1. Introduction

1.1 Adhesive joints

An adhesive may be defined as a material which when applied to surfaces of materials can join them together and resist separation. The term adhesion is used when referring to the attraction between the substances, while the materials being joined are commonly referred to as substrates or adherends (Kinloch, 1987). The adhesive properties of some substances have been used for thousands years. During Prehistory, for example, man has employed several plant resins as adhesives, either neat or with other materials to improve their properties (Regert, 2004; Wadley, 2005). However, the science and technology of adhesion and adhesives has not progressed significantly until the middle of 1940s (Kinloch, 1987), when the II World War promoted the development of different technologies, between them, the polymer science, closely related to the adhesives. Since then, great advances have been carried out in all aspects of adhesives technology. Nowadays, the practical demands upon adhesives have changed. The main aim is no longer to achieve simply strong bonds; that has been mastered. The targets are durability under a variety of harsh environments, together with enhanced toughness and, in some specialised cases, adequate performance at relatively high temperatures (Allen, 2003).

Adhesive joints offer many advantages, with regard to other ways of joining materials, like welding, brazing, riveting or bolting:

- The ability to join any type of material, even to make dissimilar joints.
- An improved stress distribution in the joint, reducing the stress concentrations caused by rivets or bolts.
- Adhesive bonding can potentially reduce the weight of a structure, mainly because of the ability to join thin-sheet materials efficiently.
- An improvement in the corrosion resistance between dissimilar materials, and also with regard to the use of mechanical fasteners.
- Adhesive joints can be used for sealing, insulating (heat and electricity) and damping vibrations.
- Less expensive than other types of joints, especially when bonding large areas.

They have some drawbacks:

- Require careful surface preparation of adherends, especially in order to attain a long service-life from adhesive joints in hostile environments.
- Limitation on upper service temperature.
- The strength of adhesive joints is relatively low compared to mechanical joints.
- Disassembly cannot be carried out without incurring significant damage to the joint.
- Non-destructive test methods for adhesive joints are relatively limited compared to those used with other fastening methods.
- Heat and pressure may be required for assembly.
- Jigs and fixtures may be required for assembly.

1.2 Mechanisms of adhesion

The mechanisms or theories of adhesion try to explain how an adhesive bond is formed between two materials. There is not a universal mechanism to explain all bonds. In fact, in adhesive joints there is usually more than one mechanism contributing to the adhesive strength.

**Mechanical interlocking:** This theory proposes that mechanical interlocking of the adhesive into the irregularities of the substrate surface is the major source of intrinsic adhesion (Kinloch, 1987). This means that the adhesion is directly related to the substrate roughness. Mechanical, like grit blasting, or chemical roughening, like anodizing, generate different values of surface roughness and also different features. The size and shape of these features have an influence on the adhesion, providing a tortuous path which prevents the separation of the adhesive from the adherend (Fisher, 2005). However, this theory is not able to explain the good adhesion strength attained in some cases between smooth surfaces.

**Diffusion theory:** The diffusion of segments and chain ends of polymers was suggested as a mechanism for the adhesion of similar polymers. This requires that the macromolecules or chain segments of polymers (adhesive and substrate) possess sufficient mobility and are mutually soluble (Kinloch, 1987). Two polymers, or a polymer and a solvent, are miscible when they have similar solubility parameters. This theory demonstrates the autohesion of plastics using hot or solvent welding, and also explains why polymers with very different solubility parameters do not present good adhesion between them.

**Electronic theory:** In adhesive joints of metallic substrates, the different nature of the materials (metal and polymer) facilitates the transfer of electrons from the metal to the adhesive, in order to equilibrate the Fermi levels of both metal and polymer. The result is the creation of an electric double layer at the interface (Allen, 2003). The existence of that layer is easy to demonstrate. For example, it causes the flashes of light and noise which occur when an adhesive tape is stripped form a solid surface (Allen, 2003). However, it is not clear if such electrostatic forces promote an increase of the joint strength or they are a result of that increase (Kinloch, 1987).

**Adsorption theory:** The adsorption theory of adhesion is the most widely applicable theory and proposes that, provided sufficiently intimate molecular contact is achieved at the interface, the materials will adhere because of the interatomic and intermolecular forces which are established between the atoms and molecules in the surfaces of the adhesive and substrate. This means that the adhesive has to spread over the solid surface. A liquid wets a solid when the contact angle between a liquid drop and a solid surface is lower than 90°; in other words, when the surface free energy of the surface is high than the surface tension of the liquid. The Young equation (Young, 1805) describes the relationship between surface free energy, \( \gamma_{SV} \), and contact angle, \( \theta \), in the three-phase contact point (Figure 1):

\[
\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot \cos \theta
\]
The work of adhesion, $W_A$, is defined as the difference between the sum of the surface free energies of the solid and liquid phases and the interfacial free energy:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$  \hspace{1cm} (2)

Combining equations (1) and (2) the relationship between the work of adhesion and the contact angle can be obtained:

$$W_A = \gamma_{LV} (1 + \cos \theta)$$  \hspace{1cm} (3)

This equation is very useful to estimate the strength of an adhesive joint, taking into account that the higher the work of adhesion, the higher the adhesive strength. The surface energy of a liquid, $\gamma_{LV}$, is a known parameter, and the contact angle is very easy to determine.

**Weak boundary layer theory:** This is not strictly a mechanism of adhesion, but it is a theory which allows explaining the lack of adhesion in many cases. Oxide layers, low molecular weight species, oils and other contaminants are weak boundary layers, poorly adhered to the substrate. If any of such layers is present on the surface of the adherend when bonding, the joint will fail between this layer and the substrate with low strength.

### 1.3 Surface preparation

In order to achieve good adhesive properties, one requirement is that the adherends must present adequate surface properties. As it was mentioned above, the surface free energy of the substrate should be higher than the surface tension of the adhesive. In some cases, especially when the adherends are polymers or polymer matrix composites, the surfaces have to be modified to increase their surface free energy. There are other reasons to apply surface treatments before adhesive bonding, like removing weak boundary layers, increasing the surface roughness, creating specific chemical groups or homogenizing the surfaces to improve the reproducibility of the results.

There are several types of surface treatments available: mechanical (grit blasting), chemical (anodizing, acid etching) or energetic (plasma, laser). In every case the most suitable treatment has to be selected, taking into account the material, shape and size of the adherend, the adhesive and other circumstances related to the manufacturing.

### 2. Nanoreinforced adhesives: potential advantages

Polymer nanocomposites manufactured from an effective dispersion of nanofillers (nanoparticles, nanofibres, nanotubes, etc) into a polymeric matrix (thermoplastic or thermosetting) have been proposed as a powerful tool for generating new multifunctional materials with improved mechanical, physical and chemical properties. Due to their small size and large surface area, nanoreinforcements would be able to provide unique...
combination of properties, which are not possible to be reached for conventional fillers with sizes in the micrometer range. Of particular importance, it is the requirement of achieving a good distribution of the nanofiller in the polymer, in order to obtain the pursued increases in properties, without loss of other characteristics of the nanocomposite (i.e. processability) because of the high tendency to particle aggregation.

The development and commercialization of nanoparticles such as nanoclays, carbon nanotubes (CNT) or nanofibers (CNF), inorganic nanoparticles and other, offer new possibilities to tailor adhesives in the nanoscale range. Due to the large surface area of the nanosized particles only small amounts are needed to cause significant changes in the resulting properties of the nanocomposite adhesives. It could provide a new generation of structural adhesives with combination of thermal, electrical or thermomechanical properties which also provide higher environmental durability because of their lower water absorption and enhanced ageing properties.

