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# Characterisation of the Interfacial Adhesion of the Different Components in Wood–Plastic Composites with AFM

Bernard Effah<sup>1</sup>  · Albert Van Reenen<sup>2</sup> · Martina Meincken<sup>1</sup>

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**Abstract** The search for innovative solutions for the reuse of solid residues has intensified with growing environmental issues and the increasing cost of most raw materials, leading to the design of eco-friendly composite materials, such as wood–plastic composites (WPCs). These materials combine the stability of wood fibres with the durability of plastic, allowing for a wide range of applications, whilst simultaneously offering the possibility of utilising waste products from the forest/wood industry and recycled plastic. Waste products that otherwise incur cost for disposal therefore become a sustainable material resource for new products. Natural fibres offer a number of advantages over synthetic fibres and are seen as a “green” alternative to other reinforcements. Commonly, the fibre-matrix adhesion in WPCs is improved by using compatibilisers that bond to the polar wood fibres and the non-polar polymer matrix. However, the problem with these is that good dispersion is not always achieved as it depends on the adhesion properties of three individual components in the WPC, which might lead to poor mechanical properties of the WPC. The ability of the atomic force microscope

(AFM) to create 3D images of topography and various interaction forces with molecular resolution made it a valuable tool for the analysis of adhesion properties in WPCs.

**Keywords** Natural fibres · Composites · Compatibiliser · Sustainability · AFM

## Introduction

In recent times, increased environmental awareness throughout the world has led to an increasing interest in natural fibres and their applications in various fields [87]. This has in turn led to the development of completely new composite materials by combining different resources in such a way that a synergism between the components results in a new material that is better than the individual components. With this in mind, the World Commission on Environment and Development in 1987 observed that “the time had come for a marriage of the economy and ecology” [90].

Composite materials are made from two or more materials with significantly different physical or chemical properties, which remain separate and distinct within the finished structure [47, 58]. Composites are used in areas such as automotive, building, appliances, packaging and biomaterials [58, 75, 80]. Composites can be classified based on the matrix, which could be metal, ceramic or polymers [3, 80]. The classifications according to the type of reinforcement are particulate composites, fibrous composites and laminate composites. The classification can even include the types of fibres used [39].

Natural fibres offer a number of advantages over traditional synthetic fibres and are widely used for the

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Endorsed by Martina Meincken.

✉ Bernard Effah  
18761569@sun.ac.za

Albert Van Reenen  
ajvr@sun.ac.za

Martina Meincken  
mmein@sun.ac.za

<sup>1</sup> Department of Forest and Wood Science, Stellenbosch University, Stellenbosch, South Africa

<sup>2</sup> Department of Chemistry and Polymer Science, Stellenbosch University, Stellenbosch, South Africa

production of wood–polymer composites or wood–plastic composites (WPCs) [47, 80]. In the composite industry, natural fibres are seen as a “green” alternative to reinforcements of other sources. Economically, the use of plant co-products for composite production avoids the use of new agricultural lands, which limits competition with alimentary products and also becomes sources of remuneration to farmers [7]. Plastic is found in all sectors of human life and the attitude of people towards the excessive use and careless disposal of the plastic has led to a drastic environmental pollution. Similarly, a large amount of wood waste is generated at different stages in the wood processing industry and a large proportion of the waste is either incinerated or deposited in landfill sites. On the other hand, the growing production and consumption of plastic worldwide has resulted in the development of waste recycling facilities, which produce the raw material for another generation of plastic products [80]. Furthermore the search for innovative solutions for the reuse of solid residues increased in the late 20th century and has intensified with growing urgency for environmental preservation [53] leading to the design of eco-friendly materials including WPCs [75].

### Wood–Plastic Composites

Wood–polymer or WPCs are a relatively new class of materials that covers a broad range of composite materials utilising an organic resin binder (matrix) and fillers composed of cellulosic material [58]. These rapidly developing materials for high technology products possess the advantage of utilising waste products from the forestry industry and recycled plastic from household waste. Waste products that would usually incur cost for proper disposal, therefore become a new material resource, allowing recycling to be both profitable and environmentally sustainable. Polymers like polypropylene (PP), polyethylene (PE), polyester, epoxy and polyvinyl chloride (PVC)—the latter mainly in the US—have an established status in composite applications. Natural fibres can originate from wood, agricultural plants and residues, grasses, water plants and a wide variety of waste agromass including recycled wood, paper and paper products [11].

Matoke et al. [59] emphasised the growing interest in the use of natural cellulosic fibres as the reinforcement for polymeric matrix and noted that, adding natural powder or fibre to plastics provides a cost reduction to the plastic industry and improves the physical and mechanical properties of the composite. For the production of high performance wood composites, a fundamental understanding of the properties of the materials involved is essential [89].

Two major constituents make up WPCs: the fibres and the matrix. The interface between the fibre and matrix is critical for the function of the composite material and as such could be added as a third constituent of the material [35, 49]. Many complex phenomena including matrix phase separation, development of chemical bonds, interdiffusion and physical interactions combine to transfer loads at the interface and lead to durable materials with excellent mechanical properties [48]. Information about the behaviour of the fibre/matrix interface can directly be obtained at the microscopic scale using micro-mechanical analysis, such as pull-out, microbond or fragmentation tests [50].

Like any other advanced product, a WPC has its own complications, especially the interfacial adhesion between the polar wood fibres and the non-polar polymer, which is normally very poor and therefore depends on coupling agents to initialise the bond [47, 98]. Wood is a hydrophilic porous composite of cellulose, lignin and hemicellulose, which are rich in functional groups like hydroxyl groups. On the other hand, many matrix polymers are hydrophobic, with very few functional groups. This incompatibility results in non-uniform dispersion of fibres within the matrix leading to poor mechanical properties. In order to improve the affinity and adhesion between fibres and polymer matrix in production, chemical compatibilising agents are normally employed [43]. The primary function of a compatibiliser is to form an interphase between the wood and the plastic, as such the compatibiliser should have a domain or functionality that is compatible with the wood fibre, as well as a domain that is capable of interacting with the polymer matrix [69]. The compatibilisers are added in small quantities to form a bridge between the otherwise incompatible materials. They act via the formation of covalent bonds, secondary bonding, polymer molecular entanglement or mechanical interlocking [52]. The type and level of compatibiliser for WPCs should be carefully selected in order to produce composites with acceptable properties and performance [69].

