Interfacial Control in Colloidal Nanocomposites for Pressure-Sensitive Adhesives

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Abstract

This work developed various two-phase colloidal nanomaterials from aqueous dispersions and applied them as pressure-sensitive adhesives. A fundamental understanding of the nano-scale interfacial friction and the macro-scale viscoelasticity and adhesive properties of these nanomaterials was developed via various existing models.

Colloidal nanocomposites were fabricated by horizontal deposition from poly(butyl acrylate-co-acrylic acid) colloids, and single-walled carbon nanotubes or multi-walled carbon nanotubes functionalized by various polymers or surfactants. A percolation threshold of 0.03 wt% SWNT was determined. The electrical conductivity is on the order of 1 S/m above the percolation threshold. A thermal conductivity increase by 80% is achieved with 0.1 wt% SWNT presence. At the percolation threshold, the nanotubes increase the adhesion energy by 85%. The adhesion energy was found to be proportional to the tanδ/E' value of the nanocomposite. It was found that the tan δ/E' value is controlled by dispersants at the matrix/nanotube interface. A high-\(M_n\) polymer at the interface is required to ensure enough interfacial strength for stress transfer and to impart high interfacial friction during stretching.

From measurements of the large-strain deformation of the nanocomposites, the shear strength, \(\tau\), of the nanotube/matrix interface was determined as a function of the interfacial polymer chain length, \(\bar{N}\), and the chain density, \(\Sigma\). The results show that the value of \(\tau\Sigma\) (friction force contributed by individual polymer chain) increases with \(\bar{N}\). \(\tau\) likewise increases with \(\Sigma\), but then levels off above a critical value. These results are explained by the molecular friction of the adsorbed polymer chains sliding along the rubbery polymer matrix.

The molecular interactions among the polymer colloids were also adjusted by pH values of the dispersions. In the films cast from acidic dispersions, hydrogen bonding dominates the particle interactions, whereas the ionic interactions are the main factor in the films cast from basic dispersions. AFM force spectroscopy and macro-scale mechanical measurements show that latex films with hydrogen bonding interactions have a lower modulus but are more deformable. They offer a high adhesion energy. The ionic interactions increase the moduli of the dried latex films: they are stiffer and consequently exhibit a lower adhesion energy.
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Chapter 1

Design and fabrication of colloidal polymer nanocomposites: from nanoscale to macroscale*

1.1 Introduction

Waterborne polymer colloids, often called latex dispersions, are firmly established for uses in many industrial products, ranging from cosmetics and pharmaceuticals to adhesives and coatings.¹ ² In these applications, single identical homogeneous particles are typically used as the “building blocks” of a larger structure. Particle identity is usually lost upon film formation so that a homogeneous material is created.³ The science of latex film formation has reached maturity as a result of decades of study.

Within the past decade there has been enhanced interest in using colloidal polymer particles in water to create nanocomposites. There are two broad strategies to make polymer nanocomposites: (1) blends of colloidal polymer particles and a second type of particle (inorganic or polymeric) can be assembled into a desired structure, or (2) hybrid particles consisting of a polymer phase and a second phase can be assembled. Each strategy will be reviewed here. A key advantage of the colloidal approach is that it offers control of structure at the nano-scale (within particles) and at the meso- and even macro-scale through the creation of ordered assemblies of particles. The fabrication of nanocomposites offers exciting new challenges and opportunities for the science and technology of latex film formation.

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The quest for novel and enhanced properties is a key driver in the development of colloidal nanocomposites. Nanocomposites with nanoscale fillers, e.g. nanoclay and carbon nanotubes, have pronounced properties that are not realized with traditional micro-scale fillers. The mechanical properties, electrical and thermal conductivity, and flammability resistance all differ in nanocomposites in comparison to conventional composites. Polymer colloids are usually dispersed in water and therefore offer a further attraction over other processing methods. Organic solvents are not emitted into the atmosphere, making the process environmentally-friendly. When the polymer has a glass transition temperature \( (T_g) \) below the ambient conditions, the use of heat energy is not essential for the processing, in stark contrast to the melt-processing fabrication method, which requires lower viscosities and therefore temperatures far above the \( T_g \) or the melting temperature. Hence, the waterborne process offers a further environmental benefit.

Our emphasis here will be on hybrid particles in which the core is polymeric and the shell or surface region is inorganic. Hybrid particles with inorganic cores and polymer shells prepared by miniemulsion polymerisation or in-situ polymerisation are not considered, as they have been reviewed elsewhere. Polymer/polymer core-shell hybrids are also not considered here. We shall show that latex technology, which was developed in the 1950s, can be applied and extended to make 21st century materials. The development of colloidal nanocomposites builds on the expertise in polymer colloid science developed over several decades.

