Progress in Adhesion and Adhesives
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The current book constitutes Volume 4 in the series “Progress in Adhesion and Adhesives” initiated in 2015. Volume 3 (published in 2018) in this vein was based on 12 review articles published initially in 2017 in the journal *Reviews of Adhesion and Adhesives* (RAA) by recognized experts and world-class active researchers in the wide domain of adhesion science and adhesive technology. The sole purpose of RAA is to publish concise, critical, illuminating and thought-provoking review articles on any topic within the broad purview of Adhesion Science and Adhesive Technology. Volume 2 (published in 2017) documented 14 review articles published originally in 2016 in RAA addressing a number of topics of current interest. The premier Volume 1 (although we did not designate it as Volume 1 as we had no crystal ball to prognosticate the future of this series) was the result of 13 review articles originally published in RAA in the year 2014.

The first three volumes were warmly received and had served the intended purpose and this motivated us to bring out the current Volume 4. We have received excellent comments from many members of the adhesion community and this provided ample justification for making these books available. These hardbound books provide an easily accessible resource for critical information on a number of topics of current interest and relevance in the broad domain of Adhesion Science and Adhesive Technology. It should be stressed here that the authors of the review articles endorsed cheerfully the idea of bringing out these hardbound books.

With the information being published at an ever-increasing rate, critical review articles serve an excellent purpose for anyone wishing to stay informed about the latest developments on a topic of his/her interest. As a matter of fact, anyone embarking on research in an area should start with a critical review article.

The rationale for bringing out Volume 4 was the same as was applicable to its predecessors, i.e., the RAA has limited circulation so this set of books should provide broad exposure and wide dissemination of valuable information published on many and varied aspects of Adhesion & Adhesives in RAA.

The chapters in this Volume 4 follow the same order as the review articles published initially in RAA in the year 2018. The subjects of these 9 review articles fall into the following areas.
O Adhesion to wood and wood bonds.
O Adhesive joints.
O Adhesion in microelectronic packaging.
O Surface modification.
O Contact angle, wettability and surface free energy.

It should be pointed out that in 2018 the reason why only 9 review articles were published was that some review articles were very long and the total number of pages printed had to be maintained.

The topics covered include: Adhesion phenomena in microelectronic packaging; adhesives for wood and lignocellulosic materials; adhesion to wood and lignocellulosic materials; adhesively bonded lap joints having bi-adhesive and modulus-graded bondlines; adhesion between compounded elastomers; applications of contact angle measurements in pharmaceuticals and foods; oxygen or ammonia plasma treatment of polyolefin surfaces; surface free energy determination of powders and particles; wood bonds; and dispersion adhesion forces between macroscopic objects.

Now comes the pleasant task of acknowledging all those who were instrumental in making this book available. First and foremost, I would like to profusely thank the authors of review articles for their whole-hearted support and enthusiastically endorsing the idea of bringing out Volume 4 as they strongly felt that this series of books was an alternative, but very useful, medium to make the information contained in these review articles to a much wider audience. Also, thanks to Martin Scrivener (publisher) for conceiving the idea of publishing this series of books and for his steadfast support in this book project.

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Adhesion Phenomena Pertaining to Thermal Interface Materials and Solder Interconnects in Microelectronic Packaging: A Critical Review

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Abstract
High performance and diverse power computing needs in desktop, server, communication, automotive, and artificial intelligence microelectronic sectors demand microprocessors with different form factors and intricate package designs. For such complex package architectures, semiconductor chips in addition to microprocessor, such as in-package memory, transceivers or a combination of both are essential to attain maximum performance. Integrated Heat Spreader (IHS) assembly with thermal interface material (TIM) layers plays a vital role in providing heat dissipation for these integrated circuit chips and aids them to perform with maximum efficiency for a long duration. Additionally, for Ball Grid Array (BGA) semiconductor packages, interfacial adhesion quality of solder attach material is very critical in determining package quality and reliability. There are numerous challenges associated with developing and optimizing such an IHS assembly process and solder attach material for high volume manufacturing with good throughput, quality and yield. Here we provide a comprehensive review of the adhesion mechanisms and challenges of polymer TIMs to IHS-metal interface and various techniques proposed in the literature to enhance their adhesion. Complexities involved in solder attach adhesion including material selection and chip assembly interaction are reviewed in detail as well.

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1.1 Introduction

Integrated Heat Spreader (IHS) assembly is an integral part of a microelectronic package to accomplish efficient thermal dissipation from one or more semiconductor chips and to attain overall device thermal performance [1–5]. State-of-the-art IHS assembly process is used in various application sectors including desktop, server, communication, automotive, and artificial intelligence. In an assembly process, semiconductor chips or dies are first placed on an organic or ceramic substrate. Front layer interconnect and an underfill layer are further used to hold the dies mechanically. Furthermore, an IHS is glued on the substrate to protect the die and aid with its heat dissipation [6–8]. During IHS assembly, a thermal interface material (TIM) is placed or dispensed on the surface of the die and an adhesive or sealant material is further applied and cured on the organic substrate layer (motherboard) to mechanically hold the IHS in place. A TIM layer is placed between the die and the IHS referred to as TIM₁ and between IHS and heat sink referred to as TIM₂ as shown in Figure 1. A Ball Grid Array or BGA package is a form of surface mount technology (SMT) that is being used increasingly for integrated circuits. It has become one of the most popular packaging alternatives for high input/output devices in the industry. Apart from the improvement in connectivity they offer, BGAs have other advantages. They offer a much lower thermal resistance between the silicon chips than the quad flat pack devices. This allows heat generated by the integrated circuit inside the package to be conducted out of the device on the PCB faster and more effectively. The whole bottom surface of the device can be used on a BGA as compared to just the perimeter on a Land Grid Array (LGA)

Figure 1.1 Schematics of multiple thermal architectures. (a) Designs typically used in laptops without an IHS (b) Architectures used in desktop, server and high-end gaming applications with an IHS. I- Heat Sink; II- TIM₁; III- IHS; IV- TIM₂; V- Silicon Die; VI- Underfill; VII- Substrate; VIII- Solder Ball [Adapted from [8]].
package. BGA packages have solder balls pre-attached to the bottom of the substrate, hence resulting in a higher stand-off height compared to LGA packages.

Thermal efficiency and reliability of TIM\textsubscript{1}, TIM\textsubscript{2} and solder balls define the performance of a microelectronic package and its long-lasting characteristics depend a lot on the interfacial adhesion between the layers [9]. In this review, focus will be mainly on the adhesion characteristics of these materials due to their quintessential role in the microelectronic packaging. This review will be divided into two sections excluding the Introduction. Section 2 provides an overview of the thermal interface material and its interfacial adhesion phenomena. Section 3 on the other hand is devoted to the solder joint adhesion characteristic and its dependence on the material quality and assembly process.

