3 Plasma Surface Treatment to Enhance Adhesive Bonding

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3.1 INTRODUCTION

Major industrial sectors such as automotive, aerospace, and others are increasingly employing polymer composites in their load-bearing structural parts, which offers benefits such as being lightweight, good thermomechanical bulk properties, low cost, and recycling [1–4]. Apart from this, the rationale behind the choice of polymeric composites lies in their superior physical, mechanical, and chemical performances, along with higher resistance to corrosion and structural weakening from radiation [5]. The use of adhesively bonded joints in these load-bearing structures is of great interest to the aerospace and automotive industries as compared with mechanical methods (welding, riveting), which generally lead to stress and failure problems.

Structural and specialty adhesives account for about 30% of the total adhesive and sealant market, with uses in many industries [6]. This is because of time and cost savings, high corrosion and fatigue resistance, crack retardance, and good damping characteristics. Adhesive bonds are more effective in assembling composite structures than other mechanical joining methods, as they provide more uniform stress distribution, lower stress concentration, and better fatigue life and corrosion resistance [7]. Any adhesive joint can distribute the applied load over the entire bonded area and is suitable for joining dissimilar materials with low manufacturing cost [8].
It has been established that for successful application of polymeric composite materials to form structural parts using adhesive bonding, they need to have special surface properties such as polarity and high surface free energy (SFE) [9]. A basic requirement for successful bonding is the spreading of the adhesive on the surface of the adherend or substrate [10]. This will occur if the SFE of the adhesive is lower than that of the adherend, but the typical values of SFE are 30–50 mJ/m² for adhesives and about 12 mJ/m² to about 70 mJ/m² for polymers [11]. This shows that although these polymers have found wide suitability for high-end applications, they still have some limitations in achieving a good structural adhesive bond. Several conventional methods such as chemical treatment, thermal treatment, and mechanical treatment are used to modify polymeric surfaces, but they suffer from problems of uniformity, reproducibility, and cost-effectiveness. The need for adequate adhesion by activating the polymeric surface without affecting the bulk properties of the polymer has resulted in the development of plasma surface modification techniques [12], which offer a uniform, reproducible, economic, and environmentally friendly alternative [13]. It has been observed that the polar component of the SFE leading to increased total SFE of the polymer increases significantly due to generation of new functional groups as a result of surface oxidation by reactive species in the plasma [14]. The changes in the physicochemical characteristics and surface morphology of the polymer brought about by plasma result in strong adhesion [15].

3.2 ADHESIVES

The automotive, aerospace, building, biomedical, and other industries have been investigating the use of various types of adhesives and sealants for numerous applications in these industries.

An adhesive or glue is a mixture in a liquid or semiliquid state that bonds items together. Adhesives cure (harden) by either evaporating the solvent or by chemical reactions that occur between two or more constituents [16,17]. The adhesives are classified into different types. A detailed description of different types of adhesives is given in Table 3.1.

The choice of proper adhesive is critical to produce strong and durable bonds [24]. Unlike thermoplastics, thermosetting adhesives do not melt or flow on heating, but become rubbery and lose strength. The molecular chains present in thermosetting adhesives undergo irreversible cross-linking during curing [25]. The most familiar thermosetting adhesives are the family of epoxies. The limitations of other adhesives for the joining of different materials have been solved by epoxy adhesives, and presently these adhesives are widely used.

It is evident from the literature that thermoplastic resins can withstand temperatures comparable to many aerospace graphite–epoxy prepregs (177°C). A common example of an adhesive system found in the automotive industry is a paint coating applied to a polypropylene (PP) bumper bar. However, it requires some pretreatments. Adhesives that have been used successfully in aerospace are, typically, modified epoxy film adhesives with brand names such as FM300 (Cytec Industries Inc.) for both poly(phenylene sulfide) (PPS) [26] and poly(ether ether ketone) (PEEK) [27,28], FM 377 [29], and FM 87 [30]. The building industries require such sealing materials in the form of sealants that have the ability to withstand thermal expansion and contraction while still bonded to the substrate [4,31,32]. Kodokian and Kinloch [33] described the use of a wide range of epoxy- and acrylic-based adhesives for bonding applications: Hysol 9309.3, FM73M, Permabond F241, F245, F246, and V501, and Bostik M890 and M896. An extensive review of adhesives for PEEK–graphite composite bonding is also given in [34], and it was found that FM300 recorded a close second-highest lap shear strength value of 23 MPa to Scotch-Weld structural adhesive film (AF-163-2K) (24.5 MPa) when tested at 25°C. When it comes to the biomedical industry, a study of the adhesion mechanism between human hepatoma cell lines and polymers such as polystyrene, poly(methyl methacrylate), and polycarbonate (PC) is of much importance [35–38]. Researchers [38,39] have made an important observation that the major factor responsible for cell adhesion to polymer substrates is the SFE of the polymer, irrespective of whether the surface has been covered by a protein layer.
### TABLE 3.1
Classification of Adhesives