To improve reinforcement and mechanical properties, such as strength and stiffness, the fibres need to be well dispersed within and well bonded to the matrix. If at a certain location, the fibres are not properly bonded to the matrix, delamination and void formation will occur. In such situation stress transfer between fibre and matrix would fail and these locations could serve as nucleus for cracks to form [11].

The major factors to determine the properties of WPCs are fibre dispersion, fibre length distribution, fibre orientation and fibre-matrix adhesion [47, 70, 80]. Poorly dispersed fibres could lead to agglomeration or the formation of voids, which should be avoided to produce efficient composites.

### Wood and Other Natural Fibres Used in WPC

The term WPC refers to any composite that contains wood of any form and either thermoset or thermoplastic polymers [15, 79]. Klysov [47] defined WPCs as products made from plastic filled with cellulose fibres and other ingredients. However, the term WPC covers an extremely wide range of composite materials using plastics ranging from polypropylene to PVC and various natural fillers ranging from wood flour to flax Tangram [91]. The polymer matrix forms the continuous phase surrounding the fibrous enforcement component [70]. With phenomenal growth of wood–thermoplastic materials in the United States in recent years, they are now most often simply referred to as WPCs with the common understanding that the plastic always refers to a thermoplastic [79] and the filler can consist of various natural fibres.

Natural fibres are fibrous plant materials produced as a result of photosynthesis. They are sometimes referred to as vegetable, biomass, photomass, phytomass, lignocellulosic fibres, agromass, solarmass, agro-based resources or photosynthetic fibres [35, 74]. The use of natural fibres dates back to about 8000 BC, specifically, the use of flax, or hemp fibre dates back to the stone age, grass and straws have been used for many generations as a reinforcement in mud bricks, whilst cotton fibres have been found in caves in Mexico that date back over 700 years [16, 35, 74, 80].

Natural fibres lost much of their interest later on, after decades of development of artificial fibres based on carbon, aramid or glass. More recently, the use of natural fibre-reinforced polymer composites has been growing again

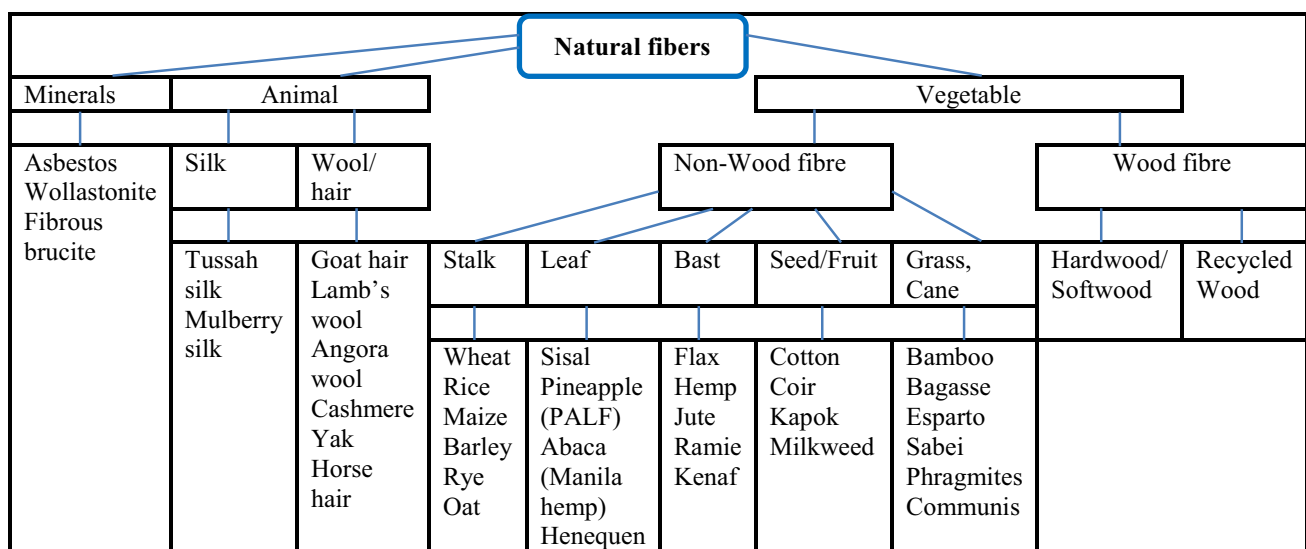
owing to their good performance, significant processing advantages, bio-degradability, low cost and low density. Natural fibre-reinforced composites with thermoplastic matrices have successfully proven their high quality in various fields of technical application [33].

Fibres like flax, hemp, coconut or jute are harvested from renewable resources, are cheap, have better stiffness per unit weight than the traditional glass and carbon fibres and have a lower impact on the environment. The advantages of natural fibres over traditional reinforcing materials, such as glass are lower cost, lower density, high toughness and a more environmentally friendly processing [35, 99, 100].

The categorisation of natural fibres is based on their origin: lignocellulosic materials, animals or minerals. The lignocellulosic fibres, also known as cellulose-based fibres, typically originate from a huge variety of softwood or hardwood species, plant fibres, such as hemp, kenaf, curaua, coir, jute, sisal, cotton or bamboo. Animal fibres include silk and leather. The most well-known mineral fibres are glass, boron and asbestos [16, 35, 53, 99]. Clearly, the most abundant are wood fibres from trees; nonetheless other fibres are also often used [16]. An overview of the classification of natural fibres from Mohanty et al. [67] is given in Table 1. All natural fibres, whether wood or non-woody, are cellulosic in nature and therefore also hydrophilic in nature.

According to Celluwood [16], Pickering [74] and Mallick [56], some of the main shortcomings and limitations of natural fibres as reinforcement for composites are related to the lower strength properties, lower interfacial adhesion,

**Table 1** Classification of natural fibres



poor resistance to moisture absorption, limited maximum processing temperature and lower durability and dimensional stability. Fibre surfaces can vary greatly, which results in varying interaction with the polymer matrix due to their natural biological variability. Regions of both low and high surface energy may exist on the same fibre. Also the surface of the fibre can be smooth or rough and fibre modifications, such as beating, may enhance surface contact area [47, 70, 84]. Other factors, which can largely affect the composite properties, are concerned with the size, geometry and dispersion of filler particles in the matrix [75].

Indeed, the performance of natural fibre-reinforced polymer composites as a structural material mainly depends on the quality of stress transfer in the interphase between fibre and polymer in the composite [68]. The interphase is the region lying between the reinforcing fibre and the polymer and as such play an important role in the performance of fibre-reinforced polymer composites [68]. The load transfer between the fibre and matrix affects the overall mechanical properties of the composite [68].