### 1.2 Colloidal particle assembly methods

We will first consider methods by which waterborne colloidal particles can be assembled to create a desired structure. When a colloidal dispersion of particles in water is deposited onto a substrate and water evaporation is allowed to proceed, either a continuous film or an array of separate isolated particles will form under the appropriate drying conditions. Highly dilute dispersions are used to create isolated particles. The three most common deposition methods for polymer colloids are
horizontal deposition\textsuperscript{11}, vertical deposition\textsuperscript{12, 13, 14} and spin-casting\textsuperscript{15, 16, 17}. There is growing interest in the use of surface patterns to assist and guide the particle deposition, and this constitutes a way to control particle deposition by the other three methods. Each of these methods will be considered individually hereafter.

1.2.1 Horizontal deposition

![Diagram of horizontal deposition process](image)

Figure 1.1 (a) Overview of the horizontal deposition process of polymer colloids (i.e. film formation). (b) AFM phase image of an ordered close-packed array of polymer colloids obtained by the horizontal deposition process. Average particle size is \( \approx 200 \) nm; image size is \( 2 \mu m \times 2 \mu m \).

In the horizontal deposition process, the colloidal dispersion is cast on a substrate horizontally such that a planar layer of uniform thickness is created. This flexible and fast method typically creates a layer with a thickness of several microns rather than nanometres. The process is illustrated in Figure 1.1a, and Figure 1.1b shows an example of close-packed polymer particles with a 3D-ordered structure obtained by direct horizontal deposition. Such a perfect structure requires a tight control over the particle size; polydispersity in size leads to randomness in the
packing. The horizontal deposition of glassy colloidal particles to produce colloidal crystals is commonly employed to create templates for the deposition of a second phase. A good example is in the creation of inverse opal structures for photonics applications.\textsuperscript{18,19,20}

Whether or not a continuous film is formed depends on the temperature of the deposition process relative to the minimum film formation temperature (MFFT) of the polymer colloids. In turn, the MFFT is dependent on the viscoelastic resistance of the polymer to deformation. If the film is cast above its MFFT, the film becomes continuous and clear (the average void size is well below the wavelengths of visible light), and the coalescence of the polymer colloid particles can occur. At a temperature below MFFT, a cracked or even powdery film results. Conventionally, the film formation is separated into three primary stages: (I) evaporation of water and particle ordering; (II) particle deformation; and (III) interdiffusion of polymers across the particle-particle boundaries. Mechanisms for particle deformation include dry sintering (driven by the reduction of the polymer/air interfacial energy), wet sintering (driven by the reduction of the polymer/water (serum) interfacial energy), and capillary deformation (driven by the capillary pressure generated across the water/air menisci).\textsuperscript{21} A mechanism in which a coalesced surface layer creates osmotic pressure that leads to particle deformation was proposed by Sheetz.\textsuperscript{22} Detailed descriptions of the latex film formation process and the drying mechanisms are developed and summarized elsewhere.\textsuperscript{23,24,25,26}

Mono-sized particles can be packed into a face-centred cubic array in which each particle has twelve nearest neighbours. When the particles deform to fill all available space, the boundaries between the particles flatten. Each particle then creates a twelve-sided geometric figure known as a rhomboid dodecahedron. If the film is sliced along a (111) plane, a hexagonal array – often called a honeycomb structure – is observed.
1.2.2 Vertical deposition

The horizontal deposition of colloidal particles across a large area usually creates a film with defects (e.g. “vacancies”) and with lateral variations in the type of packing (e.g. face-centred versus body-centred). On the other hand, vertical deposition has been found to produce superior quality colloidal films with fewer defects and a single packing type. In vertical deposition, a substrate is held vertically in a colloidal dispersion and then lifted away from it to form a well-ordered monolayer or multilayer of particles on the substrate. This method has been modified by dipping the substrate into the dispersion inclined at an angle. Alternatively, the substrate can be dipped into the dispersion and then held in a stationary position while the solvent is allowed to evaporate. The solvent can be allowed to evaporate at either the natural ambient rate or at an accelerated rate to create colloidal layers.\textsuperscript{27, 28, 29, 30} The vertical deposition is highly effective provided that the evaporation velocity of the solvent exceeds the sedimentation velocity of the particles.\textsuperscript{31}

Lifting direction

![Diagram of vertical deposition process](image)

Figure 1.2 (a) Scheme of the process of vertical deposition of polymer colloids. (b) SEM of one layer and (c) seven-layer silica micropheres on a glass substrate processed by vertical deposition. The silica diameter is ~230 nm. Reprinted from Ref. 33.
A schematic diagram of the vertical deposition process is presented in Figure 1.2a. During vertical deposition, convective mass flow and capillarity are the two main driving forces for the colloids to assemble at the substrate surface, with a thickness ranging from several nanometres (corresponding to a particle monolayer) to several microns. Examples of ordered monolayer and seven-layer ($M = 7$) silica microsphere films obtained by vertical deposition process are presented in Figures 1.2b and 1.2c, respectively. Vibrations during the lifting or liquid dropping process can detrimentally affect the deposition and packing of the colloidal layers.