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General Classification</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermosetting</td>
<td>Cross-linked by strong covalent intermolecular bonds, forming one giant molecule</td>
<td>Epoxies, polyesters, polyimides, phenolics</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td>Molecules of most of thermoplastics combine into long polymer chains alternating with monomer units</td>
<td>Polymides, cyanoacrylates, polyacrylates, poly(vinyl acetate) (PVAc)</td>
</tr>
<tr>
<td>Elastomeric</td>
<td>These consist of long lightly cross-linked molecules</td>
<td>Natural rubbers, silicones, acrylonitrile butadiene (nitrile), neoprene, polyurethane, styrene–butadiene</td>
</tr>
<tr>
<td><strong>On the Basis of Function</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural adhesives</td>
<td>Used to bond structural materials and have the ability to withstand significant loads or stresses</td>
<td>Polyurethanes, polysulfides, polyesters, acrylics, special formulations of cyanoacrylates, anaerobics, epoxy adhesives</td>
</tr>
<tr>
<td>Nonstructural adhesives</td>
<td>Also called holding adhesives, these are not required to support substantial loads but merely to hold lightweight materials in place [18]</td>
<td>Pressure-sensitive tapes, packaging adhesives</td>
</tr>
<tr>
<td><strong>On the Basis of Curing Method</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-Part Adhesives</td>
<td>Adhesives of this type consist of a ready mixture of two components and harden from melt for thermoplastics</td>
<td>Epoxies, urethanes, polyimides</td>
</tr>
<tr>
<td>Heat-activated curing adhesives</td>
<td>Light-activated adhesives are cured under a visible or UV light of appropriate wavelength. Adhesives of this type usually contain photoinitiators to enhance curing reaction</td>
<td>Acrylics, cyanoacrylates, urethanes</td>
</tr>
<tr>
<td>Light/UV-activated curing adhesives</td>
<td>Cured on reacting with moisture present on the substrate surface or in the air</td>
<td>RTV silicones, cyanoacrylates, urethanes</td>
</tr>
<tr>
<td>Moisture-activated curing adhesives</td>
<td>Adhesives of this type do not cure. These materials bond to adherend surfaces at room temperature as low pressure is applied [18]</td>
<td>Self-stick tapes</td>
</tr>
<tr>
<td>Pressure-sensitive adhesives (PSAs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two-Part Adhesives</td>
<td>A two-part adhesive is cured when its two (or more) components are mixed. The components react chemically, forming cross-links of the polymer molecules</td>
<td>Epoxies, urethanes, acrylics, silicones</td>
</tr>
<tr>
<td><strong>Description of Common Adhesives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Description</td>
<td>Advantages</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>Formed by cross-linking highly reactive isocyanates with various polyols and are frequently used for joining</td>
<td>Possess low viscosity, good wettability, and penetrating ability—which help the adhesives to spread over the substrate surface—good cohesive strength, and high impact resistance; good flexibility at low temperatures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Disadvantages</td>
</tr>
<tr>
<td></td>
<td>Pose processing problems that arise due to their reaction with water and their gaseous nature. Limited temperature resistance, sensitive to moisture in cured and uncured states [19]</td>
<td></td>
</tr>
</tbody>
</table>
3.3 ADHESION

Adhesion is a multidisciplinary topic that involves surface chemistry, physics, rheology, polymer chemistry, stress analysis, polymer physics, and fracture analysis [40]. The ASTM [41] defines adhesion as “the state in which two surfaces are held together by interfacial forces which consist of valence forces or interlocking actions or both.” When the adhesion between two surfaces is caused by valence forces, this is called specific adhesion, while when they are held together by interlocking action, this is called mechanical adhesion. Both of these play important roles in understanding the effect of surface preparation on adhesion. These various types of intrinsic forces that may operate across the adhesive–substrate interface are referred to as the mechanisms of adhesion [42].

### TABLE 3.1 (CONTINUED)

<table>
<thead>
<tr>
<th>Classification of Adhesives</th>
<th>Polysulfides</th>
<th>Adhere well to almost all adherends</th>
<th>Require higher humidity for faster cure, show poor elastic recovery; also result in poor creep resistance [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obtained by the reaction of sodium polysulfide with organic dichlorides such as dichlorodiethyl formal and ethylene dichloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyesters</td>
<td>Reaction products of dibasic acids with polyfunctional hydroxyl materials</td>
<td>Often used as hot-melt adhesives, have good resistance to water, nuclear radiation, and biodeterioration [20]</td>
<td>Generally have poor resistance to chemicals. Other undesirable properties include high flammability and tendency to brittleness and crazing [18]</td>
</tr>
<tr>
<td>Acrylics</td>
<td>Synthesized from a wide selection of acrylic and methacrylic ester monomers</td>
<td>Capable of adhering to most metals and polymers [21]. This is due to their low viscosity, good wettability, and penetrating ability that help the liquid to spread over the substrate surface</td>
<td>Possess poor cohesive and shear strengths, low elevated temperature strength, high flammability, and bad odor of uncured adhesive [19]</td>
</tr>
<tr>
<td>Cyanocrylates</td>
<td>Known as instant adhesives or superglues, cyanocrylates are also from the acrylic family tree, but having a completely different cure system</td>
<td>Very rapid curing adhesives; possess excellent lap shear strength and good shelf life [19]</td>
<td>Bond to skin instantly, posing safety risks. Unpleasant fumes, poor peel strength, poor resistance to impact loads, limited gap cure, poor durability on glass, low-temperature resistance (lose strength at about 85°C), and poor solvent resistance [22]</td>
</tr>
<tr>
<td>Anaerobics</td>
<td>Derived from methacrylates (Plexiglas), the basic ingredient in anaerobic adhesives is a special liquid of small molecules that can combine chemically to form a polymer or a group of molecules</td>
<td>Very versatile and are used in a wide variety of applications</td>
<td>Brittle, limited gap filling, cure rate is surface dependent, and very expensive [23]</td>
</tr>
</tbody>
</table>

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3.3.1 MECHANISM OF LIQUID–SOLID ADHESION

During liquid–solid adhesion, there are usually three interfaces involved: the solid–gas interface, the liquid–gas interface, and the solid–liquid interface. There are two conditions that are required to be met when a liquid spreads over a solid surface. Firstly, the SFE of the solid–gas interface must be greater than the combined interfacial energies of the liquid–gas and the solid–liquid interfaces. Secondly, the interfacial free energy of the solid–gas interface must exceed the interfacial free energy of the solid–liquid interface. The adhesion mechanisms between liquid adhesive and solid substrate have been explained on the basis of mechanical interlocking, adsorption, diffusion, and electrostatic theories. These mechanisms have been known to be dependent on the surface characteristics of the materials being used for the automotive and aerospace industries. These theories can be used, solely or in combination with each other, to describe almost any kind of adhesion phenomenon [43].

The mechanical interlocking theory of adhesion essentially proposes the interlocking of the adhesive into the irregularities of the substrate surface as the major source of intrinsic adhesion [42]. According to this theory, good adhesion occurs only when a liquid penetrates into the pores, holes, crevices, and other irregularities of the surface of the substrate, and locks mechanically into the texture of the substrate [44]. Pretreatment methods applied on a surface enhance adhesion [45], as they result in microroughness on the adherend surface, which can improve adhesion strength by providing mechanical interlocking. Beyond mechanical interlocking, the enhancement of adhesion strength is due to the roughening of the adherend substrate. Further, surface roughness increases surface area, improves the kinetics of wetting, and increases plastic deformation for better adhesion [46,47]. The size and shape of the special features created on the surface have an influence on adhesion, providing a tortuous path that prevents separation of the adhesive from the adherend [48]. However, this theory cannot explain the attainment of good adhesion strength between smooth surfaces [42].