The potential of nanofillers for adhesive formulations is promising, and their effects, most of them based on the chemical and physical interactions developed between the nanoparticle surface and the resin at the reinforcement-matrix interfaces, can be classified on the following groups:

a) **Mechanical properties.** Many of the new applications of structural adhesives (i.e. transportation application such as aircraft industry) require stable materials under service conditions which imply high temperature environments, beside to be resistant to failure resulting from vibration and fatigue loading. The addition of nanofillers to base adhesive formulations generally increases their modulus and mechanical strength. However, the main objective in these cases is to increase fracture toughness without loss of adhesive characteristics. Research in improving the fracture toughness of brittle polymers (i.e. thermosets) using nanoreinforcements holds great promise. Although the toughness of these brittle resins is usually increased by means of the addition of rubber fillers, other mechanical properties are usually degraded. For example, the improvement of the toughness of epoxy resins by incorporating nanofillers (i.e CNTs) in the resin system has been reported by numerous researchers. The participation of new mechanisms of fracture energy consumption generated by the interaction between cracks and nanofillers (crack deflection, crack bridging, fiber pull-out, etc) is considered responsible of the toughening effect associated to the nanoreinforcement addition.

Gojny et al. (2005) have published an overview in *Composites Science and Technology* over the influence of nanofiller on the fracture toughness of brittle epoxy resins and the related micromechanical mechanisms. These authors consider toughening mechanisms participate at two different dimensional levels: 1) micro-mechanical mechanisms, such as crack deflection at agglomerates, crack pinning, crack blunting and the extension of the plastic deformation zone and 2) nano-mechanical mechanisms, such as interfacial debonding, pull-out and crack bridging with participation of the nano-sized structure of CNTs.

Improvements in toughness with addition of low contents of nanofiller have been reported for numerous authors, not only in the case of nanoreinforced polymers but also in situations in which the nanoreinforced matrix is included in a more complex system such as continuous fiber reinforced composites. The manufacture of multiscale composites by incorporation of nanofiller inside the matrix composite is also considerate as a potential method to improve those properties which are highly depended on the matrix (among them, toughness). Manufacture of these composites requires that nanoreinforced resins
keep their rheological and wetting characteristics to make possible the infiltration of fibre per- forms. Both types of properties are also required by nanoreinforced adhesives. In this research line, R. Sadeghian et al. (2006) have manufactured by Vacuum Resin Transfer Moulding (VARTM) hybrid composites constituted by CNF nanoreinforced polyester/glass fiber, improving the mode-I delamination resistance $G_{IC}$ about 100 % when CNF concentration up to 1 wt% is incorporated in the polyester matrix. These authors characterized also the viscosity dependence on the CNF concentration noticing a notable increase in resin viscosity when we CNF concentration raised from 1 to 1.5 wt%. This problem, which limits the processability of multiscale composites by infiltration methods, must be considered also in the case of nanoreinforced adhesives.

**b) Electrical properties.** In relation with the electrical properties, one of the most interesting fields of application is the incorporation of carbon nanotubes or carbon nanofiber as fillers in electrical conductive adhesives. The aim is to improve the performance of conductive adhesives in comparison to common products. An increase of electrical conductivity is observed in these kinds of nanocomposites with increasing CNT or CNF contents, showing clear percolation behaviour. The conductivities of the many of the developed composites show magnitudes below materials like copper. The percolation threshold values depend on the type of nanoreinforcement, being lower in the case of CNT than for CNF. The method of dispersion also has a dramatic influence on the conductivities of the nanocomposites, both for the effectiveness of the dispersion and for the effect of the applied dispersion method (mechanic stirring, ultrasonication, calendering, etc) on the nanoreinforcement integrity. High energetic dispersion processes may damage the nanofillers decreasing their aspect ratio, which affect to the percolation behaviour.

The electrical conductivity is usually detrimentally influenced by the application of functionalization treatments to the carbon nanoreinforcement. Although these kinds of treatments (oxidation, amination, fluoridation, etc) usually improve the nanofiller dispersion and favour the formation of covalent bond with the polymer matrix, they are always connected to structural changes (i.e rupture of the CNTs, resulting in a reduced aspect ratio) and, therefore, to a reduction of the electrical conductivity. Figure 2 shows the change in specific conductivity with the percentage of nanofiller for two epoxy nanocomposites reinforced with double wall CNT (untreated and aminofuntionalizated), compared with the effect of the addition of carbon black. The lowest percolation threshold value is reached for the Epoxy/DWCNT; an increase in this value is observed in the case of the Epoxy/DWCNT-NH$_2$ because of the damage of the nanofillers during the funtionalization treatment.

**c) Thermal Properties and Thermal Stability.** Thermal stability is one of the most important properties of polymer nanocomposites for potential applications as functional or structural components at elevated temperatures. Thermal stability and degradation behaviour of nanocomposites have been studied by several researchers. For example, Sarathi et al. (2007) showed that the addition of nanoclays (i.e organo-montmorillonites) in epoxy increases the heat deflection temperature up to a critical percentage of nanoclay in epoxy, about 5 wt % above which it reaches a steady state. Addition of nanoclays also improves the thermal stability reducing, in relation with unreinforced epoxy, the loss of weight measured during a thermogravimetric analysis. Decomposition temperatures of nanocomposites generally increased with increasing nanofiller contents, indicating that the thermal decomposition of the matrix is retarded by the presence of the nanoreinforcement. These results may be
attributed to the physical barrier effect, having experimental proofs that not only nanoclays but also CNTs impede the propagation of decomposition reactions in the nanocomposites (Kim & Kim, 2006).

Other thermal property that can be controlled by the addition of low amount of nanoparticles is the coefficient of thermal expansion (CTE). In the specific case of thermosetting resins, the CTE values can be differed below and above the glass transition temperature ($T_g$). Considering the application of these resins as adhesive, the most useful CTE concerns the temperature below $T_g$, since adhesive would lose most of its mechanical properties at temperatures higher than $T_g$. Since CNT shows negative CTEs values (longitudinal CTE of SWNTs has been estimated to be $-12 \times 10^{-6} \text{ K}^{-1}$ while a transverse CTE was predicted to be $-1.5 \times 10^{-6} \text{ K}^{-1}$) (Kwon et al., 2004; Jiang et al., 2004), the additions of SWCNTs could lead to a lower CTE in SWNT nanocomposites. This effect will be so much remarkable when dispersion of nanoreinforcement is more effective. For example, S. Wang et al. have shown that the CTE of the functionalized SWCNTs–epoxy composites below $T_g$ could be diminished by 52 and 42% by the incorporation of 1% by weight of nanotubes which were subjected to simple functionalization treatments (mechanical chopping and oxidization) to improve their dispersion (Wang et al., 2007).

The addition of some kind of nanofillers (i.e. CNT) can also increase the thermal conductivity of nanocomposites. Heimann et al. (2008), have shown that the thermal conductivity rises almost linearly with rising content of CNT in the polymer matrix (epoxy matrix). The composite with the highest portion of CNT tested (10 wt %) points out an enhancement nearly 4.4 times compared to the matrix without CNT (Figure 3); no influence of the method of dispersion could be observed.

d) Gas and Liquid Barrier Properties. The barrier properties of the nanocomposites are considerably improved as compared to that of pure or macroscopically filled polymers. The reason for the dramatic drop in permeability has been attributed to the existence of well-dispersed nanoreinforcements with a large aspect ratio (nanoclays, CNT, CNF). Most studies on polymer nanocomposite barrier properties are based on the tortuous pathway concept (Nielsen, 1967), where the nanofiller phase is assumed to be impermeable for gas
and liquid molecules, which forces the gas molecules to follow a tortuous path thereby increasing the effective path length for diffusion.

One of the potential advantages of nanoreinforced adhesives related with these barrier properties is use as a moisture barrier. Moisture permeation is a measure of the ability of a material to resist moisture to penetrate through its thickness. Several important parameters must be considered, including the volume fraction ($V_f$) and the aspect ratio of the nanoparticles. Higher aspect ratios provide greater barrier improvement according to the equation:

$$\frac{P_c}{P_0} = \frac{1}{1 + (L/2W)V_f}$$

where $P_c$ and $P_0$ are the permeability coefficients of the nanocomposite and the neat polymer, respectively; $L/W$ is the aspect ratio of the nanofiller, defining the term $(1 + (L/2W)V_f)$ as the tortuosity factor. Reductions in moisture permeability in the range of 57-86\% for epoxy resins nanoreinforced with nanoclays have been determined, deducing that the very large aspect ratio of the clay platelets is the main factor to reach an effectively increased the moisture penetration path, which is responsible for the reduced permeability. (Kim et al., 2005).