1.2 Polymer Thermal Interface Material – Metal Interface Adhesion Phenomena

1.2.1 Basics of Thermal Interface Material Adhesion

Shown in Figure 2 is a simple graphical representation of a microelectronic package resistance network. The key temperatures of interest include $T_j$ or $T_{j\max}$ which refers to the maximum junction temperature in the device, $T_c$ which refers to the IHS temperature, $T_{\text{sink}}$ which refers to the heat sink temperature, and $T_a$ which refers to the local ambient air temperature. Total thermal resistance which depends on the interfacial adhesion can be described as two components: junction to IHS surface resistance or package thermal resistance and heat sink surface to ambient resistance or system thermal resistance. The maximum allowable junction temperature is one of the key factors that limits the power dissipation capability of a device. The maximum power that a device can dissipate, also referred to as thermal design power (TDP), can be written as

\[
TDP = \frac{(T_{j\max} - T_a)}{\Psi_{ja}}
\]

\[
TDP = \frac{(T_{j\max} - T_a)}{(\Psi_{jc} + \Psi_{ca})}
\]

Figure 1.2 Classical example of a one-dimensional resistance network [Adapted from [10]].
\[ \Psi_{jc} + \Psi_{ca} = \frac{(T_{j_{max}} - T_a)}{T_{DP}} \]  

In other words, TDP is the maximum amount of heat that a processor can generate for a thermally significant period while running real applications. \( \Psi_{ja} \) is the overall thermal resistance, \( \Psi_{jc} \) is the package thermal resistance and \( \Psi_{ca} \) is the system thermal resistance.

If we consider only the package level thermal resistance, equation (3) can be re-written as,

\[ \Psi_{jc} = \frac{(T_{j_{max}} - T_c)}{T_{DP}} \]  

Thermal impedance in a package is represented universally in industry as \( R_{jc} \) and is measured as package thermal resistance (\( \Psi_{jc} \)) under uniform power times the area of the silicon die \( (A_{die}) \) as shown in equation (5).

\[ R_{jc} = (\Psi_{jc})_{\text{uniform power}} \times A_{die} \]  

Poor adhesion of the TIM layer has a huge impact on the junction temperature, increasing \( R_{jc} \) and, therefore, impacts TDP leading to poor power capability of a microelectronic device.

Real TIMs in a semiconductor package look like as shown in Figure 3. Real TIMs have a finite bondline thickness (BLT) and at the interface have voids/delamination because of their inability to completely wet the surface. From Figure 3 it can be inferred that the total thermal impedance (\( R_{TIM} \)) of a real TIM can be written as

![Figure 1.3 Cross-sectional illustration of a TIM layer [Adapted from [8]].](image-url)
Adhesion Phenomena Pertaining to Thermal Interface Materials and Solder Interconnects

\[ R_{\text{TIM}} = \frac{\text{BLT}}{k_{\text{TIM}}} + R_{c1} + R_{c2} \] (6)

where \( R_{c1} \) and \( R_{c2} \) represent the contact resistances of the TIM at the silicon-TIM and TIM-metal interfaces, respectively. There is a great drive in the semiconductor industry to decrease the \( R_{\text{TIM}} \) as much as possible to provide efficient thermal dissipation on high-end packages. One way to do this is by increasing the thermal conductivity of the TIM (\( k_{\text{TIM}} \)) using novel materials and process optimization; however, it will be of no use if the TIM fails to adhere to the surface initially or the adhesion bond weakens over a period of time. Both these failures lead to quality issues either during manufacturing impacting yield and productivity or in the field during use condition affecting product users. Customer returns because of these types of quality issues are becoming a norm these days and hence understanding the fundamentals of adhesion bonds and the root cause of adhesion failures is very critical.

1.2.2 Current Status of Thermal Interface Materials and their Bonding Mechanisms

With the recent developments in TIMs, a Polymer Thermal Interface Material (PTIM) is preferred over a Solder Thermal Interface Material (STIM) due to its inherent cost benefits and comparable thermal performance to STIM [11, 12]. IHS attachment process, in particular, can be performed in two stages: room temperature assembly and high temperature curing. Room temperature assembly is, however, not sufficient enough to bond the PTIM/STIM and sealant with IHS as these materials are not cured. Both sealant and PTIM/STIM need to be cured at high temperature (~150 °C to 180 °C) with pressure on top of these to achieve their targeted material properties and BLT. Polymer to IHS bonding is caused by a combination of different adhesion mechanisms such as physical adsorption, mechanical interlocking, and chemical bonding [13–17]. Physical adsorption forces are a resultant of interatomic and intermolecular interactions due to the van der Waals bonds. On the other hand, mechanical interlocking is brought about by surface roughness of the substrate; however it is debatable whether enhancement in adhesion strength is due to mechanical interlocking or increase in the effective area through secondary bonding [18]. Primary chemical bonds are one order of magnitude stronger than secondary chemical forces such as van der Waals force (Table 1). The primary bond type also includes acid-base theory of adhesion which is very popular and has been studied extensively on various surfaces including polymers [19–21]. By increasing the number of bonds across the interface, polymer-IHS metal bonding could be enhanced considerably.

Chemists tend to associate adhesion with the energy liberated when two surfaces meet to form an intimate contact characterized as an interface as shown in Figure 4. In other words, adhesion may be defined as the energy required to dismantle the interface between two materials. Physicists and engineers describe adhesion in terms of forces, with the force of adhesion being the maximum force exerted when two adhered materials are separated. Many theories on the mechanisms of adhesion are usually attributed to adsorption, chemical bonding and mechanical interlocking all of which play significant roles in interfacial
bonding. The energy required to separate the polymer from a metal surface is a function of the adhesion level i.e. interactions at the interface, but it also depends on the mechanical and viscoelastic properties of the polymeric material.

Modern multi-chip packages have inherent manufacturing variability in chip stacks including IHS flatness, die stack-up gaps and die dynamic warpage affecting TIM1 and TIM2 adhesion and BLTs. This, in turn, affects the Rjc (equation 5) and the package reliability. Listed in Table 2 are some of the commercially available TIM1/TIM2 materials which exhibit unique adhesion property.

### 1.2.3 Chemical Bonding

The adhesion results from molecular contact between polymer and substrate due to surface forces. For these forces to develop, the polymer must make an intimate contact with the substrate surface. The process of establishing a continuous contact is termed as wetting which can be measured by contact angle. The prerequisite for wetting is a contact or wetting angle of less than 90 degrees. A complete spontaneous wetting occurs when the contact angle is zero degrees. Schematic illustration of good and poor wetting is presented in

Table 1.1 Bonding energy range for different types of bonds [22].