The diffusion theory is based on the assumption that the adhesion strength of polymers to themselves (autohesion) or to one another is due to mutual diffusion of macromolecules across the interface, thus creating an interphase [49]. This implies that the molecular chains or chain segments are sufficiently mobile and mutually soluble [50]. To describe the self-diffusion phenomenon of polymers, several theories have been proposed: entanglement coupling [51], cooperativity [52], and reptation [53]. The reptation model has been applied to study tack, green strength, healing, and welding of polymers [54]. Some studies have shown that the interdiffusion phenomenon exists in mobile and compatible polymers and increases intrinsic adhesion. The diffusion theory, however, has found limited application where the polymer and adherend are not soluble or the chain movement of the polymer is constrained by its highly cross-linked, crystalline structure, or when it is below its glass transition temperature [55].

The electrostatic theory of adhesion, as primarily proposed by Deryaguin and coworkers, states that an electron transfer mechanism between the substrate and adhesive, having different electronic band structures, can occur to equalize the Fermi levels [56]. The result is the creation of an electrical double layer (EDL) at the interface [57]. These electrostatic forces at the interface are responsible for resistance to separation of the adhesive and the substrate. Thus, the adhesion depends on the magnitude of the potential barrier at the substrate–adhesive interface [56]. However, this kind of potential barrier does not exist in some cases [58]. This theory could not be widely accepted, because the EDL could not be identified without separating the adhesive bond. Also, as argued by many researchers [59,60], the effect of the EDL on the adhesive bond strength was exaggerated.

The adsorption theory states that adhesion results from intimate intermolecular contact between two materials, and involves surface forces that develop between the atoms in the two surfaces [61]. These forces may be due to physical adsorption—mainly van der Waals forces or secondary forces. These adhesion forces may also be due to acid–base interaction [62,63] or hydrogen bonds [64,65].
To obtain good adsorption, intimate contact must be reached, so that van der Waals interaction or acid–base interaction or both can occur; hence, good wetting is essential. Thus, criteria for good adhesion essentially become the same criteria as for good wetting, although this is a necessary but not sufficient condition [55].

3.3.2 Wetting

The wetting ability of a liquid is a function of the SFEs of the solid–gas interface, the liquid–gas interface, and the solid–liquid interface. The adhesion forces between the liquid and the second material will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material (or the desire to create adhesive bonds) will tend to spread over the material. Interfacial interactions are an important factor in the prediction of adhesion [66]. Liquids with strong cohesive bonds and weaker adhesion forces will tend to bead up or form a droplet when in contact with another material [67]. One way to quantify a liquid’s surface wetting characteristic is to measure the contact angle of a drop of liquid placed on the surface of a substrate.

According to Young’s equation, the interfacial tensions (liquid–vapor: $\gamma_{LV}$, solid–liquid: $\gamma_{SL}$, and solid–vapor: $\gamma_{SV}$) at the three-phase contact are related to the equilibrium contact angle $\theta$ through:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta$$  \hspace{1cm} (3.1)

The contact angle ($\theta$), as seen in Figure 3.1, is the angle at which the liquid–vapor interface meets the solid–liquid interface. The contact angle is determined by the resultant of the adhesion and cohesive forces.

The SFE and the dispersion ($\gamma_S^D$) and polar ($\gamma_S^P$) components for any polymer are calculated using the equation shown:

$$(1 + \cos\theta)\gamma_{LV} = 2\left(\gamma_S^D\gamma_{LV}^D\right)^{\frac{1}{2}} + 2\left(\gamma_S^P\gamma_{LV}^P\right)^{\frac{1}{2}}$$  \hspace{1cm} (3.2)

Firstly, the contact angle of deionized water $\theta$ is measured on the surface. Therefore, in this equation, $\theta$ is the measured contact angle of deionized water where the surface tension of deionized water $\gamma_{LV}$ and its two components, the dispersion $\gamma_{LV}^D$ and the polar $\gamma_{LV}^P$, are known and the two unknowns are $\gamma_S^D$ and $\gamma_S^P$ for the surface. Secondly, the contact angle $\theta$ of formamide is measured on the surface and, consequently, $\theta$ is the measured contact angle of formamide where surface tension of formamide $\gamma_{LV}$ and its two components, the dispersion $\gamma_{LV}^D$ and the polar $\gamma_{LV}^P$ are known and the two unknowns are $\gamma_S^D$ and $\gamma_S^P$ for the surface. Thus, by solving these two equations, the unknowns $\gamma_S^D$ and $\gamma_S^P$ for the surface are calculated. Finally, the total SFE $\gamma_S$ is determined by Equation 3.3:

$$\gamma_S = \gamma_S^D + \gamma_S^P$$  \hspace{1cm} (3.3)

FIGURE 3.1 Contact angle on a solid surface. (From http://home.iitk.ac.in/~kbalani/vl-kb/wetting.html. With permission)
A deeper understanding of the adhesion process is achieved by calculating the thermodynamic solid–liquid work of adhesion ($W_{SL}$) required to separate a unit area of the two phases in contact [69]. The combination of the Duprée expression [70], which assumes that there is negligible liquid surface area change on adhesion to a solid surface [71], and Young's equation [72] leads to an equation that allows prediction of the bonding characteristics of a surface through two experimentally measurable parameters, the liquid surface tension and its contact angle on the solid surface [73]:

$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} (1 + \cos \theta)$$  \hspace{1cm} (3.4)

where:
- $W_{SL}$ is the solid–liquid work of adhesion
- $\gamma_{LV}$ is the surface tension or free energy of the liquid
- $\theta$ is the liquid contact angle on the solid surface

One important factor that influences adhesion strength is the ability of the liquid to spread uniformly on the substrate [74].

For spontaneous wetting to occur:

$$\gamma_{SV} \geq \gamma_{SL} + \gamma_{LV}$$  \hspace{1cm} (3.5)

However, this is an ideal case and is not possible with all polymers.

