BIO and NANO

INSPIRED ADHESION

10th April 2008

Society of Chemical Industry
15 Belgrave Square London

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This one-day symposium is one of an ongoing series organised by the Society for Adhesion and Adhesives.

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The next symposium is due to be held at the SCI on Thursday 4th December 2008.

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Insects did it first: a micro patterned tape for robotic applications.

S. Gorb

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Biological hairy attachment systems demonstrate their excellent adhesion and high reliability of contact. The structural background of this functional effect is discussed in the present paper. It is demonstrated here how comparative experimental biological approach can aid in development of novel tribological materials and systems. Biomimetic mushroom-shaped fibrillar adhesive microstructure inspired by these systems was characterized using a variety of measurement techniques and compared with a control flat surface made of the same material. Results revealed that pull-off force and peel strength of the structured specimens are more than twice those of the flat specimens. In contrast to the control system, the structured one is found to be very tolerant to contamination and able to recover its adhesive properties after being washed in a soap solution. Based on the combination of several geometrical principles found in biological attachment devices, the presented microstructure exhibits a considerable step towards the development of an industrial dry adhesive.
Switchable Adhesion between oppositely charged polyelectrolytes
Mark Geoghegan
Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK

Tuning the interactions between different surfaces is an important area of research with technological benefits. Polyelectrolytes are good candidates for this kind of study for their remarkable behaviour. By altering environmental pH, polyelectrolytes can undergo conformational transitions, which, if controlled, enable a wide range of applications in such fields of nanotechnology as microfluidics, targeted drug delivery and controlled wetting and adhesion [1]. I shall present data describing the interaction between poly[2-(dimethyl amino)ethyl methacrylate] (PDMAEMA, a polybase) chemically grafted to planar silicon substrates by atom transfer radical polymerization, with a hydrogel of poly(methacrylic acid) (PMAA).

The interaction between PDMAEMA and PMAA is of great interest because it represents a situation where the interaction between a positively charged polybase in contact with a negatively charged polyacid can be controlled simply by changing the external environment. In fact in aqueous media, there is strong adhesion and in acidic media the interaction is negligible. A JKR-type experiment has been designed to measure the strength of the interaction between the two components [2]. The process is both switchable and reversible. The adhesion can be switched off by lowering the pH to ~1. The adhesion can be re-achieved by re-immersing the components in water at pH ~6 and bringing them into contact.

We describe preliminary results to determine the mechanism of the interaction between the two components. At present it seems likely to be a combination of electrostatic attraction, hydrogen bonding, and chain entanglement (molecular Velcro). We use neutron reflectometry to observe the conformation of the grafted polymers, as well as the JKR results, which also show that the adhesion is pressure sensitive.

A practical approach to the development of a synthetic Gecko tape
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BAE Systems, ATC-Sowerby, Filton, Bristol, UK, BS34 7QW

Abstract

The fabrication and the assessment of the adhesion of bio-mimetic Gecko hair arrays is described. The objective being to assess the performance of these materials and characterise behaviour with multiple attachment on smooth glass surfaces, and on glossy and rough painted surfaces of the type likely to be encountered on an aircraft. This was with a view to using such attachment methods in, for example, the temporary attachment of panels - perhaps in field repair, the use as attachment pads in an autonomous inspection robot, etc.

Since such materials are not commercially available, examples of structures were fabricated using in-house nano-moulding and photolithographic methods of the type employed in the semiconducting industry. Specimens comprising arrays of cylindrical and mushroom shaped hairs were fabricated in both polyimide and PDMS (polydimethylsiloxane).

One essential factor responsible for achieving adhesion with maximum strength on any surface is achieving intimate contact with maximum contact area. The degree of contact and separation distance between the hair surface and glass surfaces was assessed via the use of optical interferometry and SEM examination. It was noted that better contact and larger adhesion strengths were in general obtained with mushroom shaped hairs using PDMS, rather than cylindrical materials or polyimide materials. Pull-off tensile adhesion strength measurements were made using a simple, purpose built balance, with multiple attachments both to the glass, and rough and smooth painted surfaces. Strengths of up to 220kPa were measured for first contact of mushroom shaped PDMS specimens on glass surfaces. Subsequent attachments resulted in reduced strengths with detachment of individual hairs from the backing material and also some damage to the mushroom heads. Smaller attachment strengths were measured on the rougher surfaces. It was also noted that the PDMS based structures exhibited an adhesion strength which was dependent on the residence time on a surface between attachment and subsequent detachment.