<table>
<thead>
<tr>
<th>Category</th>
<th>Bond type</th>
<th>Bond energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Bond</td>
<td>Ionic</td>
<td>600–1100</td>
</tr>
<tr>
<td></td>
<td>Covalent</td>
<td>60–700</td>
</tr>
<tr>
<td></td>
<td>Metallic</td>
<td>110–350</td>
</tr>
<tr>
<td></td>
<td>Brönsted acid-base interaction</td>
<td>Up to 1000</td>
</tr>
<tr>
<td>Secondary Bond</td>
<td>Hydrogen bonds</td>
<td>Up to 40</td>
</tr>
<tr>
<td></td>
<td>Van der Waals bonds</td>
<td>Up to 40</td>
</tr>
</tbody>
</table>

Figure 1.4 Pattern of surface effects determining the overall adhesion [Adapted from [23]].
Table 1.2 TIM materials widely used in industry and are commercially viable.

<table>
<thead>
<tr>
<th>TIM materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td>1. Conform to surfaces&lt;br&gt;2. Fail cohesively, depending on polymer chemistry</td>
<td>Physical movement and delamination failure mode</td>
</tr>
<tr>
<td>Adhesives</td>
<td>1. Conform to surfaces&lt;br&gt;2. No physical movement or migration</td>
<td>1. Low thermal conductivity&lt;br&gt;2. Cure process required&lt;br&gt;3. Delamination failure mode&lt;br&gt;4. Not recoverable</td>
</tr>
<tr>
<td>Aligned Carbon Fibers</td>
<td>1. Very high thermal conductivity&lt;br&gt;2. Easy to handle&lt;br&gt;3. No physical movement or migration</td>
<td>1. High pressure required to compress&lt;br&gt;2. Not recoverable</td>
</tr>
<tr>
<td>Gap Pads/Elastomers</td>
<td>1. Easy to handle&lt;br&gt;2. Fill larger BLT gaps&lt;br&gt;3. May be recoverable</td>
<td>1. High contact resistance&lt;br&gt;2. Low thermal conductivity in general</td>
</tr>
</tbody>
</table>

Figure 5. Wetting is favoured when the substrate surface tension (in mN/m), also known as the surface free energy (in mJ/m²), is higher than that of the adhering polymer. Low surface energy polymers, therefore, easily wet the high surface energy substrates such as metals and glass. On the other hand, substrates with low surface energy such as polyethylene, fluorocarbons, etc. will not be wetted.

Surface tension is an important factor that determines the ability of a polymer coating to wet and adhere to a substrate. The ability of a coating to wet a substrate has been shown to be improved by using solvents with lower surface tensions. Wetting may be quantitatively defined with reference to a liquid drop resting in equilibrium on a solid surface (Figure 5). The smaller the contact angle, the better the wetting. When $q$ is zero, the liquid wets the
solid surface completely at a rate depending on the liquid viscosity and the solid surface roughness. The equilibrium contact angle for a liquid drop sitting on ideally smooth, flat, and nondeformable surface is related to various interfacial tensions by Young’s equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$  \hspace{1cm} (7)$$

Where $\gamma_{lv}$ is the surface tension of the liquid in equilibrium with its own saturated vapor, $\gamma_{sv}$ is the surface free energy of the solid in equilibrium with the saturated vapor of the liquid, and $\gamma_{sl}$ is the interfacial tension between the solid and the liquid. For spontaneous wetting to occur, the surface tension of the liquid must be lower than the surface free energy of the solid. It is also possible for a liquid to spread and wet a solid surface when $\theta$ is greater than zero, but this requires the application of a force to the liquid. The ranges of van der Waals forces and the hydrogen bonds are extremely short for this purpose. For optimum adhesion it is, therefore, absolutely essential to ensure good wetting by the coating material applied, thus creating ideal conditions for causing the film forming agent molecules to approach the substrate. The condition for good wetting is always fulfilled whenever the surface free energy of the substrate is higher than that of the liquid coating material. Such a requirement can easily be fulfilled when coating metals because of their high surface free energy. With various nonpolar plastics such as polyethylene or polypropylene, with surface free energy values less than 30 mJ/m², it is not possible to achieve good adhering coatings because of the inferior wettability without appropriate surface treatments. The surface tension values of the involved materials, the liquid coating and the solid substrate, are most important for substrate wetting. Figure 6 and Table 3 highlight the surface tension in mN/m or surface free energy in mJ/m² of some of the commercially available metals and polymer materials.

It is interesting to note that the polarity of the substrate and possible surface structures (porosity, roughness) will also influence the adhesion mechanism. For example, for surfaces such as wood, the surface tension will not be the same across the whole surface and will vary. Additional surface irregularities can be due to contamination of the surface, which will then cause wetting problems in the form of craters in some areas. Finally, there is also a time aspect. The surface free energy of the substrate is constant, but the surface tension of the liquid phase changes due to solvent evaporation and cross-linking reactions. If, in this process, the surface tension of the liquid exceeds that of the substrate, dewetting can occur, if the film viscosity is still low enough. When a polymeric
Figure 1.6 Surface tension of molten metals at their melting points [Adapted from [25]].

Table 1.3 Surface tension of commercially available polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyyperfluoropropylene</td>
<td>16</td>
</tr>
<tr>
<td>Polyytetrafluoroethylene (Teflon)</td>
<td>18.5</td>
</tr>
<tr>
<td>Poly(dimethyilsiloxane)</td>
<td>24</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>31</td>
</tr>
<tr>
<td>Polyyystyrene</td>
<td>34</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (acrylic)</td>
<td>39</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>40</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (polyester)</td>
<td>43</td>
</tr>
<tr>
<td>Poly(hexamethylene adipate) (nylon)</td>
<td>46</td>
</tr>
</tbody>
</table>
coating is applied on a substrate, a chemical reaction takes place between the two materials i.e. the substrate as well as the coating. It is often desirable to modify the substrate to ensure reactivity at the interface by removing contamination and/or introducing functional groups. This simplified view of the interfacial or interphase bonding neglects physical forces between the two materials, which are influenced by surface roughness. For a comprehensive characterisation of coatings, surface analysis of the substrate (chemical as well as topographic) and thermal analysis of cured polymeric coating materials are of great importance.

Due to the higher bonding energy of the primary bonds in comparison to secondary bonds, working on different types of primary bonds has been more attractive for researchers. Various types of primary bonds, such as ionic and covalent at different interfaces have been reported in the literature. For instance, bonding of brass and rubber occurs by curing with the existence of sulfur due to the creation of polysulfide bonds [26]. Using coupling agents, such as adhesion promoter molecules, is one of the most interesting approaches for interfacial chemical bonding. These molecules are able to make a bond with both polymer and metal [27, 28]. The most common adhesion promoters are silane-based molecules. Examples of silane-based adhesion promoters are listed in Table 4.

Schuberth et al. [29] used 2,2’-Spirobi[4H-1,3,2-benzodioxasilin] and 2-(3-aminopropyl)-2-methyl-4H-1,3,2-benzodioxasilin as twin monomers in order to improve the polymer-metal bonding by introducing chemical bonding between the two. In their work, they considered the interaction of chemical adhesion promoter versus surface treatments on steel-fiber reinforced polymer (FRP) and aluminum-FRP as shown in Figure 7. Interestingly, it was concluded that using these two techniques together was not generally more effective than the individual ones, and surface treatment should be adjusted for the purpose and application.