The tendency of a drop to spread over a flat solid surface increases as the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability [75], as shown in Table 3.2.

### 3.3.3 Polymer–Polymer Adhesive Joint

The science of a polymeric adhesive joint is concerned with two steps: the formation of the adhesive bond and the physical strength of the adhesive bond. As the forces of attraction between the polymeric chains are mainly van der Waals forces, the SFE of a polymer is low. A basic requirement for successful bonding is the spreading of the adhesive on the surface of the adherend or substrate. This will occur if the SFE of the adhesive is lower than that of the adherend, but the typical values of SFE are 30–50 mJ/m² for adhesives and about 12 mJ/m² to about 70 mJ/m² for polymers [11]. Since the SFE of the adhesive can hardly be altered, attempts are made to increase the SFE of the adherend by employing different surface modification techniques. When the polymers are modified by different treatments, polar groups are formed on the polymeric surface. The presence of polar groups on the polymer surface bridges the forces of physical adsorption and chemical adsorption by the formation of covalent bonds with the adhesive, where the covalent bond is the primary force responsible for adhesion. This covalent bond plays a significant role in producing adhesive bonds that are even stronger than the cohesive strength of polymeric materials. Thus, surface treatment is critical in any adhesive bonding operation.

### 3.4 Surface Modification of Polymers

Adhesive bonds are dependent on the chemistry of the interface, and thus control of surface chemistry is critical to bond quality [42,76]. Thus, the most important step in adhesive bonding is surface modification, which not only prevents or removes contaminants that can adversely affect bonding, but also helps in creating chemically active sites on the surface to maximize bond strength. High-performance polymers very often do not possess the desired surface properties for strong adhesive bonding. They are hydrophobic in nature, and in general exhibit insufficient adhesive bond strength due to relatively low SFE [77].
Several conventional methods such as chemical treatment, thermal treatment, and mechanical treatment have been used to modify polymeric surfaces. The different treatment methods such as (1) chemical treatment, (2) thermal treatment, (3) mechanical treatment, and (4) electrical treatment, along with their merits and demerits, are discussed in the following subsections.

### 3.4.1 Chemical Treatment

The influence of chemical treatment on polymers includes surface alteration as well as other morphological changes in the surface layer, such as surface roughness [78,79]. The wetting characteristics of a polymeric surface are enhanced by the introduction of polar groups on the surface when it is treated with a heavily oxidative liquid chemical such as chromic anhydride with tetrachloroethane, chromic acid with acetic acid, or potassium dichromate with sulfuric acid. The polymer surface is then rinsed clean of the etching chemicals and dried. Oxidation may also be carried out with nitrogen oxide, cycloalkyl chromate, potassium permanganate, and sodium hypochlorite. Chlorosulfonation and flame treatment in the presence of a halogen could also be used. Bajpai et al. [80] have reported surface modification of the poly(methyl methacrylate)–poly(vinylidene fluoride) (PMMA–PVDF) blend system under the chemical environment of some organic liquids, namely, benzene, toluene, xylene, and acetone. Comyn et al. [81] reported that although the sulfuric acid–orthophosphoric acid–water treatments were ineffective in treating the surface of PEEK, the addition of 1% potassium permanganate, a strong oxidizing agent, resulted in strong bonds with failure predominantly away from the interfacial zone.

Carbon fiber (CF)-filled PEEK was chemically etched by Davies et al. [82] using a composition of 7 g K₂Cr₂O₇ + 12 g H₂O + 150 g H₂SO₄. This resulted in an increase of adhesive bond strength. Chromic acid etching increases the bondability of a plastic by introducing reactive sites, such as hydroxyl, carbonyl, carboxylic, and −SO₃H groups, to the plastic surface and forming root-like cavities that provide sites for mechanical interlocking. The effect of this treatment varies from substrate to substrate. For example, increasing the etch time and temperature increases only the etch depth when etching PP. On the other hand, both the degree of oxidation and etch depth increase with treatment time for polyethylene (PE). All these reactions take place in vessels under very strict time–temperature–pressure conditions that are difficult to handle and are not feasible for use on an industrial scale. Moreover, they require expensive waste disposal and may also pollute the environment.

### 3.4.2 Thermal Treatment

Thermal treatment plays an important role in modifying the nature and concentration of surface functional groups [83]. Thermal treatments have been used to produce activated carbons with basic character, and such carbons were effective in the treatment of some organic...
Plasma Surface Treatment to Enhance Adhesive Bonding

hydrocarbons [84]. Heat treatment of carbon in inert atmospheres (hydrogen, nitrogen, or argon) could increase carbon hydrophobicity by removing hydrophilic surface functionalities, particularly various acidic groups [85–88].

Thermal treatment also oxidizes the surface of polymers by introducing polar groups [89] such as carbonyl, carboxyl, or amide when the plastics are exposed to a blast of hot air. It also utilizes a free radical mechanism accompanied by chain scission and some cross-linking, which helps in improving the wettability of the surface. Ansari and Wallace [90] reported that the redox properties of polypyrroles were improved with mild heating but were degraded at higher temperatures. Lafdi et al. [91] used heat treatment to alter the physical properties of a nanofiber-reinforced epoxy composite. It was reported that heat treatment up to 1800°C resulted in improved flexural modulus and strength of the nanocomposite, while heat treatment to higher temperatures demonstrated a slight decrease in mechanical properties, likely due to the elimination of potential bonding sites caused by the elimination of the truncated edges of the graphene layers.

3.4.3 Mechanical Treatment

The mechanical abrasion process has been used for surface pretreatment of polymers, because it provides an effective and reliable way of ensuring improvement in adhesion of polymer surfaces [92]. It serves to increase the surface area of the material by roughening the exposed areas prior to adhesive bonding. Surface roughening increases bondability by dramatically increasing the number of mechanical interlocking sites. Mechanical abrasion is carried out by dry blasting, wet blasting, or hand/machine sanding. However, for low SFE plastics, the opposite effect can occur. Silverman and Griese [27] examined a joining method using mechanical fasteners in conjunction with FM300 adhesive for the AS4 CF–PEEK composite. Their findings revealed a comparatively low lap shear strength value of around 17 MPa, when a chromic acid-etch surface treatment was used prior to bonding and aluminum rivets were used to mechanically fasten the joint.