To overcome the shortcoming, various techniques have been developed to modify natural fibres. There are four methods used to treat natural fibres based on the modification process: physical, chemical, biological and nanotechnological [16, 70]. Physical modification is done in order to change the structural and topological properties of the fibre, with the aim of increasing the strength of the fibres. Typical methods involve thermo-treatment, beating, calendaring and stretching [16]. Chemical modification utilises chemical agents to modify the fibre surface or the entire fibre throughout. The modification can be classified into five methods: mercerisation, oxidation, cross linking, grafting and coupling agent treatment [16, 70]. The control of properties of natural fibre-reinforced polymer composites highly depends on the possibility of modifying the interfacial adhesion through the improvement of the fibre–matrix interactions. Polymer modification appears to be a quick, effective method to provide good interfacial adhesion, in contrast to fibre modification, which generally involves solvent-based processes [75]. Compatibilising is a surface-active method, which utilises the electrostatic nature of the two interfaces [47, 70]. Compatibilisers have the primary function of improving the homogeneity of dissimilar or incompatible materials. Lack of homogeneity can prevent the development of stress transfer and reduce the mechanical properties of the end product; therefore, the use of compatibilisers improves mechanical properties [47, 70]. Biological treatments involve the use of naturally occurring microorganisms, such as bacteria and fungi to alter the surface properties of fibres. Nanotechnology is used to immobilise nanoparticles on the surface of natural

fibres through layer-by-layer deposition or the sol–gel process [16].

Reinforcements for composite materials can be in the form of fibres, particles or flakes. The size of fibres used in composite materials ranges from the micrometre to the centimetre level [11, 70].

## Performance and Applications

Wood fibre/plastics composites have found many applications replacing solid wood or pure plastic materials. Several Asian countries, especially India, have continuously used natural fibres, mainly jute fibres, as reinforcement for composites and are producing natural composites for many applications such as pipes, panels and other profiles. In Japan, WPCs are applied for stairs, handrails and bathrooms. In the US building products, such as decking, cladding and window frames are very successful in the market, whereas in Europe fibre composites mainly find applications in the automotive industry [35, 74].

Cellulosic fillers/fibres have been incorporated in a wide variety of polymers, such as polypropylene, polyethylene, polystyrene, polyvinyl chloride and polyamides [74, 80].

The performance of a fibre used in WPCs depends on several factors including chemical composition, physical properties, mechanical properties, the interaction of a fibre with the composite matrix and how that fibre or fibre/matrix performs under a given set of environmental conditions [35, 47, 70]. Tensile strength is the most frequently tested property of natural fibre-reinforced composites [35] as it is a good indicator for interfacial adhesion and general performance of the WPC. Rowell et al. [18, 47, 81] and others investigated the effect of coupling agents and different matrices, and Jacoby et al. [37] and Caraschi and Leao [14] studied different chemical treatments for wood fibre composites and all these were found to improve tensile properties. Pracella et al. [75] examined the effect of chemical modification of fibres, as well as the addition of compatibilisers containing reactive groups on the morphological, thermal and mechanical properties of polypropylene (PP), polystyrene (PS) and ethylene–vinyl acetate (EVA) copolymer composites containing hemp, cellulose and oat. They observed enhanced fibre dispersion and interfacial adhesion with the occurrence of effective interactions between the functional groups on the copolymer chains and the polar groups of the fibres.

Mishra et al. [66], Rout et al. [78], Cyras et al. [21], Marcovich et al. [57] and Khan et al. [42] investigated the tensile properties of composites containing jute, sisal, coir, pineapple or leaf fibre and all reported increases in the tensile, flexural and impact strength of their composites.

McDowell et al. [61], Aramguren et al. [2], Van de Velde and Kiekens [92], Chen-Jui [19], Van Den Oever [93], Heuer [34] and Rozman [82] studied the flexural properties of wood, flax, jute, coir and oil palm fibres with regard to their effect on the moulding properties, chemical treatment, esterification, different wood species, fibre loading and surface wettability. All studies agree that mechanical performance of WPCs improves significantly when compatibilisers are used under optimised conditions [70]. Dittenber and GangaRao [24] conducted a critical review of recent publications on the use of natural fibre composites in infrastructure and emphasised that using natural materials and modern construction techniques reduces construction waste and increases energy efficiency, whilst promoting the concept of sustainability. Azwa et al. [4] published a review on the degradability of polymeric composites based on natural fibres by evaluating the characteristics of several natural fibre composites exposed to moisture, thermal, fire, and ultraviolet degradation and concluded that an optimum blend ratio of chemical additives must be employed to achieve a balance between strength and durability requirements for natural fibre composites.

In their study, Le Duigou et al. [49] evaluated the fibre surface involved in the practical adhesion of flax/epoxy system by microbond and could not explain the superficial surface chemistry evaluated by X-ray photo-electron spectroscopy (XPS). Nonetheless, they established with the FTIR that the effective surface or complex interphase is the overall area where fibre and resin are in contact. Morphology and mechanical properties of wood flour-reinforced polypropylene composites were studied by Bhandari et al. [8] and their results showed that alkali-treated wood flour was more compatible with PP matrix than a neat one and the effects were reflected in the morphological and mechanical properties of the composites. They also observed that the compatibiliser played a key role in enhancing the filler–matrix interfacial interactions.

## The Atomic Force Microscope

In 1982, the scanning tunnelling microscope (STM) was developed as a tool to image metallic and semiconducting surfaces with high resolution [1, 9, 51, 55, 88]. This discovery later prompted the development of several advanced high-resolution imaging techniques, which scan point probes in a raster pattern across the sample surface to detect various interaction forces. The limitation of the STM to conducting surfaces led to the development of the atomic force microscope (AFM) by Gerd Binnig, Christopher Gerber and Calvin Quate at Stanford University, USA [1, 10, 26, 55, 88]. Since then, the AFM has developed into the most widespread and commercially successful scanning

probe microscope. It is used not only in physical, chemical, biological, medical and material research laboratories, but also for product development and quality control. The success of the AFM is attributed to the high resolution and the versatility, with which it can map not only the topography of sample surfaces in the sub-micrometre scale, but also physical properties depending on the interaction forces between the tip and the sample surface [26, 32, 51, 55, 65]. As elaborated by Starostina and West [88] and Prater et al. [76], the AFM is capable of producing 3D topographical information from the Å to the µm level with high resolution. The AFM is, however, not limited to topographic images; it can also be used to identify and discriminate surfaces with varying chemical properties, for example, by modifying the AFM tip with self-assembled monolayers (SAMs) of specific functional groups [60]. The method of scanning surfaces with modified AFM probes is called chemical force microscopy (CFM) [60, 71]. Chemical force microscopy detects the chemical interaction between the functionalised tip and the surface and maps it as a 3D image, similar to the image of surface morphology and often both images can be acquired simultaneously [1, 32, 55, 76].