It is definite that all the mechanisms mentioned above can affect adhesion and thus bond strength. It is also undisputed that the individual mechanisms of adhesion only make significant contributions if the prerequisites have been met. If one endeavors to establish

<table>
<thead>
<tr>
<th>Adhesion promoter</th>
<th>Organic structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethoxyvinylsilane</td>
<td>(CH₂)=CHSi(OCH₃)₂⁺</td>
</tr>
<tr>
<td>(3-Chloropropyl)trimethoxysilane</td>
<td>Cl(CH₂)₃Si(OCH₃)₃</td>
</tr>
<tr>
<td>(3-Mercaptopropyl)trimethoxysilane</td>
<td>HS(CH₂)₃Si(OCH₃)₃</td>
</tr>
<tr>
<td>(3-Aminopropyl)diethoxymethylsilane</td>
<td>H₂N(CH₂)₃Si(OC₂H₅)₂</td>
</tr>
<tr>
<td>(3-Aminopropyl)triethoxysilane</td>
<td>H₂N(CH₂)₃Si(OC₂H₅)₃</td>
</tr>
<tr>
<td>(3-Aminopropyl)trimethoxysilane</td>
<td>H₂N(CH₂)₃Si(OCH₃)₂⁺</td>
</tr>
<tr>
<td>Triethoxy-(3-ureidopropyl)silane</td>
<td>H₂NCONH(CH₂)₃Si(OC₂H₅)₃</td>
</tr>
<tr>
<td>Triethoxy-(3-methacryloyxpropyl)silane</td>
<td>CH₂=C(CH₂)₃COO(CH₂)₃Si(OCH₃)₂⁺</td>
</tr>
</tbody>
</table>
the causes of interactions, numerous theories are available in the literature [30–33]. The explanations range from mechanical attachment of the coating on the cavities and fissures in the substrate (mechanical anchoring) and attachments of film forming agent molecules by diffusion or contact charges and the creation of mirror forces through interactions of polar functional groups, hydrogen bonds or chemical links between the coating and the substrate as illustrated in Figures 8 and 9. Figure 9 shows curves and ranges of the potential energies of van der Waals forces as well as hydrogen bonds as the causes for adhesion. Van der Waals forces are orientation forces (dipole-dipole), induction forces (dipole/induced dipoles) and dispersion forces. Assuming a suitable chemical structure and an appropriate substrate there are also effective hydrogen bonds.

Figure 1.7 (a) Surface roughness of steel and aluminum according to different surface treatments. Bonding strength of (b) Steel-FRP and (c) aluminum-FRP determined by shear tension test [Adapted from [29]].
1.2.4 Mechanical Interlocking

Lee and Qu studied the effect of surface roughness by presenting the outcome of different types of oxidation on interfacial fracture toughness [34]. In their study, it was shown that copper as a function of oxidation time from exposure to the environment creates different oxidized forms. Within the first 30 seconds of copper exposure, pebble-like cuprous oxide (Cu$_2$O) was formed on the surface with an approximate thickness of 0.2 μm. After 2 minutes, needle-shape cupric oxide (CuO) was formed. Formation of cupric oxide causes interfacial (adhesion) failure mechanism in the polymer coating (Figure 10).

Schaubroeck, et al. exposed a polymer resin surface to KMnO$_4$/NaOH solution for different time periods to roughen the surface by means of etching [35]. By controlling the time of exposure, surface roughness was controlled and after that surfaces were treated by polydopamine according to the method described by Lee et al. [36]. Afterward, copper deposition was carried out on polydopamine (DOPA)-modified and non-modified etched surfaces. Peel strength of the deposited copper on non-modified Epoxy Cresol Novolac (ECN) resin substrates increased by an increment in surface roughness. Moreover, it shows that lower electroplating bath temperature leads to higher peel strength in comparison to higher temperatures as indicated in Figure 11.

Figure 1.8 Physical and chemical bonding of polymer coatings to the metal surface [Adapted from [23]].
On both polydopamine modified substrates as well as non-modified surfaces, peel strength does not have a linear correlation with surface roughness. This result has a striking similarity with Schuberth et al. work which showed that employing both adhesion promoter and surface roughness does not necessarily lead to higher bond strength of metal-polymer bonds in comparison to their individual effect [29].
1.2.5 Weak Boundary Layer

According to a theory proposed by Bikerman, adhesion failures occur due to the presence of a weak layer at the interface between the adhesive and target surface as illustrated in Figure 12 [37]. This theory suggests that the root cause of adhesion failure is the cohesive failure within the weak boundary layer. One of the common weak layers is the hydrocarbon contamination on the target surface [38]. Plasma surface treatment is one of the well-known ways to remove hydrocarbon layer from the surface [39].

Jang et al. investigated the nonconductive film (NCF)-SiO$_2$ adhesion improvement by oxygen plasma cleaning [40]. Applying the oxygen plasma to the oxidized silicon wafer causes removal of the hydrocarbons and increase in silanol groups and hydrophilicity of SiO$_2$ surface. However, strikingly, surface roughness decreased after plasma treatment in comparison with non-treated surfaces and due to this plasma treatment could not enhance the adhesion despite increment in surface energy. However, de-ionized water (DIW) rinse was applied after surface plasma cleaning. This step could change the surface roughness during plasma treatment due to the presence of hydroxyl groups on the oxidized silicon surface [41, 42]. With DIW rinse step, NCF-SiO$_2$ bond strength was improved as shown in Figure 13.

In another study, Coulon et al. carried out plasma surface treatment on the polymer resin and then covered the surface with 1 μm thick evaporated aluminum film [43]. It was demonstrated regardless of the roughness of the surface, plasma treatment brought about surface energy and adhesion strength increments (Figure 14). X-ray photoelectron spectroscopy (XPS) analysis of treated and non-treated polymer resin surfaces revealed that atmospheric plasma created reactive carbonyl groups and metal-carbonyl bonds led to higher adhesion strength [44, 45].

1.3 Ball Grid Array Solder Attach Adhesion Phenomena

Ball grid array packages have solder balls pre-attached to the bottom of the substrate, hence resulting in a higher stand-off height compared to land grid array packages. This higher
stand-off height and improved planarity of the package have been shown to positively affect the temperature cycle performance of the electronic devices [46]. The adhesion/joint quality and reliability of these solder joints and the yields during the surface mount process heavily depend on the material and process selections. The materials involved in the ball attach process are solder sphere, flux, or solder paste. The solder sphere selection determines the strength and reliability of the joint and hence affects its performance under stress and temperature that the devices go through in the field. The flux or solder paste serves to clean the oxide on the solder sphere and the pad on the substrate and attaches the solder sphere through a metallurgical joint.