Bhowmik et al. [93] investigated the effect of mechanical polishing prior to surface modification of high-density polyethylene (HDPE) and PP sheets by exposure to dc glow discharge on the SFE and their adhesive joint strength to steel. Mechanical polishing of the HDPE and PP sheets by abrading with 800-grade emery paper prior to glow discharge treatment increased the adhesive joint strengths over those observed in the case of unpolished polymers exposed to glow discharge only. However, the use of prior mechanical polishing increases the joint strength only by a little more than 10%, compared with a five-to-seven-times increase in strength observed as a consequence of exposure to glow discharge of untreated samples. Mechanical processes are operator dependent and labor intensive, produce dust, and are usually only employed in situations with low production volumes. The abrasive materials that are used to remove particulates or residues are hazardous and require disposal [94].

3.4.4 Electrical Treatment

While these traditional procedures are well tested and reliable, they are also time-consuming manual processes. If not properly administered, these techniques can yield poor bond strengths, and can even result in damage to composites that are fabricated with high-modulus fibers [95,96]. They also suffer from problems of uniformity, reproducibility, and cost-effectiveness. The need for adequate adhesion by activating the polymeric surface without affecting the bulk properties of the polymer has resulted in the development of the plasma surface modification industry [12], which offers uniform, reproducible, economic, and environmentally friendly alternatives [13]. Electrical treatment under atmospheric-pressure plasma (APP or normal plasma) [97] and low-pressure plasma (LPP) (glow discharge) [98,99] are popular techniques that have been employed to modify the surfaces of polymers.
3.4.4.1 Electrical Treatment by Generation of Plasma

Electrical treatment by generation of ionized plasma is a suitable technique that is used to modify polymer surfaces without affecting their bulk properties. The term plasma was coined by Irving Langmuir. A distinct fourth state of matter, it is broadly defined as partially or wholly ionized gas with approximately equal numbers of positively and negatively charged particles. Ionized means that at least one electron is not bound to an atom or molecule, converting the atoms or molecules into positively charged ions. Plasma contains active species, such as electrons, ions, radicals, photons, and so on, that initiate chemical and physical modifications on the polymer surface [100,101] by making the surface electrically conductive and strongly responsive to electromagnetic fields. Ions and electrons present in plasma break polymer chains due their high kinetic energy [102]. At the same time, free radicals in plasma modify the chemical properties of polymers by introducing functional groups on the polymer surface [103,104]. The interactions of the polymer with the plasma also alter the molecular weight of the surface layers by scissoring, branching, and cross-linking. Thus, when the material whose surface is to be modified is placed in the plasma chamber, these energetic particles collide with the surface of the material and cause molecular disruptions. This leads to a drastic modification of the structure and properties of the surface [105], although this depends on the composition of the surface and the gas used. There are mainly two types of plasmas: (1) thermal plasma and (2) cold plasma.

Thermal plasma is used to destroy solid, liquid, and gaseous toxic halogenated and hazardous substances or to generate anticorrosion, thermal barrier, antiwear coatings, and so on. Cold plasmas are used for surface modifications of materials, ranging from simple topographical changes to the creation of surface chemistries and coatings that are radically different from the bulk material [106]. Cold plasmas are generated by glow discharges at reduced pressures of 0.01–10 torr, and pressure of around 1 torr is sufficient for surface modification of polymers [107]. LPP using glow discharge and APP using corona discharge are convenient methods for surface modification of polymers enhance their adhesion characteristics.

3.4.4.1.1 Low-Pressure Plasma (Glow Discharge)

A glow discharge is an ionized gas consisting of equal concentrations of positive and negative charges and a large number of neutral species. It is generated by applying a potential difference (of a few hundred volts to a few kilovolts) between two electrodes that are inserted in a cell filled with a gas (an inert gas or a reactive gas) at a pressure ranging from a few millitorr to 10 torr [108]. Due to the potential difference, electrons emitted from the cathode by the cosmic radiation are accelerated away from the cathode, and give rise to collisions with the gas atoms or molecules (excitation, ionization, dissociation). The excitation collisions give rise to excited species, which can decay to lower levels by the emission of light. The ionization collisions create ion–electron pairs. The ions are accelerated toward the cathode, where they release secondary electrons. These electrons are accelerated away from the cathode and can give rise to more ionization collisions. In its simplest form, the combination of secondary electron emission at the cathode and ionization in the gas gives rise to self-sustained plasma [109], as shown in Figure 3.2.

Due to the various collision processes occurring in the plasma, a large number of different plasma species are generated: electrons, atoms, molecules, several kinds of radicals, several kinds of (positive and negative) ions, excited species, and so on. These active species activate the surface of the polymer and cause the surface layer to be oxidized or cross-linked, enabling it to become significantly active for participation in adhesion. There are different variants of glow discharge plasma:

- Direct current (dc)
- Radio-frequency (RF)
- Microwave (MW)

In dc glow discharge, a continuous potential difference is applied between cathode and anode, giving rise to a constant current. However, this setup gives problems when one of the electrodes is
Plasma Surface Treatment to Enhance Adhesive Bonding

noncon ducting as, due to the constant current, the electrodes become charged up, which may lead to burnout of the glow discharge. This problem is overcome by applying an alternating voltage between the two electrodes, as in the capacitively coupled radio-frequency (CCRF) glow discharge. The charge accumulated during one half of the cycle is neutralized by the opposite charge accumulated during the next half-cycle in the RF glow discharge. RF plasmas can be sustained at lower gas pressure, and are characterized by higher ionization efficiency as compared with dc plasmas.

The majority of plasma processing has been carried out at low pressure in a vacuum chamber and is viewed as a necessary processing requirement. In principle and practice, however, APPs provide a critical advantage over widely used LPPs, as they do not require expensive and complicated vacuum systems. Without a vacuum system, the costs of materials processing are reduced substantially and materials issues related to vacuum compatibility are not of concern. Therefore, the use of APPs is beginning to greatly expand the current scope of materials processing.