Although nanoplatelets have been shown as very effective gas and liquid barriers in polymeric matrices, recent studies on the transport properties, sorption and diffusion of water vapour carried out on epoxy resin filled with multi-walled carbon nanotubes, have also showed the improved effect of the barrier properties with increasing MWCNT concentration (Guadagno et al., 2009).

Water absorption is other of the properties of polymer which can be improved by the dispersion of nanofillers. This improvement can be significant for resins which preset pourer behaviour under prolonged water exposure, such as epoxy. The substantial decrease of permeability brought about by nanocomposite structures is a major advantage of polymer-clay nanocomposites, due to the tortuous path presented by high aspect ratio clay. The Toyota researchers determined that the rate of water absorption in their polyamide 6-clay nanocomposite was reduced by 40\% compared with the pristine polymer. However, these results are more contradictory in the case epoxy matrix nanocomposites where only the rate of absorption is reduced, while the equilibrium water uptake is relatively unaffected.
In spite of those potential advantages of the nanoreinforced adhesives, the incorporation of nanofillers into the adhesive may originate problems associated to the increase in viscosity and the modification of the wetting behaviour with regard to the neat adhesive. It is enough shown that the addition of nanoparticles into liquid resins increases their viscosity; and for the particular case of CNTs, it has been found that increase in the viscosity of the nanocomposites filled with CNTs was much higher than increase in the viscosity of polymer composites filled with carbon fibers (CF) or carbon black (CB). Beside, nanocomposites filled with functionalized CNTs, that have better dispersion of the CNT, show a complex viscosity at low frequency.

### 3. Adhesives reinforced with inorganic nanoparticles

Due to the novelty of the nanocomposites, there are not much scientific researches which analyse the viability for the use of nanoreinforced polymers as adhesives. Further, the most of the found publications about nanoreinforced adhesives are centred in the reinforcement of epoxy adhesives with different kinds of carbon nanotubes. This is probably associated to the fact that the epoxy resins reinforced with carbon nanotubes are being currently the most studied nanocomposites by the scientific community. Even so, several researches have been found about the reinforcement of adhesives with inorganic nanoparticles. The nature of the added nanofiller is varied, being nano-sized particles of silica and alumina some of the most used. Also, the published results are varied. Among other reasons, the study of the adhesive ability of a resin, modified or not, depends on several factors, such as the nature of the adherends and the applied surface treatments on them, the geometry of the joints (single lap, butt, T-joing, etc) and the type of test carried out to determine the strength of the joints (lap shear, peel, pull off, wedge, etc). Besides all these variables, new ones are added, which are associated with the own manufacture of nanocomposites, like the dispersion techniques and methods applied, the previous chemical treatments carried out over nanofiller surfaces and the geometry, structure and other characteristics own of nanoreinforcements, among others. Despite of this, this section of the chapter contains a summary of some of the most interesting published results on adhesives reinforced with nano-sized particles of inorganic nature.

The most of bibliography found about the addition of nanofiller into the adhesives is mainly based on epoxy adhesives. Compared with other adhesives, epoxy ones produce joints with high shear strength and excellent creep properties. The delamination resistance and impact of the epoxy joints are, however, relatively low. Due to their good properties, these adhesives are frequently used in high responsibility applications where their relative high cost is not as relevant. It is expected that the advantages obtained by the addition of the relative expensive nano-scale filler compensate the increase of price of the adhesive. In fact, the addition of nanofiller into epoxy adhesives could enhance the main debilities of the epoxy joints, such as their strength and toughness. Moreover, it should increase the electrical conductivity of these resins, becoming from isolator to conductive materials. This is especially interesting because of the epoxy adhesives are frequently used for joining metals and carbon fiber reinforced composites. Both are electrical conductors and it will be very profitable that their joint remains this electrical behaviour, using an electrical conductive adhesive.

Lanlan Zhai and collaborators have published several researches on the effect of the addition of alumina nanoparticles in epoxy adhesives (Zhai et al., 2006; Zhai et al., 2008),

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analysing their pull-off strength over steel. Some of the extracted results are shown in Figure 4a, together with a scanning electron micrograph of the alumina nanoparticles added (Figure 4b) and image of the nanoreinforced epoxy surface captured by transmission electron microscopy (Figure 4c).

![Fig. 4. (a) Effect of nano-alumina additive content on the adhesion strength, (b) SEM micrograph of alumina nanoparticles, (c) TEM micrograph of the nanoreinforced epoxy surface (Zhai et al., 2008).](image)

It is probed that the addition of alumina nanoparticles causes a drastic increase of the adhesive strength, which reaches the maximum value when the nanofiller content is 2 wt %. The pull-off strength of this nanoreinforced adhesive is almost five times higher than that of pure epoxy adhesive. This increase is intimately associated with a change in failure mode, which becomes from interfacial failure for non modified adhesive to a mixed cohesive-interfacial failure mode for the joints bonded with nanoreinforced adhesives. At high nano-alumina contents, the adhesive strength falls because the surface wetting ability of the adhesive is reduced by the increase of its viscosity.

The modification of adhesives by the addition of alumina nanoparticles has been also studied in epoxy-based film adhesives, which are incrementing their use for joining aluminium and polymer composite parts in the aircraft industry. These applications typically require the modification of epoxy formulations to increase the adhesion, toughness and peel strength of the joints, because they are usually subjected to vibration and fatigue loads besides high service temperature environments. The most widely used modifiers of epoxy-based film adhesives consist of reactive liquid elastomers, which increase the toughness of the joints but limit their modulus, thermal stability and hot-wet performance. Also, the phase separation of the rubber can imply a reduction in shear strength. Gilbert et al. (2003) confirmed that the addition of 5 wt % nano-alumina into an epoxy formulation that was filmed on polyester random mat scrim achieved increases in the peel strength of almost 50% and in shear strength of 15% for joints of aluminium substrates. Contradictory results were obtained in the measurements of mode I and mode II fracture toughness of nanoreinforced epoxy adhesives when the nature of substrate was carbon fiber/epoxy.
Nanofibers laminates. They were strongly dependent on whether the composite systems were cocured or bonded. Mode I fracture toughness of the cocured composites increased, while values for the bonded systems drastically fell down by the addition of the nanofiller.

Other kinds of inorganic nanoparticles have been added to adhesives in order to enhance their properties and behaviour. In particular, several researches have been published using nanosized particles of silica. It is well known that thermophysical and thermomechanical properties, such as thermal conductivity, coefficient of thermal expansion, tensile and breaking strength of epoxy resins improve considerably due to the silicate nanopowder into the matrix polymer. Also, the addition of low concentrations of nanosilica particles to a typical rubber toughened epoxy adhesive leads to very significant increases in the toughness and single lap shear strength of the joints (Klug & Seferis, 1999; Kinloch et al., 2003). This increase is related to the enhancing of the plastic deformation of the epoxy matrix due to the appearance of different toughness mechanisms, such as crack deflection and crack twisting around the nanoparticles. On the other hand, Bhownik et al. (2009) probed that the exposure under high-energy radiation of a nanosilica reinforced epoxy resin causes an increase of its crosslinking density, essentially affecting the overall behaviour and mechanical properties of the nanoreinforced polymer. In fact, they report an increase of more than 100% of the lap shear strength of the titanium joints when the adhesive was reinforced with nano-silicate particles and exposed to high energy radiation regard to the adhesive strength of non-modified adhesive. Patel et al. (2006) analysed the strength of acrylic-silica hybrid adhesives, prepared in situ by sol-gel, through both peel and lap shear tests using aluminium, biaxially oriented polypropylene (PP) and wood as substrates. They found enhancements on the joint strengths with hybrid nanoreinforced adhesives compared to neat acrylic ones, which were associated to changes in the failure mode from interfacial failure for neat acrylic adhesive to slip-stick failure in the case of the hybrid composites. As with alumina nanoparticles, the joint strength increases with increase in nanofiller loading up to certain content due to the higher cohesive strength and higher interaction between the substrates and the nanoreinforced adhesives. High contents of nanoreinforcements imply the fall of adhesive and mechanical properties because of both an increase of the adhesive viscosity and problems to disperse rightly the nanofiller, appearing micro-sized agglomerations.