### 1.3.1 Solder Alloy Selection

Tin-silver-copper alloys are widely used as a lead-free alternative in the semiconductor packaging industry. This is because they possess an attractive combination of wettability to the pad surface, good mechanical properties, microstructural stability and availability [47]. However, the melting range of tin-silver-copper (SnAgCu, also known as SAC) alloys is...
high and requires a typical reflow peak temperature of 245 °C. This leads to higher warpage of the package during assembly and may lead to poor joint formation or adhesion [48]. Since Sn is a reactive species, the same intermetallic compounds are formed with both Cu and Ni surfaces during solder/substrate interaction between all common Sn-based solders such as Sn-Ag-Cu, Sn-Cu, and Sn-Bi alloys [49]. With a Cu surface, these alloys form Cu$_3$Sn and Cu$_6$Sn$_5$ as can be seen in the phase diagram that these two are the stable intermetallic compositions in the temperature range of interest [50]. With a Ni surface, these alloys primarily form Ni$_3$Sn$_4$ and it can be seen that this is one of the stable compositions in the phase diagram and forms at the lowest temperature upon cooling among all intermetallics [51]. When Cu is present in the solder, even in much lower amount than Sn, (Cu, Ni)$_6$Sn$_5$ intermetallic is observed as well.

Figure 1.14 (a) Surface energy evolutions on different surfaces before and after atmospheric plasma treatment, (b) adhesion strength of physical vapor deposited Al on top of the un-treated and plasma treated composites and resin [Adapted from [43]].
Once the joint is formed, it is important that the adhesion holds or the joint survives through mechanical shock and severe thermal changes due to operation of the device as well as external changes in temperature [52]. Under mechanical shock, the primary mode of failure is cracking along the intermetallic layer as seen in Figure 15. This is primarily because at high strain rates, the yield strength of the bulk solder increases drastically making the intermetallic layer the weaker portion of the joint [53]. This is referred to as strain-rate sensitivity. It has been found that a decrease in elastic modulus, which is modulated primarily by the composition of the solder, and a decrease in yield strength can help in increasing the overall toughness of the joint during shock, for example SAC105 showed better shock resistance than SAC405 [54]. A lower silver content was found to be generally associated with higher ductility and lower strength of SAC solders in the 0-5% range [55]. The other method to improve shock resistance would be to change the nature and properties of the intermetallic layer itself. This has been achieved by addition of Ni to SAC alloys for example [52]. The effect of Ni addition, in the right proportion, was found to decrease intermetallic thickness or growth through void reduction and also through increasing the liquidus temperature of the solder [56, 57].

Under thermal cycling, however, the crack originates and propagates through the body of the solder [52]. The crack nucleation sites include the interfaces between the intermetallics and the bulk solder and the grain boundaries of the bulk solder created by localized recrystallization reactions due to differential plastic strain stored within the solder [59]. The crack growth has been proposed to be an intergranular propagation along the recrystallized network of high angle grain boundaries as illustrated in Figure 16 [59, 60]. Due to the dependence of recrystallization on the critical strain energy, higher strength alloys were shown to be beneficial, however, this could also result in poor drop shock performance as discussed earlier.

Sn-Bi solders are lower melting alternatives to SAC solders. It was found that Sn-Bi solders wetted Au/Ni/Cu surface better than bare Cu or bare Ni [61]. In addition, the

![Figure 1.15](image)

**Figure 1.15** An example of a typical failure mode of solder joint (SAC 405) under mechanical shock or high strain rate deformation [Adapted from [58]].
interfacial tension between the liquid solder and substrate decreases with an increase in Bi content leading to better wetting at higher Bi concentrations [61]. The relationship between wettability, surface energy and adhesion/joint strength has been discussed [62]. One study found that a Sn-30Bi-0.5Cu alloy had a much lower contact angle or superior wettability to an SAC305 solder [63]. However, a composition beyond the eutectic concentration of Bi (58%) leads to embrittlement due to the presence of Bi-rich phase [64]. In addition, once the Sn is depleted for intermetallic compound formation, a Bi-rich layer forms adjacent to the interface leading to potential weakness in the solder joint [65].

1.3.2 Flux Selection

Flux type, composition and quantity play a crucial role in controlling the adhesion of the solder to the pad. In addition, they also might modulate the adhesion of other materials such as the underfill (though not directly relevant to second-level interface), when a no-clean flux is used [66]. Fluxes used for soldering in the microelectronics industry including the ball attach process fall into two major categories: no-clean and water washable. No-clean fluxes do leave a residue while any water washable flux can be removed by washing with water, which is typically heated and sprayed. However, no-clean flux residues are hydrophobic in nature and cannot be water washed but these are tolerated since they are nonconductive and noncorrosive [67, 68]. The flux reactions with the substrate pad and the solder sphere are much more than just oxidation-reduction and involve acid-base, co-ordination and adsorption type reactions as well. Most fluxes form salt and water with metallic oxides and the salt further helps in promoting solder wetting [69].

In general, for proper adhesion, fluxing of lead-free solders such as SAC alloys is more challenging than lead containing solders. This has been attributed to 3 different factors: 1.

![Figure 1.16 Intergranular crack propagation during thermal cycling of an SAC alloy [Adapted from [60]].](image)
Tin salt that forms at high temperatures is harder to clean than lead salt, 2. Higher flux activity is needed to boost the wetting of an SAC solder leading to more side reactions, and 3. Higher reflow profile is needed for SAC compared to an eutectic Sn-Pb solder. There are other challenges caused by lead-free solder alloys other than SAC alloys, prevalent in the industry today. Low temperature solders such as Sn-Bi need fluxes with a lower activation temperature and highly oxidizable alloys such as the ones containing Zn need a flux with a high oxygen barrier capability or needs to be reflowed under an inert atmosphere [67]. Hence modern fluxes need to have a superior compatibility to lead-free solders based on factors such as superior thermal stability, etching ability, and a temperature range of activity that is compatible with the melting range of the solder. This often necessitates custom development based on solder alloy package/board pad surface finish selection.

1.4 Summary

In this review paper, a detailed overview of interfacial adhesion phenomena of the polymer layers to a metal surface is given. Various bonding mechanisms which play a key role in polymer to metal bonding are discussed in detail. For optimum adhesion, it is absolutely essential to ensure good wetting. Ideally, for good substrate wetting the surface tension of the polymer material should be lower than the surface tension of the substrate. The quality and durability of polymer to metal bonding are directly related to the nature of adhesion. Many theories influencing the mechanism of interfacial adhesion including adsorption, chemical bonding and mechanical interlocking are discussed. The energy required to separate the polymer from a metal surface also depends on the properties of the polymer material. It is definite that all the mechanisms mentioned could modulate the adhesion and thus the bond strength.