3.4.4.1.2 Atmospheric-Pressure Plasma

APPs [97] are gaining greater acceptance than other plasma techniques, because they are easy to integrate into existing production lines and can treat specific parts of a substrate selectively [110,111]. Also, in contrast to most corona treatments (and dielectric barrier discharges) [112], APPs are not limited to flat and thin substrates, but can also be used for large three-dimensional objects. APP shows significant potential for improving interfacial adhesion. It minimizes downstream wastes from subsequent surface preparation. Since it can be automated, it reduces process variability while increasing reliability and processing rates [113].

APP is the name given to the special case of plasma in which the pressure approximately matches that of the surrounding atmosphere—the so-called normal pressure. It is generated by alternating current (ac) excitation (corona discharge and plasma jets). By means of high-voltage discharge (5–15 kV, 10–100 kHz) in the plasma jet, a pulsed electric arc is generated. A process gas, usually oil-free compressed air flowing past this discharge section, is excited and converted to the plasma state. This plasma then passes through a jet head to arrive on the surface of the material to be treated. The jet head is normally at earth potential and, in this way, the potential-carrying part of the plasma stream is largely held back [114]. In addition, it determines the geometry of the emergent beam. It is
observed that during APP discharge, ion bombardment physically and chemically removes oxides and reducible compounds from surfaces and many other contaminants are vaporized. In addition, gas molecules are accelerated to an excited state, releasing active free radicals and ultraviolet (UV) energy [115]. Free radicals activate chemical reactions on surfaces, inducing intermolecular cross-linking. When compared with corona discharges, APPs produce significantly more homogeneous and uniform surface activation across material surfaces, and increase the microroughness of surfaces, with introduction of active species.

### 3.5 EFFECT OF PLASMA TREATMENT ON PHYSICOCHEMICAL PROPERTIES OF POLYMERS

Many researchers have documented well that plasma treatment of polymer surfaces not only increases the polarity of the polymer surfaces, but also results in surface roughening [116–118]. These surface properties, such as polarity and roughness, play an important role in successful application of polymers to form structural parts using adhesive bonding [116,119].

The presence of polar groups is readily established by determining SFE through contact angle measurements [120]. According to Williams et al. [121], adhesion is correlated with the fraction of the polymer surface sites that are oxidized and converted into active functional groups. This physicochemical change brought about on the polymer surface is determined by x-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy. The change in surface morphology on the polymer surface is measured by atomic force microscopy (AFM) analysis. Further, it is worthwhile to note that the physicochemical change on the surface of polymers plays an important role in contribution to adhesion strength.

#### 3.5.1 CONTACT ANGLE MEASUREMENT AND SURFACE FREE ENERGY DETERMINATION

Pelagade et al. [122] studied the effect of low-energy (300 eV) argon plasma treatment on the surface of PC. They observed that the SFE increased from 38.5 mJ/m² to 74.9 mJ/m² on increasing the treatment time, as shown in Figure 3.3. The corresponding water contact angle decreased from 63° to 17°.

Pandiyaraj et al. [98] studied the effect of dc glow discharge air plasma on poly(ethylene terephthalate) (PET) films. It was observed that the contact angle on the untreated PET surface was...
86.2° for distilled water and decreased by 50% after plasma treatment. The SFE of plasma-modified PET films increases on increasing the exposure time, as shown in Figure 3.4a. It reaches a maximum value at 15 min of exposure time, and thereafter tends to saturate. This may be due to lack of any further change in the oxygen content incorporated onto the surface. Figure 3.4a clearly demonstrates that the total SFE of the PET film attained a higher value when the film was exposed to

![Graph](image-url)

**FIGURE 3.4** Variation of the (a) total SFE and (b) polar component of PET film with time of exposure to dc glow discharge plasma treatment at different discharge potentials. (From Pandiyaraj, K.N. et al., *J Phys.: Conf. Ser.*, 208, Paper ID: 012100, 1–7, 2010.)
higher discharge potential compared with lower potentials. A similar kind of trend was observed in
the increase in polar components, as shown in Figure 3.4b.

Kitova et al. [123] studied the RF plasma treatment of PC substrates, and found that all RF
plasma treatments led to an increase in the polar component of SFE of PC. Narushima and Ikeji
[102] used oxygen plasma to improve the adhesion strength at Cu–PEEK interfaces. It was observed
that the water contact angle on the untreated PEEK surface was 98°, which decreased to 62° and
66°, respectively, after pulsed oxygen plasma and conventional oxygen-plasma treatments. They
concluded that both pulsed oxygen plasma and conventional oxygen plasma introduced hydrophilic
oxygen functional groups that resulted in an increase in SFE of the polymer.

Iqbal et al. [124] investigated the adhesion performance of CF- and glass fiber (GF)-reinforced
PPS after surface modification with APP. It was observed that surface modification by APP resulted
in a substantial increase in the polar component of SFE of these materials, as shown in Table 3.3. In
the case of CF-reinforced PPS composite, the increase in SFE was 52% after the plasma treatment.

Lommatzsch et al. [125] used an APP jet to activate PE samples. The presence of polar func-
tional groups on the polymer surface was revealed by contact angle measurements, where it was
found that the water contact angle on an untreated PE surface was 93.3°, which decreased to 21.6°
after air-plasma treatment.

Arpagaus et al. [126] found that a plasma exposure time of 0.14 s effectively improved the wetta-
bility of HDPE and copolyamide (Co-PA) powders. The water contact angle was reduced from more
than 90° (untreated powder) down to 65° for HDPE and to 76° for Co-PA powder as a consequence
of O2–Ar-plasma treatment, indicating a more hydrophilic surface. The total SFEs increased by a
factor of 1.5, showing an increase from 31.2 mJ/m² to 47.9 mJ/m² for HDPE and to 44.9 mJ/m² for
Co-PA.

Bhatnagar and coworkers [116,127] used low-pressure air–N2 plasma under RF glow discharge as
well as APP to alter wetting, chemical, and morphological characteristics of PEEK. It was observed
that the contact angles of deionized water and formamide on the PEEK surface decreased sig-
nificantly when the surface of the PEEK was modified by LPP and it decreased more with APP
treatment.