By measuring strengths both in air and in a vacuum chamber it was demonstrated that the mushroom shaped PDMS structures showed adhesion on glass with a contribution from both a molecular and a “suction pad” atmospheric component. The material showed superhydrophobic properties, and simple cleaning experiments showed that washing with water after contamination with dust and foreign hairs could restore a proportion of the strength.

It is likely that further optimisation of the present mushroom shaped structures could be undertaken by addressing their geometry and size, and also the time and strength dependent material properties. These could be optimised in order to reduce stress concentrations within the hair array, improve conformity to surfaces and reduce material tearing and failure. With further development to improve compliance on a greater range of length scales by the manufacture of structures with increased levels of geometrical hierarchy, then it is anticipated that improvements in contact to rough surfaces, like the rough painted surface used here, could also be achieved.
Adhesion in dentistry – why and how

R van Noort, Department of Adult Dental Care, University of Sheffield.

The story of adhesion in dentistry can be traced back to the 1950’s when Michael Buonoocore discovered a means of bonding resins to enamel using an acid etching process. However, it was not until the 1980’s that adhesive dentistry really began to take off. Nowadays there isn’t a single branch of dentistry where adhesive procedures are not used. In restorative dentistry, procedures such as the placement of ceramic veneers are now routine and all tooth coloured filling materials are placed using an adhesive procedures. In orthodontics, the placement of brackets used in tooth realignment are bonded rather than banded. The success of dental implants owes much to the fact that titanium allows bone growth onto its surface such that the implant becomes locked in place, a process referred to as osseointegration. Thus part of the reason for the recent developments in adhesive dentistry is that it has allowed the introduction of new treatment techniques not previously possible. Yet, there are a number of other reasons why the ability to bond successfully to enamel and dentine has been a preoccupation in dentistry, particularly restorative dentistry, for the last 20 years.

For some 150 years the restorative material of choice for the posterior teeth has been dental amalgam, a material based on a mixture of mercury and a silver/tin alloy. Despite its excellent track record of durability it has a number of fundamental drawbacks, one being the fact that it has no capacity to bond to tooth structures. Consequently it requires the use of retentive design features, which are highly destructive of tooth structure and require students of dentistry to learn about complex design concepts. The excessive removal of tooth tissues weakens the tooth and this will eventually lead to catastrophic failure of the tooth. If failure does not arise from that source, then it comes from the recurrence of dental decay. This happens because there is inevitably a small, but highly significant, gap between the restoration and the tooth. This is a source of bacterial invasion, which eventually leads to demineralisation of the tooth tissues, i.e. caries. Whereas one may think that this is no big deal and it would be a simple matter of replacing the filling, studies have shown that general dental practitioners can spend up to 50% of their time replacing failed restorations. In any other clinical discipline this sort of performance would cause outrage, yet in dentistry it is accepted, partly because the perception is that the replacement of a single filling or crown is not that expensive. However, one has to remember that millions of fillings are placed annually in the UK alone. The cost of this to the NHS runs into many billions of pounds and therefore restorative materials that can create a durable bond to tooth tissues can have a profound effect on the quality and cost of service provided by the general dental practitioner.

Adhesion can make a significant contribution to the improvement in the quality of life of our patients. However, the demands placed on adhesives used in dental treatments are considerable and although major strides forward have been made there is still considerable room for improvement. In my presentation I will describe the current state of play with respect to adhesion in dentistry in terms of what we have achieved and how it is done.
The adhesive strategies of marine invertebrates

N. Aldred and A. S. Clare

School of Marine Science and Technology, Newcastle University, NE1 7RU.