Novel ideas and procedures to enhance polymer to metal bonding and to mitigate adhesion failures are provided which include chemical surface modification and plasma treatment. According to Schuberth et al. [29] and Schaubroeck et al. [35] surface chemical modification and adhesion promoters used in combination on the metallic surface do not necessarily enhance the bond strength significantly compared to employing them individually on the surface. In other words, efficacy of adhesion promoters depends on the surface and it is more effective on smoother surfaces. In another section, the effect of plasma treatments of polymer substrates is reviewed. Jang et al. [40] studied the adhesion phenomena of SiO₂ substrates using oxygen plasma treatment with and without de-ionized water treatment. Coulon et al. [43] measured the adhesion strengths on carbon/epoxy composite surfaces treated with atmospheric plasma. Remarkably, from these two works, it becomes clear that there is a difference in applying plasma treatment on oxidized silicon surfaces as opposed to polymer surfaces. In Jang et al. work [40], it was shown that plasma treatment on SiO₂ showed no enhancement in its surface roughness and did not add any value to bond strength. Use of de-ionized water after plasma treatment helped to improve bond strength drastically with the formation of Si(OH)ₓ bonds. But on the other hand, Coulon et al. [43] demonstrated that plasma treatment of the polymer surface, regardless of its roughness, would help PVD coated aluminum bond strength.
To assemble latest technology BGA microelectronic packages with improved reliability and performance has been one of the challenging tasks for semiconductor industries. It involves mounting solder balls onto the land side of the substrate. The adhesion and survivability of solders depend heavily on selection of solder spheres and flux materials. The melting range of the solders has a significant effect on package warpage and its bonding phenomena. Sn-Ag-Cu or SAC solders are the common choice for lead-free solder spheres and it has been found that an increase in the silver content leads to superior thermal cycling survivability but poor shock survivability and vice versa. Bi tends to increase the strength of the solder and Bi containing low melting solder is available, however, it can lead to embrittlement of the joint. Fluxes fall into no-clean and water washable categories and selection needs to be made here based on application and tolerability. Fluxing SAC solders is much more challenging when compared to lead based solders for several reasons and the flux choice needs to be made suitably as well with regards to activation range, thermal stability and oxide-removal capability.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{die}}$</td>
<td>Area of a Semiconductor Chip</td>
</tr>
<tr>
<td>BGA</td>
<td>Ball Grid Array</td>
</tr>
<tr>
<td>BLT</td>
<td>Bond Line Thickness</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>Cuprous Oxide</td>
</tr>
<tr>
<td>CuO</td>
<td>Cupric Oxide</td>
</tr>
<tr>
<td>DIW</td>
<td>De-ionized Water</td>
</tr>
<tr>
<td>ECN</td>
<td>Epoxy Cresol Novolac</td>
</tr>
<tr>
<td>FRP</td>
<td>Fiber Reinforced Polymer</td>
</tr>
<tr>
<td>IHS</td>
<td>Integrated Heat Spreader</td>
</tr>
<tr>
<td>$k_{\text{TIM}}$</td>
<td>Thermal Conductivity of the Thermal Interface Material</td>
</tr>
<tr>
<td>LGA</td>
<td>Land Grid Array</td>
</tr>
<tr>
<td>NCF</td>
<td>Non-Conductive Film</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
</tr>
<tr>
<td>PTIM</td>
<td>Polymer Thermal Interface Material</td>
</tr>
<tr>
<td>$R_{c1}$</td>
<td>Contact Resistance of the TIM at the Silicon to TIM Interface</td>
</tr>
<tr>
<td>$R_{c2}$</td>
<td>Contact Resistance of the TIM at the TIM to Metal Interface</td>
</tr>
<tr>
<td>$R_{jc}$</td>
<td>Thermal Impedance at the Junction to IHS Surface</td>
</tr>
<tr>
<td>SMT</td>
<td>Surface Mount Technology</td>
</tr>
<tr>
<td>STIM</td>
<td>Solder Thermal Interface Material</td>
</tr>
<tr>
<td>TIM</td>
<td>Thermal Interface Material</td>
</tr>
<tr>
<td>TIM$_1$</td>
<td>Die to IHS Thermal Interface Material Layer</td>
</tr>
<tr>
<td>TIM$_2$</td>
<td>IHS to Heat Sink Thermal Interface Material Layer</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Ambient Air Temperature</td>
</tr>
<tr>
<td>TDP</td>
<td>Thermal Design Power</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Integrated Heat Spreader Temperature</td>
</tr>
</tbody>
</table>
$T_j$ Maximum Junction Temperature  
$T_{\text{sink}}$ Heat Sink Temperature  
XPS X-ray Photoelectron Spectroscopy  
$\psi_{ja}$ Overall Thermal Resistance  
$\psi_{jc}$ Package Thermal Resistance  
$\psi_{ca}$ System Thermal Resistance

References

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Influence of Silicon-Containing Compounds on Adhesives for and Adhesion to Wood and Lignocellulosic Materials: A Critical Review

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Abstract
Silicon (Si) is the second most abundant element in the earth's crust and it is no surprise that various contents of this element may be found in plants, and also in different lignocellulosic materials. This may have some undesired effects when products from wood or other lignocellulosic materials are produced and utilised, typically with regards to adhesion of adhesives or surface coatings. However, there are plenty of positive effects of silicon-containing compounds in wood- and lignocellulose-based products, so very often silicon-containing compounds are added into the products on purpose. Sometimes, they might decrease adhesion properties of adhesives and coatings, but their advantages are a major priority and care has to be taken to make sure the drawbacks do not become predominant. Moreover, sometimes the silicon-containing compounds in lignocellulosic products are a necessity. A typical example is silicon-containing compounds to function as coupling agents in wood-polymer composites. The number of publications on Si in lignocellulosics, including wood, is enormous. Even if we narrow our search on this topic only to reports related to adhesion, the number of papers is still astonishing. Therefore, this review does not discuss all recent publications about this topic and it must be rather regarded as a critical review, exhibiting the most important issues that must be taken into account when considering the influence of Si in lignocellulosic materials with regards to adhesion. On the basis of selected papers, it is hoped that the reader will gain a satisfactory insight into the topic. In the first part, after Introduction, there is a brief overview of the most important compounds of Si that are relevant for the field of wood science and technology. In the next section, the influence of the presence of silicon in adhesives or in coatings or substrates on adhesion is discussed. In order to understand these effects, it is essential to know about the interactions/reactions of Si—compounds with cellulose, lignin and wood, which is the topic of the subsequent section. Reactions with the components of lignocellulosics are essential for proper functioning of coupling agents in wood-polymer composites, so these agents are presented in this review as well. Finally, an insight into

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the vast field of lignocellulosic composites is given, with a focus on a variety of different compounds of silicon and their function in the composites.