It was also interesting to note that the primarily polar component of the SFE of PEEK increased
on its exposure to both LPPs and APPs, while the change in the dispersion component of the SFE of
PEEK was relatively small. Thus, an increase in the polar component of SFE results in an increase
in the total SFE of PEEK. It was observed that the SFE of the as-received PEEK was 51.1 mJ/m²,
and increased after surface modification to the corresponding highest value of 70.7 mJ/m² obtained
in this study when PEEK was exposed to APP for 30 s, as shown in Table 3.4. However, exposure to
LPP increased the SFE only to 60 mJ/m² for an exposure time of 120 s.

Consequently, the increase in the total SFE of PEEK is dominated by the polar component
(Table 3.4). It is, therefore, apparent that APP is capable of increasing SFE more as compared
with LPP.

### Table 3.3

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>γ_l(mJ/m²)</th>
<th>γ_t(mJ/m²)</th>
<th>γ_s (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated CF–PPS composite</td>
<td>24.7</td>
<td>22.9</td>
<td>47.6</td>
</tr>
<tr>
<td>Untreated GF–PPS composite</td>
<td>26.3</td>
<td>17.7</td>
<td>44.0</td>
</tr>
<tr>
<td>Plasma-treated CF–PPS composite</td>
<td>55.9</td>
<td>16.6</td>
<td>72.5</td>
</tr>
<tr>
<td>Plasma-treated GF–PPS composite</td>
<td>52.9</td>
<td>17.6</td>
<td>70.5</td>
</tr>
</tbody>
</table>

3.5.2 X-ray Photoelectron Spectroscopy Analysis

XPS analysis of O₂–Ar-plasma-treated HDPE powders revealed the formation of oxygen functional groups on the surface, such as C–O–C (alcohol or ether), O–C=O (acid or ester) and C=O (aldehyde or ketone). These polar groups enable interaction with water through hydrogen bonds, and are responsible for higher powder wettability [126].

XPS analysis of untreated PET, and that treated under RF glow discharge using pulsed argon and oxygen plasmas, shows that the C1s spectra could be decomposed into three components: C–H at 285.0 eV, C–O at 286.5–286.8 eV, and C=O at 288.9–289.1 eV. But, the pulsed Ar and O₂ plasma treatments led to a decrease in the relative concentration of the C–H group and an increase in the relative concentration of the C–O and C=O groups [128].

Narushima and Ikeji [102] compared the effects of pulsed oxygen plasma and conventional oxygen plasma on the surface of PEEK for its surface metallization with Cu. The C1s spectrum of PEEK film can be resolved into three main components: 285.0 eV (C–H group), 286.4 eV (C–O group), and 287.4 eV (C=O group) [129]. The relative intensities of the C–H, C–O, and C=O components of untreated PEEK film are 75%, 25%, and 5%, respectively. Both pulsed and conventional oxygen-plasma treatments decrease the relative intensity of the C–H group and result in the formation of a new functional group, COO, with relative intensities of 1% and 5%, respectively, as listed in Table 3.5. This is in accord with an increased oxygen:carbon (O:C) ratio.

Kim et al. [130] exposed a polyimide (PI) surface to Ar–N₂ plasmas after KOH treatment. The change in the surface functionalities of the PI was studied by XPS analysis. The chemical composition of the untreated sample was determined to be 73.1% C, 20.6% O, and 6.3% N from the integrated peak signal intensities, as shown in Figure 3.5a. After the KOH and Ar–N₂ plasma treatments, the chemical composition of the PI surface changed to 62.4% C, 21.4% O, and 12.5% N (Figure 3.5c), indicating an increase in formation of polar groups on the surface.

### Table 3.4
Surface Free Energy Values and Its Polar and Dispersion Components of PEEK

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment Time (s)</th>
<th>(\gamma^s) (mJ/m²)</th>
<th>(\gamma^p) (mJ/m²)</th>
<th>(\gamma_s) (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated PEEK</td>
<td>0</td>
<td>4.3</td>
<td>46.8</td>
<td>51.1</td>
</tr>
<tr>
<td>LPP-treated PEEK</td>
<td>30</td>
<td>24</td>
<td>29</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>30</td>
<td>26.2</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>36</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>34</td>
<td>23</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>31</td>
<td>20</td>
<td>51</td>
</tr>
<tr>
<td>APP-treated PEEK</td>
<td>30</td>
<td>54</td>
<td>16.7</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>52</td>
<td>16</td>
<td>68</td>
</tr>
</tbody>
</table>


### Table 3.5
Percentage Content of Each Component

<table>
<thead>
<tr>
<th>Sample</th>
<th>C–H</th>
<th>CO</th>
<th>C=O</th>
<th>COO</th>
<th>O:C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated PEEK</td>
<td>75</td>
<td>25</td>
<td>5</td>
<td>—</td>
<td>0.17</td>
</tr>
<tr>
<td>Conventional oxygen plasma-treateed PEEK</td>
<td>68</td>
<td>26</td>
<td>6</td>
<td>5</td>
<td>0.23</td>
</tr>
<tr>
<td>Pulsed plasma-treated PEEK</td>
<td>69</td>
<td>25</td>
<td>6</td>
<td>1</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Surface studies on PET film exposed to dc glow discharge air plasma indicate that polar groups are created on the treated surface [98]. This was analyzed from the XPS C1s high-resolution spectra for both the untreated and dc glow discharge air plasma-treated samples, as shown in Figure 3.6a and b. The spectrum of untreated PET is composed of four main components at 285 eV (component C1), 286.43 eV (component C2), 288.95 eV (component C3), and 291.37 eV (component C4), which may be attributed to C–C, C–O, O=O, and π–π* shake-up satellite in phenyl groups, respectively (Figure 3.6a) [117,131,132]. The spectrum of plasma-treated PET film (Figure 3.6b) also shows components C1, C2, and C3, and additional peaks at 286.76 (component C5), 288.10 eV (component C6), and 286.0 (component C7), which may be attributed to C–OH and/or C=O–O–H, –C=O, and C–N groups [131].