The AFM requires no special sample preparation and is adaptable to many different environments such as air, vacuum or liquid, as well as to a large variety of samples. The only limitation with regard to sample size is that it must be securely fixated and not too rough [1, 32, 55].

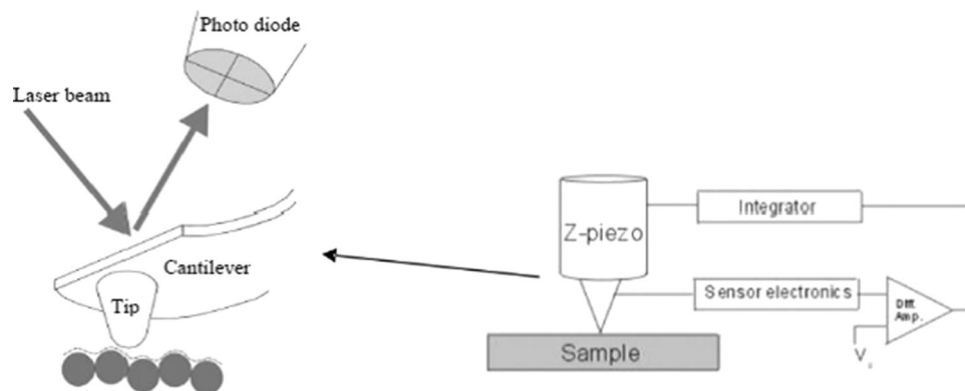
The raster pattern to create a point matrix interaction values for imaging is obtained by piezoelectric elements, which create mechanical movement to accurately move the AFM probe independently in x and y direction. The forces acting on the cantilever are measured via a laser beam that is reflected off the cantilever into a photodiode and any change in its position is counteracted by feedback control system that maintains the desired force between the probe and the sample by moving a piezo element in z direction [1, 26, 32, 55]. The force detected between the probe and the surface can be as small as 1 nN [60, 88]. Recently, an AFM-based technique where forces up to 1 mN can be applied to fibre samples has been proposed by Schmied et al. [83].

## Operation Principles of the AFM

The AFM detects forces acting between a sample surface and a sharp tip which is suspended on a very soft spring called cantilever. A feedback system which controls the vertical z-position of the tip on the sample surface keeps the deflection of the cantilever constant [26, 40, 76]. To create an image, the tip is brought into close contact with the sample and raster-scanned over the surface, causing the



**Fig. 1** Schematic diagram of the AFM



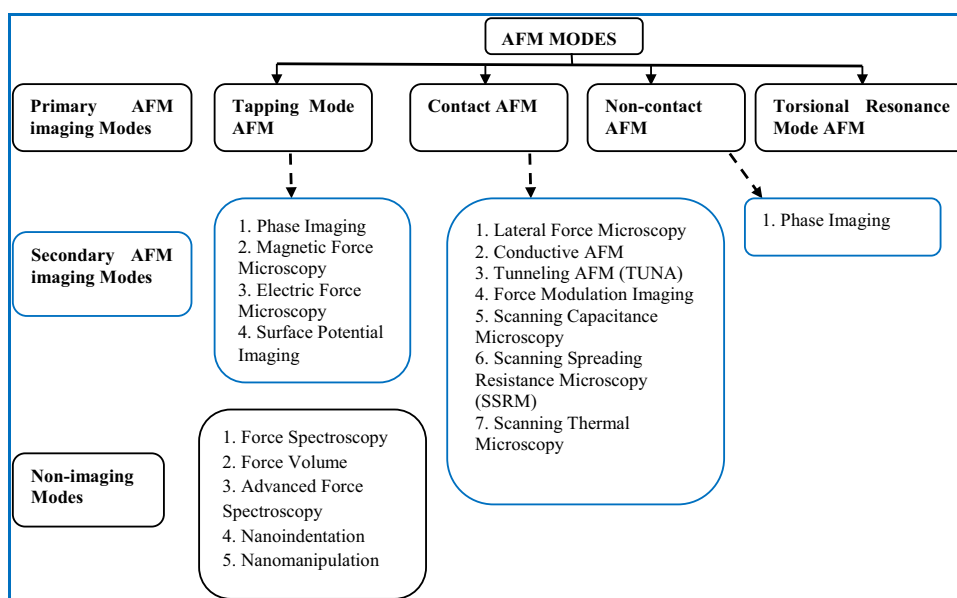
cantilever to deflect because of a change in surface topography or other interaction forces. The cantilever deflection is detected via a laser beam that is deflected off the cantilever's back side into a position-sensitive photo-diode detector [1, 51, 55, 76, 88] as shown in Fig. 1. The obtained three-dimensional data represents a 3D image of the surface topography. In non-contact mode, this information is mostly obtained from the change in VDW forces between the tip and the sample [26, 51]. Force spectroscopy on a single point on the sample can be used to provide a quantitative measure of the interaction force [64]. In this mode, the interaction force between the tip and the sample in one point is measured by analysing cantilever deflection when the probe is moved towards and away from the substrate. This deflection of the tip occurs on a straight line normal to the surface. As the tip comes in close proximity to the surface, an attractive or repulsive force causes the cantilever to deflect. If the force is attractive, the cantilever will be pulled down towards the

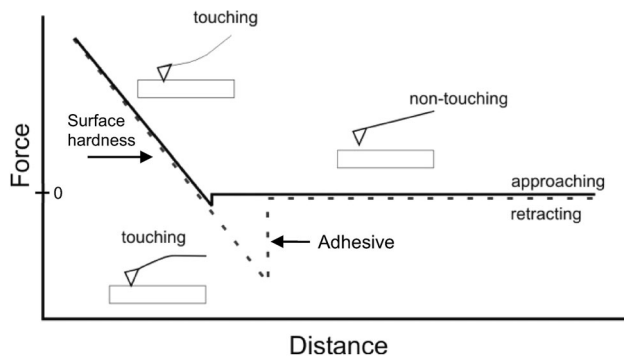
substrate and if it is repulsive, the cantilever is pushed up. The deflection signal can be converted into the actual force value if the spring constant of the cantilever is known [1, 32, 51, 55].