Lanlan Zhai et al. (2006) published a comparative study about the effectiveness of different kind of inorganic nanoparticles on the stickiness of epoxy adhesives. In particular, they used nanoparticles of Al₂O₃ (whose average diameter was 80 nm), nano-CaCO₃ (with 40 - 80 nm of diameter) and nano-SiO₂ (whose size was 10 - 20 nm in diameter). These nanofillers were added in 2 wt % regard to the epoxy adhesive mass. Low carbon steel sheets were used as adherends, which were abraded with different silicon carbide paper, polished to an optical flatness and finally degreased and dried. As shown in Figure 5, the adhesion strength, measured through pull-off adhesion test, of the epoxy adhesives incorporating three kinds of nanoparticles was greatly improved compared with pure epoxy adhesive. The highest increase is obtained by the adhesive reinforced with nanoparticles of alumina, from 3.4 to 18.4 MPa, while the strength of the nano-CaCO₃ modified epoxy adhesive was as much as that of nano-SiO₂ modified system, no more than 12 MPa.

The increase of adhesive strength by the addition of nanofillers into the adhesives implies a stronger anchoring associated to changes on the physical and chemical properties of the modified adhesives. The different enhancements found as function of nanoparticle nature may be attributed to the chemical properties of nanoparticles, which may have influence in
the chemical interaction of the surfaces of steel and epoxy adhesives, producing some chemical bonds on the interface and therefore enhancing the adhesion strength. The formation of bridges between the adhesive and the adherends was confirmed by the analysis of the interface morphology through scanning electron microscopy. Figure 6a shows the morphology of the interface of steel and epoxy adhesive reinforced with 2% nano-Al₂O₃. It is possible to observe some epoxy fibers connecting with the steel substrate, which implied that both surfaces had contacted closely. The gap between steel and epoxy adhesive was likely to result from abrading and polishing of the metallographic specimen. Figure 6b shows the morphology of the surface boundary of steel and epoxy adhesive without nanoparticles, which is radically different. The gap is evidently wider than that of nanoreinforced joint, implying a weaker adhesion. For this reason, it was easy for the contamination to fall into the gap in the process of preparing the metallographic specimen.

Fig. 6. SEM micrographs of steel – epoxy interface morphology with adhesive nanoreinforced with nanoparticles of alumina (a) and with neat epoxy adhesive (b) (Zhai et al., 2006).

Polyhedral-oligomeric-silsesquioxanes (POSS) are other kind of inorganic silica particles which are actually commercialized, being nanocages of 1.5 nm in size with organic substituents. The substituents can be inactive, physically compatibles with the matrix, or reactive, which promote curing or grafting reactions with the polymer. The effect of the addition of low amounts of POSS into epoxy adhesives is strongly dependent on the nanostructure of the epoxy/POSS network, which in turn depends on the functional groups...
(reactive or nonreactive) of the POSS (Dodiuk et al., 2005). The highest values of shear and peel strength are obtained when the crosslinking degree of nanoreinforced adhesive is high. Due to the large surface area of POSS, only relatively small amounts (< 4 wt %) are needed to cause significant changes on the properties of the epoxy resin. In fact, excess of POSS amount implies the plasticization of the matrix, decreasing the joint strength. Finally, Patel et al. (Patel et al., 2006) analysed the effect of the addition of an organically modified montmorillonite nanoclay, commonly named Cloisite 10A, on the joint strength bonded with a very soft acrylic adhesive. With a high surface energy adherend, like aluminium, clay nanoreinforced adhesives displayed gradual increment in peel strength with the increase of filler content, measuring enhancements of up 45% regard to neat adhesive. However, the observed improvement with low surface energy substrate, polypropylene, was lower. This indicates a favourable interaction between the silicates and aluminium substrate. The lap shear strength spectacularly increases with the nanoclay addition, up to 146, 130 and 142% in joints of aluminium-aluminium, wood-wood and polypropylene-polypropylene, respectively. Besides the adhesive properties, the addition of nanoclay into the adhesives enhances their barrier performance. This is especially interesting in the use of polyurethane adhesives (Osman et al., 2003). They are commonly used in producing laminates for food packing due to their flexibility and wide application temperature range. However, their use is limited due to their low barrier performance, as oxygen and humidity barriers. The inclusion of small volume fractions of montmorillonite in polyurethane adhesives decreases their gas transmission rate due to the impermeability of the inorganic nanoparticles.

4. Adhesives reinforced with carbon nanotubes

One of the nanosized filler which has generated higher expectation are the carbon nanotubes (CNTs). CNTs, composed of one grapheme layer (SWCNT) or many grapheme layers (MWCNT), are a novel crystalline carbon form. The growing interest of these materials is associated with their spectacular and new properties theoretically expected. Independently of nanotube type and its diameter, the value of the plane elastic modulus should reach the reported one for the graphite, which is 1.06 TPa (Nelly, 1981). Its yield strength is still unknown, although it must be also similar to that calculated for the graphite, which is estimated around 130 GPa (Perepelkin, 1972). The mechanical strength of MWCNTs has could be measured by Atomic Force Microscopy, giving values around 14 GPa (Wong et al., 1997). Due to its very low diameter and in spite of its high stiffness, the carbon nanotubes present very high flexibility, bending fully reversible up to 110° critical angle for SWCNT (Salvetat et al., 1999). In addition to their mechanical properties, the nanotubes present very interesting physical properties. They have metallic and semiconducting electrical character, field emission properties and high thermal conductivity, among others. Therefore, these materials have been widely researched as nanofiller in the manufacturing of composites, using different matrix materials, polymers, ceramics and metals. As it was said above, research in improving the fracture toughness of brittle thermosets using nanotechnology holds great promise. As it is well known, in order to reach the best properties of nanocomposite, CNTs must be totally dispersed into the composite matrix. For it, numerous alternatives have been proposed (Xie et al., 2005; Vaisman et al., 2006; Prolongo et al., 2008) such as the use of solvents and surfactants to disperse rightly the CNTs with the epoxy monomer. Other
proposals are based on the application of high mixing forces, using high shear mechanical mixers or ultrasonic. One of the last proposals with higher success is the use of a three roll mini-calander (Gojny et al., 2005). This procedure consists of passing the CNT/epoxy mixture through several rotating cylinders with a very small gap between them, around 50 – 5μm.

Among other difficulties, the increase of the viscosity of epoxy monomer by the addition of CNTs is high due to the very high specific area of these nanofillers (200 – 700 g/m²). This usually hinders the manufacturing of the nanocomposite. S. G. Prolongo et al., in *Journal of Adhesion Science and Technology*, (2009) analysed the rheological behaviour of mixtures of epoxy monomer with different contents of MWCNTs. The results are shown in the Figure 7. The used MWCNTs were partially functionalized with amino groups (0.5 wt% NH₂). For this reason, the nanoreinforced mixtures were thermally treated in order to enhance the chemical reaction between oxirane rings of epoxy monomer and amino groups of the nanotubes.

In spite of the viscosity increase, the shear rheological behaviour seems remaining constant. Both neat and nanoreinforced epoxy resins show Newtonian behaviour at the high shear rate applied and relative low temperature (< 70 ºC). This is explained by the preferential orientation of the nanoreinforcement in the flow rate at high shear rates. Other authors (Hyun et al., 2001) reported that the addition of a very small amount of nanotubes induce non-Newtonian behaviour at very low shear rate, which is probably associated with the non-orientation of nanotubes. On the other hand, at relative high contents of CNTs, the application of a thermal pre-curing treatment to the nanoreinforced mixtures implies an increase of their viscosity, indicating that the chemical reaction between epoxy monomer and amino-functionalized carbon nanotubes occurs. The more CNTs content is added, more amine groups anchored to nanotube react, decreasing the mobility of epoxy molecules and therefore increasing their shear viscosity.