This presentation will discuss our current understanding of the adhesive strategies used by some well-studied marine organisms. Emphasis will be placed on the modes of adhesion of larval and adult barnacles (*Balanus* sp.), and the blue mussel (*Mytilus edulis*). A schematic now exists that describes the processes involved in the adhesion of adult barnacles to surfaces. Several important proteins have been isolated from this material and their putative functions will be discussed. It is suggested, however, that although barnacle glue has been the subject of interdisciplinary study for decades, it is only now that we have the level of detail necessary to underpin truly ‘biomimetic’ barnacle glue development. In contrast, the relatively detailed knowledge of the byssus adhesive of blue mussels led to biomimetic developments, which unfortunately failed commercially. Blue mussel adhesive is thus a textbook example of the whole being greater than the sum of its parts. No individual component taken from the byssus structure is likely to be effective as an adhesive in isolation, although the structure in its entirety has been shown to be a highly effective adhesion system with unique force distribution, shock-absorption and ‘self-healing’ properties. Indeed, the focus of mussel byssus research has shifted in recent years from exclusively studying its adhesive properties, to viewing the material more holistically as an interesting model for future materials development. It is not only the adult forms of these organisms that use adhesives however. Indeed, in most invertebrates it is the larva that locates and initiates attachment to a surface. In the case of barnacles, this larva is known as a cyprid. Cyprids alone have two independent adhesive strategies, both discreet from that of the adult barnacle. During exploration of surfaces prior to settlement, cyprids use a poorly understood adhesive system known as temporary adhesion. This system involves, to some degree, a glycoprotein secretion that cyprids deposit in tracks across immersed surfaces. The terminal segments of the antennular structures that cyprids use for walking are also covered in nano-scale, hair-like, cuticular villi that may also contribute to adhesion. Upon location of a suitable settlement site, cyprids attach permanently using a dual-component ‘cement’ stored in granular form within specialised glands. This cement is expressed through the antennules over the course of a few minutes and hardens, in a matter of hours, embedding the terminal portions of the cyprid antennules, and committing the barnacle to a sessile future. This cement is also poorly understood with its composition and properties receiving little attention compared to that afforded to the adult barnacle system. Finally, it is suggested that these organisms do not simply use adhesives. They use complex, multi-component, systems of adhesion, involving sequences of behaviour that must be understood, as well as the adhesive materials themselves, if these systems are to be effectively mimicked and developed commercially.
AFM studies of adhesion-related phenomena:  
Approaches other than the measurement of force-distance curves

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In addition to imaging surfaces with a high spatial resolution, Atomic Force Microscopy (AFM) allows for nanomechanical characterisation of surfaces and nanostructures. The most common technique for the nano-scale measurement of adhesion forces using AFM is via the analysis of force-distance curves. In combination with chemical functionalisation of the AFM tip, this approach is a well-established tool, for example for studying molecular recognition or the folding of biomolecules. Yet it is worthwhile considering that AFM also provides additional nanomechanical measurement modes, such as Lateral Force Microscopy (LFM) and nanoindentation. The wider potential of AFM for the investigation of nano-scale adhesion phenomena is demonstrated in this talk via two applications.

(1) LFM was employed to characterise the adhesion between nanoparticles and a support surface. An increasing number of products involving nanoparticles (NPs) attached to a surface are being developed, such as industrial catalysts containing Pt NPs dispersed on porous oxide supports. If the NPs fall off the surface or get washed away after a short period of usage the functionalty of the product would be impaired. To ensure the reliability and safety of such products, the strength of the adhesion between the NPs and the support surface needs to be tested.

The lateral force applied by an AFM tip when scanning across a NP can be used to detach the NP from the support surface. We investigated arrays of W-NPs deposited on a surface of template-stripped gold [1]. The W-NPs were generated by means of Electron Beam Deposition (EBD) involving W(CO)₆ as a precursor gas. The interparticle distance was ~280 nm, and the dwell time of the electron beam was used as a parameter to generate NPs of various sizes. With beam dwell times in the ms range, the height of the NPs was bound to be between ~0.6 and ~4.2 nm. One array for each dwell time was generated, with each array extending over a 100 micron square region.

![Figure 1: Topography images of an array of W-nanoparticles, measured with normal forces of ~3 nN (a) and ~45 nN (b), respectively. Total height 5.2 nm and 4.2 nm, respectively. Scan range 2.5 microns.](image)

Using microcantilevers of ~0.06 N/m stiffness, the arrays of NPs were imaged in contact mode. Starting from low values, the normal force was successively increased to identify the critical force from which NPs are detached from the supporting surface. For NPs of a 2 ms
beam exposure time, the critical force was found to be ~45 nN. Scanning at this force resulted in complete removal of the NPs (Fig. 1).

(2) It is widely accepted that in the vicinity of an adhesive junction between two materials a third phase, the interphase (IP), tends to be formed. Upon loading, the spatial distribution of mechanical stresses around such interfaces is governed by IP stiffness variations. Owing to its high spatial resolution, nanoindentation can be utilised to map such variations in Young’s modulus and hardness.

The system under investigation was a sandwich-like sample consisting of a thermoplastic and an amine-cured epoxy. The epoxy resin and the amine curing agent were diglycidyl ether of bisphenol A (DGEBA, DER332 type) and 4,4'-diaminodiphenylsulfone (DDS), respectively. The thermoplastic adherend was poly(vinylpyrrolidone) (PVP). The temperature of isothermal curing (170°C) was close to the glass transition temperature of PVP, and the interphasial property variations were found to extend over a comparatively wide range, of up to ~235 microns [2]. Owing to the large extent of the IP, artefacts potentially resulting from the mechanical bias effect can be ruled out.