The result of an AFM image is a force map, which is obtained by tracking the laser displacement between the tip and the sample ( $z$ ). A force–distance ( $F/D$ ) curve is obtained in the spectroscopy mode to assess the physical and mechanical properties of the sample. In a  $F/D$  curve, the approach and retraction curves are obtained for a point on the sample and a force image can be obtained by acquiring several  $F/D$  curves at different points in the  $x$ – $y$  plane. Different parts of the  $F/D$  curve contain different information of the sample, such as surface hardness or adhesion between tip and sample and all this can be represented in different images. The information of  $F/D$  curves becomes clearer when a modified tip is used to investigate specific interactions.

Figure 2 gives an overview of the different AFM modes.

**Fig. 2** AFM operation modes [95]





**Fig. 3** Schematic force–distance relationship of cantilever deflection and vertical distance

### Force Spectroscopy

Force spectroscopy is used to determine the interaction between the probe and the sample with nN resolution and provides valuable information on molecular scale with regard to the adhesion force between tip and sample [51, 60, 76].

In this mode, the cantilever is pushed into the sample at a certain point and subsequently retracted and the deflection of the cantilever is monitored as it moves towards and away from the surface resulting in a F/D curve, as shown in Fig. 3. The x-axis is the vertical distance between tip and sample. The y-axis shows the cantilever deflection as the tip is moved towards the sample surface. The F/D curve provides useful information about both long- and short-range forces as well as surface hardness [51, 76]. As the tip begins to approach the sample surface, there is no deflection. The initial contact between the tip and the surface is mediated by attractive van der Waals forces, which leads to a small negative deflection of the tip towards the surface. As the tip is further indented into the sample, the cantilever deflection increases and this part of the curve is a measure of the surface hardness, which is proportional to the gradient of the deflection. As the cantilever is retracted again, various adhesive forces between the sample and the tip maintain contact between tip and sample. These adhesive forces can be directly measured from the F/D curve. Eventually, the tip loses contact to the surface upon overcoming the adhesive forces and the cantilever is free and no deflection is measured. Forces acting between the tip and the sample surface can therefore be measured localised with nm resolution by obtaining F/D curves [32, 51, 64, 76, 85].

F/D curves can be obtained at several different surface points in order to generate a map of adhesion forces. This can be advanced by functionalising end of the tip with specific molecules to measure the specific binding strength between molecules [60] which results in an image of the distribution of functional chemical groups [51].

Many studies have made use of AFM from the biological sciences to material sciences. In his review on the application of AFM, Wallace [96] indicated that approximately 150 articles addressed the application of AFM-based techniques to investigate bone, dentin, tendon and other collagen-based tissues. In their study on the application of AFM to the characterisation of industrial polymer materials, Bar and Meyers [6] concluded that the AFM has been an enabling technology for understanding the structure and property relationships in polymeric materials including homopolymers, blends, impact-modified polymer systems, porous polymer systems and semi-crystalline polymers. Burnham and Colton [12] and DiNardo [23] demonstrated the use of the AFM as a nanoindenter and to measure surface forces on surfaces, whilst Ganser et al. [29] recently investigated the hardness and modulus of elasticity of cellulose fibres with AFM nanoindentation.

Yan and Li [97] used chemically modified –OH-functionalized AFM tips to evaluate the inter-fibre bonding properties of typical wood pulp fibres. The pull-off forces and adhesion forces were measured in aqueous media and they showed that van der Waals forces are the major contributing factor to adhesion on non-swollen solid regions of fibre surfaces.

In demonstrating the increasing number of AFM capabilities useful in studies of polymer materials, Magonov and Heaton [54] stated that the application of AFM goes far beyond high-resolution profiling by providing local properties, maps of sample composition and the ability to examine underlying surface layers.

Meincken and Sanderson [64] confirmed the advantages and capabilities of the AFM in polymer science over other analytical techniques like scanning electron microscopy, differential scanning calorimetry and the dynamic mechanical analysis with regard to the sample preparation and environment of study. To further demonstrate the versatility of the AFM, Meincken [62] determined the surface roughness and surface polarity of fibres, parenchyma cells and vessel elements of four hardwoods commonly used for pulping and observed a clear distinction between the cell types and species for the surface roughness and polarity. Frybort et al. [28] recently utilised the AFM to study the adhesion force between AFM tips and freshly cut wood surfaces. They found clear differences in polarity between freshly cut cell walls and inner cell surfaces at the microstructural level. Similarly, the surface polarity of wood fibres was determined after pre-treatments and bisulphite pulping by Meincken and Matyumza [63]. They observed differences in polarity between the various wood species using the AFM in pulsed-force mode. George et al. [30] recently demonstrated how the AFM can be used as a tool to estimate the surface forces and roughness of modified fibres. They also



concluded that enzymatic and chemical methods can be used to improve the surface properties of natural fibres for composite applications. AFM in combination with image analysis was used to study the ultrastructure of transverse fibre cross sections and also identify the existence of pores across the fibre wall by Fahlen and Salmen [27]. In a related study and for the first time Keplinger et al. [41] used the scanning near-field optical microscopy (SNOM) on secondary plant cell walls of spruce, beech and bamboo and found their segmented circumferential nanostructure pattern to be consistent among various plant species. They also indicated that the limiting factor of conducting in-depth analysis with high-resolution characterisation techniques like AFM and TEM is that they provide structural but hardly chemical information, whilst chemical characterisation with FTIR and Raman spectroscopy also leads to disassembly of components or does not reach the required nanoscale resolution [41].

### Interaction Forces and Interfaces

Chemical and physical interactions play an important role in many applications with the increasing use of nanotechnology. The force acting between two surfaces through an intervening medium is called surface force [13, 36, 101]. The characterisation of interfaces can give relevant information on interactions between fibre and matrix in WPCs. Jose et al. [39] identified four methods available for interface characterisation:

- (1) Micro-mechanical techniques, such as fibre pull-out, micro-debonding, or micro-indentation and fibre fragmentation.
- (2) Spectroscopic techniques, such as chemical analysis/X-ray photo-electron spectroscopy, mass spectroscopy, X-ray diffraction studies, electron-induced vibration spectroscopy and photoacoustic spectroscopy.
- (3) Microscopic techniques using optical microscopy, scanning electron microscopy, transmission electron microscopy and atomic force microscopy.
- (4) Thermodynamic methods, which include wettability, inverse gas chromatography and zeta potential measurements.