![Fig. 7. Shear viscosity versus temperature plots for non-cured epoxy monomer (DGEBA, squares) and the epoxy mixtures with 0.1 (circles), 0.25 (triangles) and 0.5 wt % (stars) amino-functionalized MWCNTs non-thermal treated (solid lines) and precured at 130 ºC for 1 hour (dot lines) (Prolongo et al., 2009).](www.intechopen.com)
The addition of CNTs to epoxy resins modifies many of their properties, but this chapter is centred in the application of these nanoreinforced composites as adhesives. Several works have been found about the addition of CNTs on epoxy adhesives in order to enhance the mechanical strength and toughness of the bonded joints. Suzhu Yu et al. (2009) studied the mechanical behaviour and durability in humid environments of the A2024-T3 aluminium joints bonded with an epoxy adhesive reinforced with MWCNTs. Figure 8 shows some of the obtained results.

The wedge test has a relatively high stress concentration at or near the interface of the joint and is sensible to environmental attack. Therefore, it is usually used to provide quantitative durability data for a joint. As it can be observed in the figure, the crack developed in three steps for almost all the specimens: initial crack, crack propagation in about 3 – 8 h of immersion, and crack propagation after the first 3 – 8 h of immersion. The initial crack length was reduced up 70.3% for the epoxy resins randomly reinforced with 0.5 wt % CNTs compared to the obtained for the joint with neat epoxy adhesive. The decrease of the initial crack length occurs from 0.5 to 1 wt % CNTs, then the length increases with increasing CNTs fraction from 1 to 5 wt %. Obviously, the addition of CNTs into the epoxy adhesive causes a significant improvement in the bond strength of the joints, which is attributed to the excellent properties of the nanofiller. From a theoretical point of view, the strength of the adhesives should be monotonously increased with increasing CNT loading; thus, the initial crack length of the specimen would have monotonously decreased with the nanotube fractions. This is true at low CNTs contents (< 1 wt %). At higher contents, adverse effects of CNTs might have resulted from aggregation and poor dispersion of the nanofiller into epoxy matrix. The agglomerates can act as defects and reduce the strength of the adhesives. The propagation crack rate at first 3 – 8 h of immersion is also reduced by the addition of CNTs. In fact, the joint bonded with neat epoxy adhesive failed and broke after 3 h of immersion in water. This suggests that the water resistance of the adhesive increases with the CNT loading. The nanoreinforced epoxies must be able to resist water attack, so its adverse effects on the strength and durability of joints are not so significant. This is explained because carbon nanotubes are hydrophobic in nature and therefore their addition into the adhesive enhances the water resistance of the joints. The failure mode of the joint with neat epoxy adhesive is cohesive failure, referring to crack propagation on the adhesive (figure 8b). Interestingly, for the joints with CNT filled epoxy adhesives, more interfacial failure, referring to crack propagation on the adhesive-adherend interface, is developed with increasing nanofiller content. In fact, for epoxy adhesive reinforced with 5 wt % CNTs, only one surface is covered with adhesive in most areas; the other one mainly showed the metal surface.

Several works (Hsiao et al., 2003; Meguid & Sun, 2004) have studied the mechanical strength of CNT reinforced epoxy adhesives to join carbon fiber reinforced polymer (CFRP) composites. The shear strength increased by 31.2 and 45.6% when 1 and 5 wt % MWCNTs, respectively, were added in the epoxy system (Hsiao et al., 2003). These increments are associated with the enhanced mechanical properties of the nanoreinforced adhesives and the change of the failure mode of joints. The fracture of joints bonded with non-modified epoxy adhesive occurred at the epoxy along the bonding interface. In fact, no significant damages were observed on the composite adherends. In contrast, the failure observed for nanoreinforced joints was cohesive in the adherends. The nanotubes effectively transferred the load to the graphite fibers in the adherends and the failure was in the composite. For this reason, the graphite fibers of the composite adherends were highly damaged after the test.
Meguid and Sun studied the adhesive properties of nanoreinforced epoxy adhesive using dissimilar joints, formed by carbon fiber/epoxy laminate and aluminium alloy 6061-T6. The results reveal that the presence of uniformly dispersed carbon nanotubes causes an increase of the bonding strength. A remarkable improvement in Young’s modulus as well as ultimate tensile strength of the nanoreinforced adhesives is also appreciated. The increase continues with the increase in the weight percentage of nanofiller. However, as other authors have already observed, there is an optimum content of nanofiller. At very high carbon nanotubes contents, above 10 wt %, the properties degrade to below the ones of the neat epoxy adhesive. These results indicate the sensibility of the shear and tensile properties of the adhesive to the concentration of the nanofiller. Taking into account the fracture study of the tested specimens, this behaviour is attributed to the following. The nanotubes are characterised by large areas per unit gram. As the number of adhesively joined points increases, the adhesive strength of the epoxy increases leading to a higher strength of the joint. However, it seems that there is a limit to the number of dispersed nanotubes beyond which a drop in the properties is observed. Once the CNTs fully fill the gaps and porosities and all contact points are established, the addition nanotubes could not interact effectively within the epoxy adhesive and consequently poor matrix infiltration occurs. The additional nanotubes may force the polymer molecules to take up a strained conformation and thereby considerably modify molecular structures of polymer and interfaces that can be easily debond. Also, the agglomeration of CNTs could act as failure initiation sites, which could results in lowering the strength and stiffness of the adhesive.

Finally, Saeed & Zhan (2007) analysed the adhesive properties of several thermoplastic polyimides filled with MWCNTs, using steel as adherends. They confirmed that the addition of CNTs to this kind of adhesives also enhance their adhesive properties. In
particular, they measured the lap shear strength and the adhesive energy of the joints. Also, according to other authors, they found a maximum content of CNTs (0.5 – 1.0 wt %) from which the joint strength decrease, due to a change in the failure mode. The joint with high percentages of CNTs failed in adhesive mode, showing poor wetting of adherend surfaces. These authors also probed that the increase in the lap shear strength by the CNTs addition remains even up to 200 °C.

In addition to the improvements of the mechanical and adhesive properties, the addition of carbon nanotubes into epoxy adhesives implies other important physical change of the resin. Their electrical conductivity radically changes. In fact, the epoxy thermosets are typically electrical insulator. In contrast, the nanotubes have metallic or semiconducting behaviour depending on their structural configuration. S. G. Prolongo at., in a work published in the Journal of Nanoscience and Nanotechnology (2009) studied the reduction of the electrical resistivity of the epoxy resins by the addition of MWCNTs, which was measured in 14 magnitude orders, from $10^{17} \ \Omega \cdot cm$ for non-modified epoxy resin to $10^3 \ \Omega \cdot cm$ for the reinforced resin with 0.25 wt % CNTs. In fact, it was probed that the percolation threshold should be lower than a content of CNTs of 0.1 wt %. Tao Wang et al. (2006) also measured the modification of the electrical conductivity of pressure-sensitive adhesives by the CNTs addition. This property changes from $10^{-11} \ \text{S/m}$ for the neat adhesive to 1 S/m for nanofilled ones. In this system, they determined that the percolation threshold reaches 0.3 wt %.

5. Adhesives reinforced with alumina nanofibers

The nanoscale alumina fiber powder is usually produced by the electron-explosion of metal wire, appearing linear insulate nanofibers together with co-mingled in a bundle. These nanofibers are usually thin (2 – 4 nm in diameter) with a very high aspect ratio (20 – 80) and therefore a high surface area (300 – 700 m²/g). The Young’s modulus of the alumina nanofibers is 300 GPa and their tensile strength is 2 GPa (Meguid & Sun, 2004). The fibers have unique sorption properties, cationic and anionic chemisorption properties, such as scavenging precious and heavy metals from water.

The addition of alumina nanofibers into epoxy adhesives causes a light increase of the peel and strength of the joints of aluminium substrates (Gilbert et al., 2003; Meguid & Sun, 2004). However, the effect of nanoreinforcement of epoxy adhesives with nano-alumina fibers on the toughness of the carbon fiber/epoxy composite joints significantly varies as a function of the manufacturing method applied, depending on whether the adhesive had been bonded to the composite or cocured with the prepreg. Gilbert et al. (2003) published an interesting work about the effect of alumina nanofibers in these systems. Figure 9 shows some of the obtained results.