**Keywords:** Wood, lignocellulose, silicon, silica, silicate, silicone, silane, adhesive, coating, coupling agent, wood-polymer composite

### 2.1 Introduction

Silicon (Si) is the second most abundant element in the earth’s crust [1-2], making up over a quarter of its mass [3]. Being an element of almost all parent materials from which soils develop, Si is one of the basic components in most soils [4]. Commonly, Si is considered as a ‘Metalloid’ [5]. ‘Metalloids’ is a term that is frequently used to group elements that possess physical and chemical characteristics that are intermediate between those of metals and non-metals. For instance, they conduct heat and electricity better than non-metals but not as well as metals (i.e., they are semiconductors). Also, they generally form amphoteric oxides, being an acid and a base. They are grouped along a diagonal line through the p block of the periodic table from boron to astatine. In addition to silicon, commonly the following elements are also considered metalloids: boron (B), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), polonium (Po) and astatine (At) [5]. Si rarely occurs as a pure free element in nature but it rather occurs in more than 370 rock-forming minerals [4], because of the tendency to form strong bonds with oxygen. This is why Si generally exists as silica or silicate compounds [6]. The majority of metalloids are toxic when present in large concentrations, with the exception of Si [5]. Because Si is such a frequent element, the use of its compounds has a long history. For instance, silica for the production of glass dates back to the early stages of human civilisation [5].

Si is a crucial element for various plant species [7]. In the element mobility classification, Si can be regarded either as stationary or mobile element. Mobile Si substances play a primary role in the so-called global biogeochemical cycle, and so also in the so-called global biological cycle [8]. So, Si enters the cycle in the various soil-plant systems which can be accessed via the determination of mobile Si forms in the soil and of the total content of Si in the plant associations [8]. For instance, there was a study on the concentrations of monosilicic acid, polysilicic acids and acid-extractable Si in unmowed meadow, mowed meadow, birch-aspen forest, spruce wood and agricultural land soil-plant systems. Concentrations were measured at soil depths of 0-10, 20-30 and 50-60 cm in a Russian region, south of Moscow [8]. The investigation showed that the biological cycle of Si was characterized by 40 to 80 kg Si ha\(^{-1}\) annually removed from a specific soil type, according to the Russian Classification called the Grey Forest Soil, or Luvisol, with respect to the classification of Food and Agriculture Organization (FAO) of the United Nations [8]. In another study in the field of agriculture it was shown that Si plays a number of important roles in the mineral nutrition of plants [1]. The principal crops in the US collectively can annually take up 9.55 million tons of Si, as estimated from Si content in very young plants on agricultural plantations (shoots), or remove as much as 11.1 million tons from the planted soils [1].
Phytogenic Si was defined as Si precipitated in roots, stems, branches, leaves, or needles of plants. Silicon is taken up by plants from soil solution either passively with the mass flow of water or actively, e.g., by rice plants [5]. Although silicon (Si) is generally considered non-essential for plant growth and development, Si uptake by plants can alleviate both biotic and abiotic stresses [2].

Therefore, Si can be found also in wood where it is usually categorised into the group of ash-forming elements [9]. Typically, the ash content (0.2–0.7 %) in four wood species – spruce, pine, birch and aspen - harvested in Scandinavia was low compared to the ash content in the bark tissues (1.9–6.4%) and the foliage (2.4–7.7%). Si in the wood ash was determined to be in the range between 50–190 ppm [9]. On the other hand, even 5000–11,300 ppm of Si was determined in the ash of spruce needles [9]. In another study, the variation of wood elements in wood of six species with anatomically distinct to rather indistinct tree rings from a Thai monsoon forest was investigated [10]. In all species, the X-ray images showed crystals. It was shown that the crystals consist of calcium or silicon in the case of Chukrasia tabularis species, as major elemental components [10]. If we look at some other lignocellulosic tissues, we can see that, for example, the amounts of holocellulose (which is the total polysaccharide fraction of a lignocellulosic material, made up of cellulose and all of the hemicelluloses and is obtained by removing the extractives and the lignin), lignin and cellulose in the date palm rachis and in Posidonia oceanica were similar to those found in softwoods and hardwoods. But, extractives in different solvents and ash contents were relatively high and it was shown that silicon was the major component of ash (17.7%) of P. oceanica. Some other lignocellulosic materials contain even higher contents of silicon [11]. A typical and well-known example is rice husks. The average composition of rice husk according to Ugheoke and Mamat [12] exhibits that there is 17 % of ash in rice husk, consisting of 94 % of Si. Genieva and co-authors report that rice husks contain nearly 20 mass % silica, which is present in hydrated amorphous form [13].

The issue of Si content in wood and lignocellulosic materials becomes highly important with regards to utilisation of biomass for the production of energy and in biorefineries. Biorefineries aim to convert low value biomasses into high value products. The feedstock biomasses are often high-silica agricultural waste products such as rice straw, wheat straw, corn stover, sugar cane bagasse, or empty fruit bunches. But, this causes challenges, since the presence of silica may cause problems in industrial processes, where it forms water-insoluble precipitates that are hard to remove, block filtration systems, and cause instrumental defects [14]. There are also many studies on undesired role of Si in woody and other lignocellulosic tissues in the field of utilisation of biomass for burning. Just as an example, pointed out by Werkelin and co-authors, there is no doubt that the high Si content in the spruce needles has a large impact on the ash chemistry, and may cause problems in combustion devices. For instance, ash with a high Si content may adhere to the heat transfer surfaces, causing fouling and corrosion [9]. Also, silicon dioxide was identified in the exhaust gases from engines powered using sewage and landfill gas. The production of energy from biogas is severely compromised by its volatile organic silicon compound content. In this case, the Si present is of an anthropogenic origin. The cycle starts with the production and use of poly(dimethylsiloxane)polymer in a wide range of industrial
and domestic applications and its further dispersion into the environment. Silicon dioxide from biogas in power plants deposits on valves, cylinder walls, and liners, causing abrasion and blockage of pistons, cylinder heads, and valves. In gas turbines, siloxane deposits usually form on the nozzles and blades, causing erosion of the turbine blades and subsequently decreasing the operating efficiency [15].