The XPS C1s spectra (Figure 3.7) show significantly higher oxygen peaks when PEEK is exposed to APP using air as the process gas as compared with LPP using air–N\textsubscript{2} as the process gas, indicating extensive oxidation of the polymer surface [116]. The XPS C1s spectrum (Figure 3.7b) of LPP-treated PEEK shows a new peak at 289.0 eV (COO group) (which is not present in the untreated PEEK), along with peaks at 285.0 eV (C–H group), 286.5 eV (C–O group), and 287.9 eV (C=O group). The C1s peak of APP-treated PEEK (Figure 3.7c) can also be deconvoluted into four components: 285.0 eV (CH group), 286.5 eV (C–O group), 287.9 eV (C=O group), and 289.0 eV (COO group), but with higher concentrations of all the three functional groups, C–O, C=O, and COO, as is evident from Table 3.6.

### 3.5.3 Atomic Force Microscopy Analysis

According to some investigators [133–135], changes in surface morphology on polymer surfaces also play an important role in improving adhesion through a process known as mechanical interlocking. Various researchers have studied polymer surfaces by AFM to investigate the topographical changes on the surface of polymers when they are exposed to plasma.

The variation in surface roughness after the surface treatment of PI films was determined using AFM [130].
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The untreated surface of the PI showed a root mean square surface roughness ($R_{rms}$) of 1.42 nm, as shown in Figure 3.8a. After KOH + Ar–N$_2$ plasma treatment, root mean square surface roughness rose to 28.52 nm, as shown in Figure 3.8b.

Pandiyaraj et al. [117] examined the topography of untreated PET films and of those exposed to dc glow discharge air plasma by AFM. It was observed that the surface of untreated PET film was relatively smooth (Figure 3.9a), but after plasma treatment, the surface of the PET film showed rough morphology, as shown in Figure 3.9b.

**FIGURE 3.6** XPS spectra of (a) untreated PET and (b) plasma-treated PET. (From Beamson, G., and Briggs, D., *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, John Wiley, Chichester, UK, 1992.)
When PC is exposed to low-energy Ar plasma, the roughness of the PC sample increases, as shown in Figure 3.10b, which helps in the enhancement of its adhesion property [122].

O’Kell et al. [136] have examined by AFM the topography of untreated PE surfaces and those exposed to RF glow discharge under air and nitrogen gases at 13 MHz. It was observed that both plasmas caused the polymer surface to roughen, with nitrogen plasma treatment having a more pronounced effect. AFM studies by Gupta et al. [132] on RF glow discharge-exposed polyester films
revealed that the polymer surface became progressively rougher on exposure to glow discharge Ar plasma followed by O₂ exposure, while the virgin film had a relatively smooth surface.

Studies using AFM carried out by Bhatnagar et al. [116] also show that exposure to plasma results in significant transformation on the polymer surface. After the LPP treatment with air–N₂, the surface of the PEEK showed a rough morphology, as shown in Figure 3.11b, and after APP treatment using air, there was a further increase in surface roughness, as is evident from Figure 3.11c. This apparent increase in surface roughness results in improvement in wettability and bond strength.

3.5.4 ADHESION CHARACTERISTICS OF SURFACE-MODIFIED POLYMERS

The work of adhesion increases with the increase in SFE, which results in higher adhesive joint strength [10].

Williams et al. [121] observed that the lap shear strength and crack delamination resistance of CF–epoxy composites increased by 50% for surfaces prepared by helium–oxygen plasma activation instead of solvent wiping and abrasion. Zhang et al. [137] used air plasma to modify PPS film to improve interfacial adhesion and mechanical properties of PPS–GF cloth composites. They observed that tensile strength and notched impact strength of plasma-treated PPS–GF cloth (50:50) composite increased by 11% (from 248.49 MPa to 275.70 MPa).

Iqbal et al. [124] compared the tensile lap shear strength of PPS–CF-bonded joints before and after APP treatment with neat epoxy adhesive and nanofilled epoxy adhesive. The joint strength
increased from 6.1 to 21.5 MPa after APP treatment, resulting in a more than three times improvement in the adhesion properties of the composite joint after the plasma treatment. Analysis of failed surfaces of untreated PPS–CF composites revealed that the failure was essentially interfacial between composite and adhesive, but APP treatment resulted in cohesive failure of the substrate material.

Bhatnagar and coworkers [127] observed that the tensile lap shear strength of PEEK bonded with epoxy adhesive was significantly influenced by surface modification of PEEK under APP. The result revealed that the tensile lap shear strength of adhesive joints increased from 0.5 MPa to 4.00 MPa after LPP treatment using air–N₂ gas and further increased to 8.00 MPa after APP treatment with air. The fractured surfaces of untreated, LPP-treated, and APP-treated PEEK revealed that APP treatment resulted in a shift of locus of failure from the adhesive–substrate interface to within the adhesive or substrate material. This is in accord with the 15 times increase in the joint strength as compared with untreated PEEK.

FIGURE 3.9  AFM micrographs of (a) untreated PET film and (b) plasma-treated PET film. (From Pandiyaraj, K.N. et al., Surf. Coat. Technol. 202, 4218–4226, 2008.)
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FIGURE 3.10 AFM photomicrograph of (a) untreated PC and (b) Ar plasma-treated PC. (From Pelagade, S. et al., *J Phys.: Conf. Ser.* 208, Paper ID: 012107, 1–8, 2010.)
FIGURE 3.11  AFM micrographs of (a) untreated PEEK, (b) low pressure plasma-treated PEEK, (c) atmosphere pressure plasma treated PEEK [116].
3.6 SUMMARY

Surface modification of polymers on exposure to plasma results in the formation of polar groups on the polymer surfaces. This leads to an increase in the polar component of SFE, which further results in an increase in total SFE. As a result, the wettability of the polymer surface increases, resulting in better spreading of the liquid resin (adhesive) and increasing work of adhesion due to polar groups, which could form covalent bonds with the resin. The resin solidifies by cross-linking occurring due to hardener. Also, the high temperature generated during exposure of the polymer surface to plasma and, in particular, to APP, raises the surface temperature to a level that exceeds the glass transition temperature ($T_g$) of the polymer, which could create micropits on the polymer surface and make the surface rough. Thus, both SFE and surface roughness, which play a significant role in increasing the joint strength, have been found to increase manifold by modifying the polymer surface on exposure to plasma, especially APP.

ACKNOWLEDGMENTS

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