For the unmodified system, the bonded adhesive performed almost twice as effectively as the cocured adhesive. Nevertheless, the fracture toughness of the cocured samples tended to increase with the addition of nanoscale modifiers, while the values resulting from bonded samples tended to decrease substantially with the addition of the nano-modifiers. This behaviour is difficult to explain. The reduction of mode I fracture toughness may have been associated with an increase in the matrix stiffness by the addition of the nanofiller, causing the adhesive crack propagation. In contrast, the increase of toughness on cocured joints is usually attributed to increased crack tortuosity, blunting of the crack tip or increased matrix strength. These mechanisms seem to be enhanced by the presence of nanofibers in the cocured adhesive because of the modified adhesive may have formed covalent chemical
Fig. 9. Effect of alumina nanofibers content on the mode I and mode II fracture toughness of adhesives cocured with and bonded to high performance carbon fiber/epoxy prepregs (Gilbert et al., 2003).

bonds and undergone molecular entanglements with the prepreg matrix when the adhesive system was cocured with the prepreg. It is worthy to note that the effect of the nanofiber introduction into the epoxy adhesive on the mode II fracture toughness is exactly opposite. For cocured samples, the mode II fracture toughness decreases with the addition of nanofibers. It is difficult to state the cause. Gilbert et al. (2003) have observed that in these samples the crack propagated out of the adhesive layer, indicating that the shear strength of the adhesive had exceeded that of the composite material. In contrast, results of the nanomodified adhesives in the bonded system could indicate that the addition of alumina nanofibers increase the strength of the matrix.

6. Adhesives reinforced with carbon nanofibers

The carbon nanofibers (CNFs), grown through vapour carbon deposition, usually present diameters in the order to 20 - 200 nm and very different lengths from 10 to 100 μm. Their estimated axial Young’s modulus is in the range of 100-1000 GPa, depending on the nanofiber configuration. This parameter is particularly sensible to the shell tilt angle. The nanofibers with small tilt angles form the axial direction present much higher stiffness than the ones with large tilt angles. The mechanical strength of CNFs is usually around 2.5 and 3.5 GPa (Tibbetts & Beetz, 1987). It is known that the expected mechanical properties of carbon nanofibers are lower than those corresponding to carbon nanotubes. However, the nanofibers usually have higher length and they are also less expensive than CNTs. The high length of nanofibers is an important aspect to use them as structural nanofillers. Several researches (Bucknall et al., 1994; Zerda & Lessner, 2001) have demonstrated that the effective toughening may not be energetically favourable at nano-length scale, being generally necessary filler lengths greater than 100 nm. It has been probed (Odegard et al., 2003) that long fiber reinforced composite can effectively arrest the crack propagation, which determines the material strength and fracture toughness. However, short fillers might not have this positive effect on the mechanical properties of the composite. Other interesting
property of the carbon nanofibers is their high electrical conductivity, which is about $4 \times 10^3$ S/cm (Al-Saleh & Sundararaj, 2009). This value is similar to the reported for other traditional fillers, such as carbon fibers or carbon black, which are also electrical conductive materials, the electrical conductivity of traditional long carbon fibers is $1.7 \times 10^3$ S/cm (Al-Saleh & Sundararaj, 2009). However, the main advantage of the nanofibers is their high aspect ratio and their high specific surface area, which allow manufacturing composites with high electrical conductivity at very low filler content, meaning a very low increase of density.

It is widely known that a “good adhesive” must have a high wettability over the adherend. This behaviour is frequently determined by the measurement of the contact angle. The smaller the contact angle, higher wettability on the substrate is obtained. S. G. Prolongo et al. (2009) have published the effect of the addition of CNFs into an epoxy adhesive on its contact angle, using carbon fiber epoxy laminate as adherend. As it is expected, the measurement of contact angle depends on the adhesive nature and substrate but it is also dependent on the characteristics of the surface of the adherends, such as their surface energy, roughness, etc. Therefore, several surface treatments, commonly used for composites, were tested. The obtained results are shown in Figure 10.

Fig. 10. Contact angle of neat epoxy adhesive and modified adhesives reinforced with 0.25, 0.5 and 1 wt % CNFs on carbon fiber/epoxy laminates (non-treated and surface treated with grit blasting, peel ply and plasma) (Prolongo et al., 2009).

The contact angle generally decreases by the addition of nanofibers, meaning an increase of the wettability of the adhesive. This could be explained by the nano-scale size of the nanofiller and the higher chemical compatibility between the carbon/epoxy composite and the nanoreinforced epoxy adhesive with carbon nanofibers. The nano-scale size of the nanofibers could enhance their permeation on the porous and grooves of the adherend surface, which would increase the wettability of the adhesive. The increase of the CNFs content implies an increase of the contact angle although the measured value is lower than that of neat epoxy adhesive in most cases, except to the epoxy adhesive reinforced with 1 wt % CNFs. This increase seems be associated with the worse dispersion of the nanofiller into the adhesive. It was demonstrated, in works published in Composites Science and Technology (Prolongo et al., 2008; Prolongo et al., 2009), that the epoxy nanocomposites with 0.25 wt % presented a suitable dispersion of filler, although at high magnifications, it was possible to observe that the nanofibers tend to be tangled. However, at relative higher nanofibers
contents, it was observed the appearance of large agglomerates, with one or more microns of diameters. These agglomerates increase the effective size of used filler, causing a decrease of the adhesive wettability. In these works, the technique of dispersion used to manufacture the nanoreinforced adhesives is based on the use of chloroform as solvent and ultrasonic and high shear mechanical stirring as mixing techniques.

The rheological behaviour of the adhesives is especially interesting to analyse their primer ability. In order to define the application conditions, it is necessary to determine the variation of the viscosity as function of the temperature and its dependence with the shear rate. It is well known that the addition of nanofillers into the non-cured resins causes an important increase of their viscosity. In this chapter, it was demonstrated that the viscosity of an epoxy monomer nanoreinforced with carbon nanotubes is higher than the one of neat monomer (Figure 7). However, for the same content of carbon nanofiller, the viscosity of the reinforced epoxy resin is much higher with CNTs than with CNFs (Prolongo et al., 2009, *Journal of Adhesion Science and Technology*), as it is shown in Figure 11. This figure shows the dependence of the viscosity with the temperature for an epoxy monomer commonly used in formulations of epoxy adhesives, diglycidyl ether of Bisphenol A (DGEBA), which is reinforced with different contents of carbon nanotubes and nanofibers. It can draw attention that the amount of nanofiller added is different but it was chosen with the criterion of not greatly increase the viscosity.

![Fig. 11. Viscosity as function of the temperature of epoxy monomer (DGEBA, diglycidyl ether of Bisphenol A) reinforced with different contents of CNFs (a) and CNTs (b) (Prolongo et al., 2009).](image)

The higher viscosity of the mixtures with CNTs could be associated to the higher specific surface of the added nanotubes, close to 300 m$^2$/g, than the one of nanofibers, in the range of 150 – 200 m$^2$/g. Other reason is the better dispersion degree observed for the nanocomposite reinforced with CNFs regard to the resin with nanotubes. In spite of the increase of viscosity, the rheological behaviour is not affected by the addition of nanofillers, remaining constant their dependence with the temperature. Due to an increase of the adhesive viscosity could cause difficulties in the manufacture of the joints associated to the decrease in the wettability of the adhesive, the study of the rheological behaviour seems a suitable method to determine the optimum content of the nanofiller to add into the epoxy resin. In principle, a higher content of nanoreinforcement would imply better mechanical properties of the adhesive, provided the dispersion of the nanofiller is right. However, high
contents of nanofibers usually originate the appearance of agglomerates, which commonly cause a decrease of the mechanical properties of the adhesive.