Figure 2: Distance dependence of (a) $E_s/E_s^b$ and (b) $(E_s/H)/(E_s^b/H)^b$. Open symbols correspond to the left-sided IP and filled symbols correspond to the right-sided IP, respectively. The grey solid line drawn in vertical direction indicates the average width, $W_{DDS}$, of the amine depletion zone, as deduced from EDX measurements. $|x-x'|$ denotes the distance from the interface.

Non-monotonic profiles of the epoxy mechanical properties were detected, in particular for the hardness, $H$. In addition to $H$ and the Young’s modulus, $E$, also their ratio, $E/H$, was analysed, a measure for the relative amount of plastic deformation (Fig. 2). In particular, within the IP zone next to the adherend, a strong increase in $E/H$ is observed, in agreement with the finding of the residual imprints being ~1.3 times larger than on the other IP zones.

As complementary techniques, energy-dispersive analysis of X-rays (EDX) and dynamic-mechanical thermal analysis (DMTA) were employed. The resulting knowledge on the spatial variations in the amine-epoxy concentration ratio as well as on the concentration-modulus relationship gives us an idea of the polymer physics governing the observed variations in modulus.

References
[1] M. Munz, D.C. Cox, P.J. Cumpson, accepted for publication in *physica status solidi (a)*.
Nano-particle modification of epoxy adhesives for increased toughness

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Introduction

The epoxy polymers used as adhesives and as the matrices of composite materials are amorphous and highly-crosslinked (thermosetting) materials. This structure results in many useful properties, such as a high modulus and low creep. However, they are relatively brittle materials, with a poor resistance to crack initiation and growth.

These materials can be toughened by a micro-phase of a rubbery polymer, e.g. [1-3], without significantly impairing many of the other desirable properties. These rubbers are soluble in the epoxy prior to crosslinking. Hence, as long as the modifiers do not increase the viscosity of the resin significantly, this method of toughening may be used with resin-infusion processes for the production of fibre composite materials. These processes are attractive due to their relatively low tooling costs. However, the addition of these rubbers, at the high concentrations required to achieve significant toughness increases, typically does lead to an increase in the viscosity of the epoxy which may be unacceptable for resin-infusion.

The addition of rigid particles has also been shown to increase the toughness of thermosetting polymers [4-6]. However, these particles have conventionally been tens of microns in diameter, and hence are not suitable for use with resin-infusion processes, as they are larger than the inter-fibre spacing. Indeed, they are strained out of the resin by the fibres during infusion. More recently, the availability of nanometre-sized inorganic particles has allowed rigid particles to be used in the formulation of resins for use with infusion processes, e.g. [7]. The authors have previously shown that bulk and fibre composite materials may be successfully manufactured using 20 nm diameter silica nanoparticles, and that these particles increase the toughness of the material, e.g. [8].

The formation of ‘hybrid-toughened’ epoxy polymers, by combining both rubber toughening and silica nanoparticles has been shown to give a synergistic toughening effect [9, 10]. In the present work, the microstructure and properties of bulk materials, plus the results of fracture tests on glass-fibre reinforced polymer (GFRP) composites produced by a resin infusion under flexible tooling (RIFT) process are reported.

Experimental

The epoxy resin was diglycidyl ether of bis-phenol A (DGEBA), ‘DER332’ (Dow). The organosilane-modified silica nanoparticles were obtained at 40wt% in DGEBA: ‘Nanopox F400’ (Nanoresins), and had an average particle size of about 20nm [7]. The rubber was a carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber: ‘Hycar CTBN 1300x8’ (Emerald Performance Materials), which was pre-reacted with DEGBA resin to give a 40wt% CTBN-epoxy adduct: ‘Albipox 1000’ (Nanoresins). The curing agent was an accelerated methylhexahydrophthalic acid anhydride: ‘Albidur HE 600’ (Nanoresins), and a stoichiometric amount was used. The formulations were prepared by mixing together the components, to give the required levels of nanoparticles and rubber.

The GFRP composite plates were manufactured by resin infusion under flexible tooling (RIFT). The glass fibre was a non-crimp unidirectional glass fabric with polyester weft stitching: ‘UT-E500’ (SP Systems). Composite plates approximately 7mm thick were prepared using 16 plies, laid up in a unidirectional orientation [11]. Poly(tetrafluoroethylene) (PTFE) film was inserted into the fabric prior to resin infusion to act as a starter crack for the fracture specimens. The degassed resin was drawn through the fibres at 50°C, using a vacuum to achieve a void-free composite [12]. Four formulations were used – unmodified epoxy; epoxy with 9% CTBN; epoxy with 10% silica nanoparticles, and epoxy with 9% CTBN & 10% silica. The plates were cured for 2 hours at 100°C, with a post-cure of 10 hours at 150°C. Bulk plates were also manufactured, and similarly cured.