When using the AFM to measure interfacial forces, knowledge of the interaction between the tip and the sample is critical to interpret any data correctly [55]. According to Amelinckx et al. [1], on atomic and molecular scale the electromagnetic interaction dominates over other interaction types. Nonetheless, the electromagnetic interaction gives rise to a variety of different forces which not only complicate the AFM image interpretation, but also give the potential of measuring many different physical

properties [55]. In relation to the physics and chemistry of the interacting surfaces, the adhesion property of surfaces is a consequence of interatomic and intermolecular surface forces such as van der Waals forces, electrostatic forces, chemical forces, capillary forces and others [101]. Gnanou and Fontanille [31] stated that three interaction types are responsible for the cohesion in polymers: van der Waals interactions (Keesom forces, Debye forces and London forces), hydrogen bonds and ionic bonds. In polymer composites the interaction between the polymer and the filler is developed during processing in the melt state and is a combination of van der Waals (VDW) interactions, specific chemical interactions and chemical bonds between the polymer and the filler surface [25]. In their study, Chau et al. [17] stated that the adhesion force between two surfaces physically originates from van der Waals forces, electrostatic forces, intermolecular forces, Casimir forces or meniscus forces depending on physical and/or chemical properties of those surfaces. Wallace [96] reports that a combination of interactive forces including magnetic, electrostatic and capillary forces is important in AFM depending on the separation distance; however, van der Waals forces usually dominate at small distances.

Persson et al. [73] studied the effect of capillary adhesion between cellulose fibres and found that plastic flow must occur in order to maintain good contact in the dry state.

Amelinckx et al. [1] stated that the most important forces in conventional AFM are Pauli repulsion and ionic repulsion. Three issues are of particular importance for any interaction: the strength of the force, the distance over which it acts and the environment through which it acts. Magonov and Whangbo [55] established that adhesion between two macroscopic bodies is a consequence of the long- and short-range force interactions, involving VDW forces, electrostatic force, capillary force and frictional force. Some of the long-range forces between tip and surfaces include the VDW attraction, capillary force due to the presence of fluid films at the surface when imaging in liquid or air, and electrostatic forces [13]. Table 2 gives an overview of all forces encountered in AFM, depending on the tip/sample distance as it is observed in force spectroscopy mode.

The AFM has become one of the most advanced methods for the investigation of polymer surfaces and composites in recent years due to its developmental and instrumentation successes and the invaluable information it provides on morphology, nanoscale structure and chain order of polymers [8, 40]. Consideration of the hydrophobic attraction and hydrophilic repulsion is necessary in the AFM analysis of polymer samples [8, 40, 76]. In polymers, the structure and morphology of the topmost surface layers always differ from those of the bulk

**Table 2** Interactions occurring in AFM force spectroscopy (JPK Instruments)

	Interaction
<b>Approach</b>	
Tip far away (10–100 $\mu\text{m}$ )	No interaction
Tip approaching (few $\mu\text{m}$ )	Electrostatic forces
	Long-range interactions from adsorbed molecules
Tip close to surface (several nm to $\text{\AA}$ )	van der Waals
	Capillary forces (in air)
	Double-layer forces/screened electrostatics
	Chemical potential
	Magnetic
	Solvation forces (water layering)
<b>Contact</b>	
Tip indenting sample	Stiffness (Young's modulus, elastic response)
	Surface hardness
	Viscoelastic response
	Measurement of active forces (e.g., generated by cells)
<b>Retract</b>	
Tip lifting off surface (few $\text{\AA}$ to nm)	Adhesion:
	Non-specific (including chemical affinity, surface coatings)
	Ligand-receptor
	DNA hybridisation
	Cell surface interactions
Tip further away (nm to hundreds of nm)	Stretched molecules between tip and surface:
	Protein unfolding, pulling out of membranes
	Entropic elasticity
	Structural transitions and "melting"
	Other conformational changes in stretched molecules
Tip far from surface (1–5 $\mu\text{m}$ )	Connections broken between the tip and surface, no further interactions

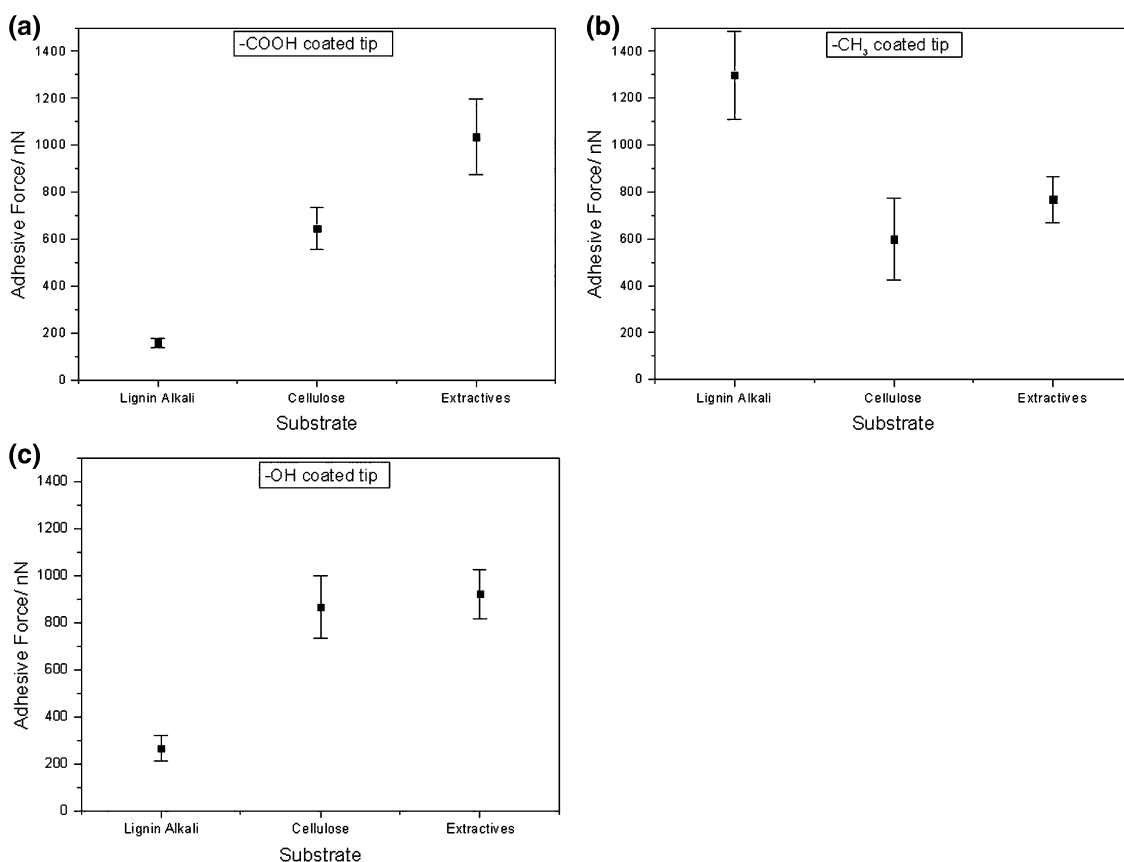
polymer, whilst the surface also influences properties such as adhesion, friction, wetting, swelling, penetrability and compatibility [8, 40].