There are several works published concerning to the effect of the addition of carbon nanofibers into adhesives in order to enhance the strength and toughness of the joints. Xu et al. (2007) studied the tensile strength of joints bonded with a commercial epoxy adhesive reinforced with carbon nanofibers. The nature of adherends varied from aluminium to poly(methylmetacrilate) (PMMA). The bonding surfaces of both were sand-blasted before the adhesive was applied to these bonding areas. The CNFs were directly added into epoxy adhesive, which was later treated at high temperature and sonication. The obtained results are shown in Figure 12.

![Fig. 12. Tensile strength of Al/Al (a) and PMMA/PMMA (b) joints bonded with an epoxy adhesive reinforced with different fiber weight percents. Left dark bar corresponds with the strength of joints bonded with pure epoxy adhesive (Xu et al., 2007).](image)

All the tensile strengths of Al/Al joints bonded with nanofiber reinforced adhesives are below the tensile strength featuring neat epoxy. In contrast, the strength of PMMA/PMMA joints bonded featuring nanoreinforced adhesives with different fiber weight contents, from 0.3 to 0.8%, exceed the value measured for the joint bonded with non-modified adhesive. The maximum increase observed was up to 30%. Seeing the discrete results obtained, the authors of this work postulated that discontinuous nanofibers or nanotubes with high strength and stiffness, when they are added as reinforcement to matrices, could generate high stress at the fiber-matrix interface and an inefficient interfacial shear stress transfer could be occur. Thus the strong nanofibers can not carry high load. It is necessary continuous forms of nanofibers or nanotubes without finite ends, precluding the presence of extra matrix material at the end of nanofiller, in order to eliminate stress concentrations. Therefore, the nanofibers should be very long or at least being aligned to reach important increases of strength or fracture toughness.

Prolongo et al., in *The Journal of Adhesion* (2009), analysed the effect of the addition of carbon nanofibers into epoxy adhesives on the lap shear strength of joints of carbon fiber/epoxy laminates. Besides the enhancement of the mechanical properties of the nanoreinforced adhesives, the very small size of the filler could enhance the adhesion on the substrate, generating new anchor-points on them. This mechanism could be enhanced when the adherend is a composite of epoxy matrix reinforced with long fibers due to the high chemical compatibility with the epoxy adhesive reinforced with carbon nanofibers. Figure 13 shows the lap shear strength of the joints bonded featuring neat epoxy adhesive and the
ones reinforced with different CNFs contents. The adherends were treated with different surface treatments such as plasma, grit-blasting and peel ply in order to increase the wettability of the adhesive and therefore to increase the adhesive strength. It is observed that the addition of carbon nanofibers scarcely affects the joint strength in spite of the nanofilled adhesives showed lower contact angles (see Figure 10), which implies an enhancement of the wettability. In contrast, as it is expected, the lap shear strength strongly depends on the surface treated applied to the composite. The highest strength is obtained for the laminate treated by plasma due to the higher wettability of the adhesives on these surfaces. Grit blasted joints also present high strength due to the increase of the roughness of the adherends, enhancing the mechanical adhesion.

![Graph showing average lap shear strength of joints bonded with neat epoxy adhesive and modified adhesives reinforced with 0.25, 0.5 and 1 wt % CNFs using carbon fiber/epoxy laminates as adherends, treated with grit blasting, peel ply and plasma (Prolongo et al., 2009).](image)

**Fig. 13.** Average lap shear strength of the joints bonded with neat epoxy adhesive and modified adhesives reinforced with 0.25, 0.5 and 1 wt % CNFs using carbon fiber/epoxy laminates as adherends, treated with grit blasting, peel ply and plasma (Prolongo et al., 2009).

![Scanning electron micrographs of the fracture surface of tested joints with peel ply treated adherends, whose failure mode was adhesive at the interface: (a) non-modified epoxy adhesive and (b) epoxy adhesive reinforced with 0.5 wt% CNFs (Prolongo et al., 2009).](image)

**Fig. 14.** Scanning electron micrographs of the fracture surface of tested joints with peel ply treated adherends, whose failure mode was adhesive at the interface: (a) non-modified epoxy adhesive and (b) epoxy adhesive reinforced with 0.5 wt% CNFs (Prolongo et al., 2009).

Despite the fact that the measured values of lap shear strength are similar, the fracture surfaces generated by the tested joints with the neat epoxy adhesive and the reinforced ones
presented significant differences. For example, Figure 14 shows the fracture surfaces of the joints whose adherends were treated by peel ply. While the surface of the non-reinforced adhesives scarcely showed deformation, the surface of the epoxy adhesives reinforced with CNFs present long cracks on the peel ply texture and even micro-scale zones of cohesive failure, meaning small pieces of pulled out epoxy matrix of the laminates. These evidences indicate higher adhesion ability of the reinforced adhesives.

Figure 15 shows some micrographs obtained at higher magnification for fracture surfaces of epoxy adhesive reinforced with 0.5 wt % CNFs, whose adherends were treated by plasma. Figures 15a and 15b correspond to the cohesive failure zones while Figures 15c and 15d show the adhesive failure zones. This detailed study of fracture surfaces shows some interesting points. The cohesive failure zone (Figures 15a and 15b) in the composite adherend can be distinguished by the presence of the fiber imprints. Within the imprints of the carbon fibers, it is possible to observe striations, which are the bright bands. These striations, running along the fiber axis, correspond to the characteristic surface roughness of PAN-based carbon fibers (intermediate modulus, IM7) used to manufacture the laminate. These marks on the epoxy matrix of the composite are generated during the test and provide a clear indication of the adhesive shear failure mode at the matrix/fiber interface. The presence of shear forces at the crack tip causes the delamination of the interface, sliding the fiber surface over the matrix. It is known that the fracture energy in mode II is higher than in mode I for thermosetting carbon fiber/epoxy composites. On the other hand, the epoxy matrix of the composite present the typical pattern of shear cusps or hackles (Figure 15b) characteristic of mode II shear failure observed by other authors both in epoxy carbon fiber laminates and in adhesively bonded CFRP joints during shear testing. The cusps are

![Scanning electron micrographs of the fracture surface of tested joints whose adherends was treated by plasma and whose adhesive was reinforced with 0.5 wt % CNFs. Its failure mode was mixed adhesive-cohesive (Prolongo et al., 2009).](www.intechopen.com)
oriented perpendicular to the fibers, bent over along them with a width approximately equal to the distance between the fibers. Figures 15c and 15d correspond to the adhesive failure zone. In particular, they are SEM micrographs at very high magnifications of the face with nanoreinforced epoxy adhesive, which show the roll played by CNFs in the crack propagation and final formation of shear cusps. Small void with sizes in the range of the nanofiber diameters found on surfaces of the cusps could show the participation of these carbon nanofibers in pull-out mechanisms from the adhesive matrix. The shear sliding of those CNFs oriented on the fracture plane (white arrow in Figure 15d) favour the matrix deformation in mode II.

Finally, although the shear and tensile strength of the joints seem not to be widely increased by the addition of carbon nanofibers, it is known that the electrical resistivity of the epoxy resins markedly decreases. Table 1 shows the decrease of the electrical resistivity of epoxy resin when different contents of carbon nanofibers are added. It is seen that the studied epoxy nanocomposites follow typical percolation behaviour. The percolation threshold of the electrical resistivity is the sharp jump by several orders of magnitude which is attributed to the formation of a three-dimensional conductive network of the fillers within the matrix. In the studied system, an epoxy resin reinforced with CNFs, the electrical percolation threshold seems to occur between 0.25 and 0.50 wt %. In fact, the resulting nanocomposites are electrically conductive while the neat epoxy resin is an insulating material. The low percolation threshold of the nanocomposites is justified by the large aspect ratio of the nanoreinforcements, forming a percolating network throughout the epoxy matrix. The decrease of the electrical resistivity with an increase in reinforcement content is attributed to the probably of reinforcement contact.

| wt % CNF | ρ (Ω cm) |
|----------|----------|
| 0        | 10^{17}  |
| 0.25     | 1.8 \times 10^7 |
| 0.5      | 1.2 \times 10^5 |
| 1.0      | 3.2 \times 10^4 |

Table 1. Electrical resistivity of epoxy resins reinforced with different contents of CNFs (Prolongo et al., 2009)

Similar conclusions was drawn by Thao Gibson et al. (2005), who studied the development of epoxy based adhesives formulated with coated and uncoated vapour-grown carbon nanofibers. They confirmed that the shear strength of metal-metal and composite-metal joints remained constant with the addition of CNFs into the adhesive. However, this modification caused an important decrease of the electrical resistivity and an increase of thermal conductivity, from 5.10^{10} Ω cm and 0.8 W/mK for neat epoxy to 0.2 Ω cm and 2.8 W/mK for the adhesive reinforced with 20 wt % CNFs. It is worthy to note that the desired properties for a high electrically/thermally conductive adhesive in the aerospace industry are an electrical resistivity lower than 10^8 Ω cm and a thermal conductivity higher than 1.0 W/mK.

