]. Another development direction concerns volatile organic compound (VOC) emissions, because until now aeronautical coatings still have had relatively high solvent content. Fast reacting coatings requiring dual sprays show promise for very low or even zero VOC. Recently, a second generation paint removable systems devised for the A380 superjumbo by Akzo Nobel Aerospace Coatings (ANAC) enabled the topcoat to be quickly removed during maintenance, cutting the required time by up to 40% by avoiding the need to strip to bare metal [158,159].

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