### Adhesion and Surface Energy

Adhesion and the interphase play a very important role in determining composite properties such as strength, toughness, creep and moisture stability [70]. Adhesion refers to the tendency of two different bodies to be held together, whilst the mechanical force that is needed to separate both bodies from another is the adhesion force or pull-off force. In theory, the work of adhesion upon separation of the surfaces is defined by the surface energy and interfacial surface tensions of the interacting materials. Adhesion allows stress transfer between two bodies and is quantified by the amount of work required to pull the two surfaces apart [70]. Differences in surface tension or free surface energy of different substances are a result of different interatomic forces. These intermolecular forces could be

ionic, dipole–dipole, ion–dipole interactions, induced dipolar forces, VDW interactions, hydration forces, steric and fluctuation forces [36].

Adhesion is very relevant to many scientific and technological areas and as such has become a very important field of study in recent years [77]. There are a number of theories on how adhesion works [36]. Practically, the adhesion phenomenon observed by AFM results from two fundamental features: the surface properties (roughness, chemical heterogeneity, adsorption layer) of the materials in contact and the interaction forces between the two surfaces. These forces depend strongly on the interaction medium (air, water, vacuum) and the four fundamental contributions due to VDW forces, capillary forces, electrostatic forces for charged surfaces and static forces [72]. In polymer composites, the interaction between the polymer and the filler is developed during processing in the melt state and is a combination of VDW interactions, specific chemical interactions and chemical bonds between the polymer and the filler surface [25]. In general, the adhesion force between an AFM tip and a sample surface



**Fig. 4** Adhesive forces determined between the different substrates and **a** -COOH-, **b** -CH<sub>3</sub>- and **c** -OH-coated tips [45]

should include the capillary force, as well as the solid–solid interactions consisting of VDW forces, electrostatic forces and the chemical bonding forces.

In AFM pull-off measurements, continuum contact mechanics models are commonly used to describe the probe/substrate system [85]. The JKR and DMT models developed by Johnson et al. [38] and Derjaguin et al. [22], respectively, are frequently used to interpret the pull-off forces measured by the AFM. The difference between the two models lies in the nature of forces assumed to be acting between particle and substrate [36]. The JKR model assumes that attractive forces act only inside the particle–substrate contact area, whereas the DMT model includes long-range surface forces operating outside the particle–substrate contact area. Both models describe the correlation between pull-off force ( $F$ ) and work of adhesion ( $W_A$ ) through a simple analytical equation of the following form:

$$F = c\pi RW_A, \quad (1)$$

where  $R$  is the radius of the particle (probing tip), and  $c$  is a constant (where  $c = 2$  in the DMT model and  $c = 1.5$  in the JKR model).

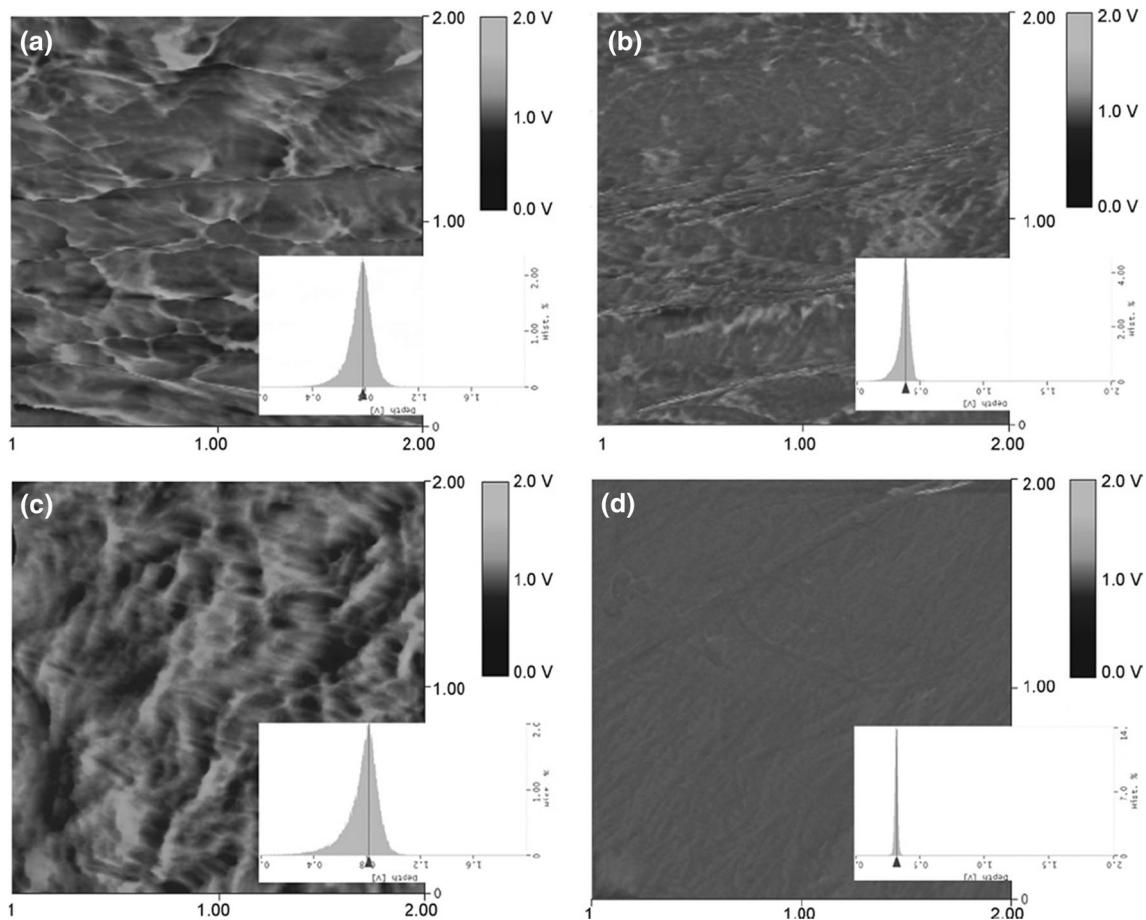
The DMT model is more appropriate for systems with hard materials having low surface energy and small radii of probe curvature. The JKR model applies better to softer materials with higher surface energy and larger probes.