The glass transition temperature, Tg, was measured using differential scanning calorimetry at a rate of 10°C/minute. Single edge-notch bend specimens were machined from the bulk plates, and tested in three-
point bending at a rate of 1mm/min. Double cantilever beam (DCB) specimens were used to measure the mode I fracture energy, $G_c$ [13] of the composites at a test rate of 1mm/min. The results were analysed using the 'corrected beam theory (CBT)' method [14].

Microstructure
Atomic force microscopy (AFM) of the bulk samples showed that the materials were homogeneous. The silica nanoparticles were dispersed through the epoxy, as shown in Figure 1. The CTBN undergoes reaction-induced phase-separation upon curing of the epoxy to produce rubbery particles of about 0.5 μm in diameter. The addition of the silica nanoparticles, to form the hybrid, did not change the morphology of the rubber particles, see Figure 2.

The glass transition temperature, $T_g$, of the unmodified epoxy was 143°C. The results show that $T_g$ was 140 ±4°C for all the formulations using epoxy with silica nanoparticles. The addition of rubber does reduce the $T_g$ of the epoxy slightly, with $T_g$ values of 129 ±7°C for the rubber-modified and hybrid formulations. The values of $T_g$ measured from the composite samples agreed well with the bulk values.

Results – Bulk
The results of the bulk fracture tests gave a fracture energy of 105 J/m² for the unmodified epoxy, see Figure 3. The addition of silica nanoparticles increased $G_c$, and a maximum of 460 J/m² was measured for the formulation with 20% silica. A similar fracture energy was measured for the rubber-modified epoxy. The hybrid-toughened epoxy gives the highest bulk fracture energies, of up to 1480 J/m², and shows a considerable synergistic toughening effect.

Figure 3. Fracture energy, $G_c$, versus the concentration of nanosilica particles.
Results – Composite
Extensive fibre-bridging was observed in the composite fracture tests, and resistance curves (R-curves) were observed for all samples. As the measured fracture energies increase significantly with crack length, the initiation values are quoted. Figure 4 shows the measured mode I initiation fracture energy values for the GFRP versus the bulk values. A fracture energy of 330 J/m² was measured for the control composite. The addition of CTBN or nanosilica increased the fracture energy of the epoxy significantly. However, the measured \( G_{IC} \) for the hybrid composite is lower than that of the bulk. A similar effect has been reported by Hunston et al. [15], who observed that thermoset polymers which have a high bulk toughness do not necessarily give high composite fracture energies. They reported that, at low fracture energies, the bulk polymer toughness is transferred fully to the composite. However, above a threshold value of \( G_{IC} \) of approximately 750 J/m², although the bulk toughness increases, this increase is not fully transferred to the composite. The results in the present work agree well with this proposition. Hunston et al. [15] suggested that for the high-toughness composites, the fibres restrict the size of the crack-tip deformation zones, and hence limit the interlaminar fracture energy.

![Graph showing fracture energy values](image)

Figure 4. Interlaminar initiation values of \( G_{IC} \) for the GFRP composites vs. \( G_{IC} \) for the bulk matrix.

Toughening Mechanisms
The rubber particles show cavitation and plastic hole growth, as expected from previous work [2, 16]. Scanning electron microscopy of the fracture surfaces of the silica-modified epoxy showed that there had been debonding of the epoxy matrix from the silica nanoparticles, and subsequent void growth, as shown in Figure 5. Although the samples are coated to prevent charging in the electron microscope, the voids are not an artefact of the coating as they could not be observed on a coated fracture surface of the unmodified epoxy.

![Scanning electron micrograph](image)

Figure 5. Scanning electron micrograph of the fracture surface of the epoxy polymer containing silica nanoparticles. (Voids with nanoparticles are circled).
Conclusions
The use of silica nanoparticles and micron-sized rubbery particles to form hybrid-toughened epoxy polymers has been shown to give a range of novel materials. These formulations show a significant increase in the bulk toughness. Most importantly, the synergistic effect of having a multiphase structure based upon both nanosilica particles and rubbery particles is clearly demonstrated. These materials can also be used to manufacture composite laminates by a resin infusion under flexible tooling (RIFT) process. The interlaminar fracture energy of glass-fibre reinforced composites is also increased.

These multiphase 'hybrid' epoxy polymers have considerable potential for a wide range of applications, such as adhesives, composite matrices and electronic encapsulating resins, where a high toughness is often required but without any accompanying significant loss of other important properties such as modulus and thermal resistance.

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References