While the presence of Si in biomass can be undesired, as described in the previous paragraph, it can also be regarded as a useful one, finding various useful ways of application, some of them are mentioned in the subsequent text. A perfect example is high content of Si in rice husks. Rice husks have now become a great source of raw biomass material for manufacturing value-added silicon composite products, including silicon carbide, silicon nitride, silicon tetrachloride, magnesium silicide, pure silicon, zeolites, fillers of rubber and plastic composites, cement, adsorbents, and supports of heterogeneous catalysts [13], as also shown in the review by Ugheoke and Mamat [12]. With the aim to improve selected properties of wood and lignocellulose-based products, silicon compounds have found a number of applications, so it is a common practice to add silicon compounds into wood, wood based composites and similar products and not just exploit the benefits of naturally present compounds of silicon. Probably, the most well-known example is the application of silicon compounds to function as coupling agents in various composite materials [16, 17]. By the way in [16], there is an extensive review about the formation of an effective interphase and the characterization of silane-treated surfaces and interphases in composites. Also, in this paper there is also a review about coupling agents in composites (section 4.3.2), however this overview focuses on a variety of composites (e.g. particleboards, medium dense fiberboards (MDFs), wood-flour composites, fiber-reinforced composites, etc.) where the coupling agents have found application. Otherwise, the coupling agents have been extensively studied, e.g. see [17], [18] and [19]. In addition, due to their expected function, silicon-containing compounds are not only added into or on wood or lignocellulosic substrates but also into various other products that are used in the field of wood science and technology, typically into adhesives and surface coatings. For instance, quite recently geopolymer binders have been identified as an emerging class of mineral polymers that can be manufactured from natural raw materials and industrial by-products containing high amounts of silica and alumina in mineral compositions. Geopolymers (mineral polymers resulting from geochemistry or geosynthesis) are materials produced by the activation of aluminosilicate powder components with an alkaline solution and an activator [20, 21]. Another example is modification of soy-based adhesives made from soybean seed with sodium montmorillonite clay [22]. Similarly, silicone resins have recently attracted a great deal of interest, especially in the construction industry, where products such as silicone resin emulsion paints and renders (the first, underlying coats) are gaining in popularity [23].

The aim of this review paper is to provide an overview of the applications of silicon-containing compounds in the field of wood science and technology and also in relation to some other lignocellulosic compounds, with regards to adhesion between a substrate and an adhesive or surface coating. The other equally important topic in this review is an overview of silicon-containing coupling agents and of silicon compounds in various wood
Influence of Silicon-Containing Compounds on Adhesives for and Adhesion in other lignocellulosic composites. Si compounds in lignocellulose substrates and in adhesives and coatings have found numerous other applications. Most probably, the predominant ones are related to hydrophobic properties of wood, wood-based and some other lignocellulosic materials, and fire retardant properties are also a very interesting area. However, the number of publications about these topics is much too large for all to be included in this review.

2.2 An Overview of Compounds and Natural Minerals Containing the Element Si, which are the Most Relevant in the Science and Technology of Lignocellulosics

2.2.1 Silica – \( \text{SiO}_2 \)

The English word silica has a very broad connotation: it includes silicon dioxide in all its crystalline, amorphous, soluble, or chemically combined forms in which the silicon atom is surrounded by four or six oxygen atoms. This definitely excludes all the organosilicon compounds made by man in which carbon atoms have been linked directly to silicon atoms—commonly referred to as “silicones”, which do not occur in nature [24]. Combined with the oxides of magnesium, aluminum, calcium, and iron, silica forms silicate minerals in rocks and soil [24]. The building block of silica and the silicate structures is the \( \text{SiO}_4 \) tetrahedron, with four \( \text{O}^2- \) at the corners of a regular tetrahedron with a \( \text{Si}^{4+} \) at the center cavity or centroid. The \( \text{O}^2- \) is so much larger than the \( \text{Si}^{4+} \) that the four oxygens of a \( \text{SiO}_4 \) unit are in mutual contact and the \( \text{Si}^{4+} \) is said to be in a tetrahedral hole (Figure 1).

Natural silicas can be crystalline, as in quartz, cristobalite, tridymite, coesite, and stishovite, or amorphous, as in opal. Crystalline silica polymorphs are divided according to their network density (\( \text{SiO}_2 \) groups per 1000 Å\(^3\)) into pyknosils and porosils, and the latter are further divided into clathrasils and zeosils depending on whether the pores are closed or open, i.e., accessible to adsorption [24]. Although in most silicas and silicates, the silicon atom is surrounded by four oxygen atoms, forming the tetrahedral unit \( [\text{SiO}_4]^{4-} \), a sixfold octahedral coordination of the silicon atom has also been observed in stishovite and coesite. The arrangements of \( [\text{SiO}_4]^{4-} \) and \( [\text{SiO}_6]^{8-} \) and the tendency of these units to form a three-dimensional network structure are fundamental to silica crystal chemistry [24]. The polymorphism of silicas is based on different linkages of the tetrahedral \( [\text{SiO}_4]^{4-} \) units. Quartz has the densest structure, and tridymite and cristobalite have a much more open structure. All three forms exist in \( \alpha \)- and \( \beta \)-forms, which correspond to low- and high temperature modifications, respectively [24]. In the Introduction in the paper of Pabst and Gregorová [25], it is cited from various sources that 12 silica phases exist, and that some other authors have identified 14 and even more than 20 phases of silicon dioxide.

Apart from crystalline silicas, the amorphous ones have attracted considerable attention as well. In amorphous silica the bulk structure is determined, as opposed to the crystalline silicas, by a random packing of \( [\text{SiO}_4]^{4-} \) units, which results in a nonperiodic structure (Figure 2) [24].
One reason for such an importance lies in the fact that amorphous silica and silica based materials have been widely developed for optoelectronics and optical telecommunication technology [26]. So silicon dioxide in its crystalline form, also in the glassy one, is of immense technological importance, with applications ranging from cladding skyscraper facades to manufacturing microchips [27].

Since nanotechnology is rapidly sweeping through all vital fields of science and technology such as electronics, aerospace, defense, medical, and dental, it is normal that considerable attention has been dedicated also to the preparation, characterisation and utilisation of nanosized silica, SiO$_2$ [28]. Nanosilica, also known as the nanoform (<100 nm) of silicon dioxide or silica nanoparticles (SiNPs), possesses distinct physico-chemical characteristics compared to its bulk form. So it has been prepared in a crystalline as well as in an amorphous form [29]. Nano-silica has found a range of applications also in wood science & technology and related areas, from applications in wood-polymer composites (WPCs), as reported, for example by Zhou et al. [30], as components in flame retardants for wood [31–33], in relation to hydrophobicity and superhydrophobicity [34–36], in adhesives [37, 38], in coatings [39], and others.

Mesoporous silica materials should be mentioned as well. Mesoporous silica and silicate materials have attracted an increased attention in the past decades owing to their interesting properties that include tunable pore size, stability and shape selective coatings [40]. The most common mesoporous silica materials have the pore size ranging from 2-10 nm and 2D-hexagonal and 3D-cubic structural characteristics [41]. They also possess extremely high surface areas (>700 m$^2$ g$^{-1}$) and narrow pore size distributions [42]. It was shown that mesoporous silicas free from any metal ions can act as an efficient oxidation catalyst in the process of oxidation of lignin model compounds under microwave activation [40]. Also, silicates (see the next section) are being used in a mesoporous form, as demonstrated by Chen et al. in the case of preparation of Ultralow Density Wood Fiber Composite [43].

2.2.2 Silicates and Clay

According to Belton et al. [44] the term silicate means a chemically specific ion having negative charge (e.g. SiO$_3^{2-}$), and the term is also used to describe salts (e.g. sodium silicate,