To quantify adhesion energies from AFM measurements, the JKR model is frequently used for the analysis of data obtained by force–distance spectroscopy [44]. In the JKR model, the adhesion force (AFM pull-off force) is related to the work of adhesion,  $W_{adh}$ , and the reduced radius,  $R$ , of the tip–surface contact:

$$F_{adh} = -3/2(\pi RW_{adh}). \quad (2)$$

The work of adhesion is a combination of the tip–surface ( $\gamma_{ts}$ ), tip–solvent ( $\gamma_l$ ) and surface–solvent ( $\gamma_{sl}$ ) interfacial energies ( $W_{adh} = \gamma_{ts} + \gamma_l - \gamma_{sl}$ ). For tip–surface combinations that have the same chemical composition, the surface energy may be estimated directly from the adhesion measurement as  $W_{adh}$ .

One can, however, also directly and quantitatively determine the adhesive force from the calibration of the cantilever deflection. The deflection of the cantilever spring is directly proportional to the tip–sample interaction



**Fig. 5** Adhesive force images and histograms of grey values obtained on the fibre surface of pulped *E. grandis* with **a** –COOH- and **b** –CH<sub>3</sub>-coated tips and on the fibre surface of pulped *A. mearnsii* with

**c** –COOH- and **d** –CH<sub>3</sub>-coated tips, showing the removal of lignin on the fibre surfaces [45]

force, and once the deflection of the cantilever is known as a distance  $x$ , the adhesive force  $F$  can be calculated with Hooke's law:

$$F = kx, \quad (3)$$

where  $k$  is the spring constant of the cantilever.

The spring constant of the cantilever depends strongly on its shape and material. Typical silicon or silicon nitride contact cantilevers have low spring constants of about 0.05 N/m and shorter non-contact cantilevers have spring constants in the range of 50 N/m.

### Localisation and Quantification of Functional Groups

As mentioned above, the incompatibility between cellulosic fibres and polymer matrices requires the introduction of compatibilisers in WPCs. The AFM has in that respect recently opened remarkable opportunities, because it allows not only the imaging of a surface on molecular

scale, but through the measurement of F/D curves allows the determination of adhesive force measurements on any given point in this image.

Klash et al. [45] studied the distribution of different free chemical functional groups on wood and pulp fibres by means of CFM with chemically modified tips, which showed different sensitivities towards the major functional groups present in the different wood components. The cellulose and lignin content on fibre surface was thus not only localised, but could also be quantified [46]. Yan and Li [97] also used AFM with chemically modified tips to evaluate the inter-fibre bonding properties of typical wood pulp fibres. In a related study, Vancso et al. [94] reviewed the recent developments in the field of high-resolution lateral mapping of the surface chemical composition of polymers by AFM and other complementary imaging techniques to unravel the lateral distribution of chemical surface groups, the stability of various types of functional groups in various environments and the interactions with controlled functional groups at the tip surface.

Figure 4 shows the quantified adhesive forces detected in air between different functionalized tips and different wood components [45].

Carboxyl (COOH) and hydroxyl (OH) groups are polar and are attracted to the polar hydroxyl groups on the cellulose surface. Lignin, on the other hand, has many non-polar functional groups that will experience higher adhesion to non-polar methyl (CH<sub>3</sub>) groups.

The resulting AFM images then show the predominant distribution of cellulose and lignin on the wood fibre surface and can also be used to show the removal of lignin after pulping, as displayed in Fig. 5.

This information can be used to analyse differences in surface morphology of wood fibres originating from different wood species and more importantly detect possible binding sites for the compatibilisers on the wood particles. The polar ends of the compatibilisers would bind to the polar functional groups on the wood fibres, as highlighted, for example, in the image obtained with a –COOH-coated tip. From AFM measurements, it is possible to determine the distribution of binding sites, as well as the strength of the adhesive force that will hold the compatibiliser and wood fibre together. The same analysis can of course be performed in order to determine the interaction between the non-polar end of the compatibilisers and the polymer matrix. Understanding of the interaction of the WPC components on molecular scale will allow for a better understanding of macroscopic properties, such as wood fibre dispersion and general strength properties.

## Conclusion

Over the last few years, WPCs have received considerable attention from the wood and plastic industries [5, 20, 86]. There are a number of advantages that natural fibres can offer compared to synthetic materials, such as sustainability, bio-degradability and environmental friendliness and reduced weight compared to synthetic reinforcement fibres. The combination of good mechanical and physical properties together with their environmentally friendly character led to an increased use of natural fibres for composite reinforcement. Nevertheless, there are also many shortcomings, specifically lower strength properties, lower interfacial adhesion, poor resistance to moisture absorption, limited maximum processing temperature and lower durability and dimensional stability. These drawbacks can be overcome by adding compatibilisers such as maleated ethylene or maleated propylene, which possess polar and non-polar functional groups that allow them to attach to the polar wood fibre surface, as well as to the non-polar polymer matrix surface. The ability of AFM to create 3D, high-resolution images of surface morphology, as well

as interaction forces, has made it an essential tool for material characterisation in general. Specifically, for WPCs this technique can potentially be very useful, as they typically consist of three different components and their mechanical properties depend strongly on the interfacial adhesion between all three of them. AFM can be used to characterise the surface structure, as well as chemical functionalities of the main components and localise and to a degree quantify functional groups and therefore give an indication of the adhesive forces on a molecular scale. Other techniques, such as contact angle measurements that are typically used to determine polarity yield average values that characterise wide macroscopic areas. The high resolution of AFM allows localised measurements that take heterogeneous fibre into account and can potentially explain why certain components work in some cases better than others. For example, not all compatibilisers work equally well on all wood fibres and studying the interfacial adhesion between different compatibilisers and different wood fibres with AFM can help understand this phenomenon.

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## Compliance with Ethical Standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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