7. Summary of main results

The following tables collect a summary of the most relevant results published about the mechanical properties of the joints bonded with neat and nanoreinforced epoxy adhesives,
which were determined by lap shear (Table 2), peel (Table 3) and double cantilever beam tests (Table 4). Table 5 shows the same properties for other kinds of adhesives.

| Filler                  | Adherend | Neat adhesive | Nanoreinforced adhesive | Variation (%) | Reference      |
|-------------------------|----------|---------------|--------------------------|---------------|----------------|
| **Al₂O₃ nanoparticles** | Al       | 237 MPa       | 273 MPa                  | +15           | Gilbert, 2003  |
| **SiO₂ nanoparticles** | Al       | 25.5 MPa      | 28.5 MPa                 | +12           | Klug, 1999     |
|                         | Al       | 20.8 MPa      | 23.0 MPa                 | +11           | Kinloch, 2003  |
|                         | Ti       | 25 MPa        | 40 MPa                   | +60           | Bhownik, 2009  |
| **POSS**                | Al       | 21 MPa        | 24 MPa                   | +14           | Dodiuk, 2005   |
| **MWCNT**               | CF/epoxy | -             | -                        | +46           | Hsiao, 2003    |
| **Al₂O₃ nanofibers**    | Al       | 237 MPa       | 265 MPa                  | +12           | Gilbert, 2003  |
|                         | Al-CF/epoxy | -         | -                        | +30           | Meguid, 2004   |
| **CNF**                 | PMMA     | 28 MPa        | 32.5 MPa                 | +16           | Xu, 2007       |
|                         | CF/epoxy | 11.9 MPa      | 12.8 MPa                 | +8            | Prolongo, 2009 |

Table 2. Lap shear strength of different adhesive joints: comparison between neat and nanoreinforced epoxy adhesive

| Filler                  | Adherend | Neat adhesive | Nanoreinforced adhesive | Variation (%) | Reference      |
|-------------------------|----------|---------------|--------------------------|---------------|----------------|
| **Al₂O₃ nanoparticles** | Al       | 87 N          | 130 N                    | +49           | Gilbert, 2003  |
| **SiO₂ nanoparticles** | Al       | 3.1 N/mm      | 5.5 N/mm                 | +77           | Kinloch, 2003  |
| **POSS**                | Al       | 0.19 N/mm     | 0.49 N/mm                | +158          | Dodiuk, 2005   |
| **Al₂O₃ nanofibers**    | Al       | 87 N          | 119 N                    | +37           | Gilbert, 2003  |

Table 3. Peel strength of different adhesive joints: comparison between neat and nanoreinforced epoxy adhesive

| Filler                  | Adherend | Neat adhesive | Nanoreinforced adhesive | Variation (%) | Reference      |
|-------------------------|----------|---------------|--------------------------|---------------|----------------|
| **Al₂O₃ nanoparticles** | CF/epoxy | 0.47 kJ/m²    | 0.85 kJ/m²               | +81           | Gilbert, 2003  |
| **SiO₂ nanoparticles** | CF/epoxy | 0.59 kJ/m²    | 0.74 kJ/m²               | +25           | Klug, 1999     |
|                         | Al       | 1.2 kJ/m²     | 2.3 kJ/m²                | +92           | Kinloch, 2003  |
| **Al₂O₃ nanofibers**    | CF/epoxy | 0.47 kJ/m²    | 0.79 kJ/m²               | +68           | Gilbert, 2003  |

Table 4. Mode I fracture toughness (GIC) of different adhesive joints: comparison between neat and nanoreinforced epoxy adhesive
Nanoreinforced Adhesives

### Table 5. Mechanical properties of different adhesive joints: comparison between neat and nanoreinforced adhesive

| Filler          | Adhesive | Adherend | Test     | Neat adhesive | Nanoreinforced adhesive | Variation (%) | Reference   |
|-----------------|----------|----------|----------|---------------|-------------------------|---------------|-------------|
| SiO₂ nanoparticles | Acrylic   | Al       | Lap shear | 106.3 kPa     | 339.6 kPa              | +219          | Patel, 2006 |
| Wood            |          |          |          | 40.7 kPa      | 128.9 kPa              | +217          |             |
| PP              |          |          |          | 34.8 kPa      | 185.6 kPa              | +433          |             |
| PP              |          | Al       | Peel     | 1.36 kN/m     | 1.98 kN/m              | +46           |             |
| PP              |          | PP       | Peel     | 0.16 kN/m     | 0.25 kN/m              | +56           |             |
| Nanoclay        | Acrylic   | Al       | Lap shear | 131.7 kPa     | 323.6 kPa              | +146          |             |
| Wood            |          |          |          | 147.9 kPa     | 339.5 kPa              | +130          |             |
| PP              |          |          |          | 86.0 kPa      | 208.5 kPa              | +142          |             |
| PP              |          | Al       | Peel     | 1.49 kN/m     | 1.98 kN/m              | +33           |             |
| PP              |          | PP       | Peel     | 0.20 kN/m     | 0.27 kN/m              | +35           |             |
| MWCNT Polyimide | Steel     | Steel    | Lap shear | 18 MPa        | 22.5 MPa               | +25           | Saeed, 2007 |

8. Concluding remarks

The addition of nanofillers causes an important increase of the mechanical properties of different adhesives, although the obtained enhancements depend on numerous factors, such as the nature of the adhesive and adherends, the applied surface treatment or the tested property. Also, they depend on the nature and content of nanofiller. It seems that the best results were obtained with the addition of nano-sized silica particles and carbon nanotubes. Specially, the effect of these nanofillers is more noticeable in the peel strength and mode I fracture toughness. In general, it is observed that there is an optimum content of nanofiller for which the adhesive properties measured are the maximum. At higher contents, the properties fall back. This fall is usually accompanied with a change of the failure mode of the joints. Frequently, the joints bonded with neat adhesives present failure at the interface while the failure shown for the joints bonded with nanoreinforced adhesives is cohesive. Finally, at relative high contents of nanoreinforcement, the failure mode of the joints is interfacial again. The improvement of the adhesive properties by the addition of nano-sized filler has been associated to different phenomena. Between them, the nanoparticles and nanofibers can fill the gaps and porosities of the adherend, establishing new contact points and enhancing the interfacial strength due to the mechanical anchoring mechanism. On the other hand, it was probed that the nanoreinforced adhesives present higher wettability than the neat epoxy resins, which justifies a high adhesive strength of the joints. Some authors affirm the formation of chemical bonds between nanoreinforced adhesive and the surface of the substrates. Other works justify the increase of the strength and toughness of the joints by the enhancement of mechanical properties of the adhesive. The worsening of the joint properties at relative high nanofiller contents can be also explained by different
mechanisms, such as the increase of the adhesive viscosity or the appearance of agglomerations due to dispersion problems.

Finally, the addition of nanofillers into adhesives can improve other interesting properties, like the gas permeability, thermal conductivity and electrical conductivity. It is worthy to note that the addition of carbon nanotubes or nanofiber implies an increase of the electrical conductivity of the adhesives, becoming from insulate to semiconductor or electrical conductor material, which is the special relevance in the joint of electrical conductive substrates.

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“There’s Plenty of Room at the Bottom” this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

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