The number of particle layers, $M$, in a colloidal film deposited from a dispersion of particles of diameter $\sigma_e$ at an initial volume fraction $\varphi$ is controlled by various factors described by the formula:

$$M = \frac{\beta L}{0.605} \frac{j_e \varphi}{\sigma_e V_p (1 - \varphi)}$$  \hspace{1cm} (1.1)

where $\beta$ is a constant varying from 0 to 1, which depends on particle-particle and particle-substrate interactions, $L$ is the meniscus height (i.e. the width of the wet particle array on the substrate), $j_e$ is the evaporation rate of the solvent (water), and $V_p$ is the liquid-surface dropping velocity or the lifting speed of the substrate.

The stronger the particle interactions, the smaller is the value of $\beta$. For non-adsorbing particles and dilute suspensions, $\beta$ can be taken as 1. The evaporation rate is influenced by the temperature and humidity of the surrounding atmosphere. Besides the above parameters, the tilt angle of the substrate when dipped into the colloidal dispersion has been found to affect the thickness of colloidal crystals. An investigation of poly(styrene)(PS)-water dispersions demonstrated that $M$ is proportional to the surface tension, but this parameter is not included in Equation 1.1.

Because of the tendency for sedimentation of larger colloidal particles, there is a limitation to the maximum particle size that can be deposited on a substrate by the vertical method. Both the aqueous phase viscosity and the relative densities of the particles and the water phase affect the sedimentation velocity. Using water as the continuous phase, the maximum colloid size able to be deposited on a substrate is as
large as 2 µm. As can be deduced from Equation 1.1, the solvent can be chosen to control the colloidal layer thickness. For example, under otherwise identical conditions, the colloidal layers will be thicker when using water rather than ethanol as a solvent, as water has a lower evaporation rate. The solvent's evaporation rate and surface tension also affect the deposition rate and the packing order. For example, when a surfactant is added to decrease the surface tension, a simple cubic array of spaced particles is more favourable, rather than a densely-packed, hexagonal array, which is favoured by a higher surface tension. Particles are drawn together as a result of the negative capillary pressures generated by a concave meniscus in the neck region between particles. This pressure is directly proportional to the surface tension, so that decreasing the surfactant concentration below the critical micelle concentration decreases the extent to which particles are drawn together into a dense array.

1.2.3 Spin-casting

Whereas horizontal and vertical depositions generally take hours or even days to create colloidal structures, spin-casting methods take only seconds. In this type of processing, the colloidal particles are dispersed in a suitable solvent and then cast onto a rotating substrate, so that shear forces induce two- or three-dimensional film patterns ranging from nanometer to micrometer thicknesses. Figure 1.3a shows a scheme of the spin-coating process. In the spin-casting process, the evaporation rate of the continuous medium, the spinning velocity, the dispersion concentration, and its viscosity are all key parameters to control the particle packing and thickness of the structure. Unlike horizontal and vertical deposition methods, which usually result in close-packed colloidal particles, spin-casting can fabricate either close-packed or isolated particle arrays depending on the process conditions. An example of a non-close-packed polymer particle array spin-cast on mica is presented in Figure 1.3b.
Figure 1.3 (a) Scheme of the spin-coating process of polymer colloids. (b) AFM phase image of an array of separated polymer colloid particles obtained by spin-coating. Image size is 2 μm x 2 μm.

1.2.4 Surface pattern-assisted deposition

Patterns on the surface of the substrate can be used to control the assembly of colloidal particles. This method has gained considerable attention for reasons of fundamental understanding and for advanced device fabrication. Patterns on the substrate can be either chemical or topographical. Particle assembly is achieved by any of the three methods of particle deposition (horizontal, vertical or spin-casting), but the surface pattern directs the particles during the process. Spatial confinement leads to the colloidal assembly.

Chemically-patterned surfaces usually have a lateral variation or modulation of electrostatic forces or charges, wettabilities, hydrophilicities, and so on. A scheme of colloidal assembly with chemical patterning is provided in Figure 1.4a, with an experimental example in Figure 1.4c. Colloidal particles with a certain surface chemistry will selectively locate on the patterned regions. For instance, electropositive particles will attach to negative regions, or hydrophobic particles will preferentially adsorb onto hydrophobic regions of the substrate.

In topographical patterning, various arrays of holes, grooves or microchannels on substrates are used to guide particle assembly, as illustrated schematically in Figure 1.4b with an experimental example in Figure 1.4d. Both methods of surface
patterning require a sequence of complex manufacturing processes to fabricate the substrate.

Figure 1.4 (a) Colloidal particle assembly on a chemically-patterned surface using the vertical deposition process. (b) Colloidal particle assembly on surface channels using the horizontal deposition process. (c) Optical micrograph of polystyrene latex particles on a patterned polyelectrolyte surface. Reprinted from Ref. 45. (d) SEM image of poly(styrene) latex particles assembled within a channel with a 10 μm width and a 1.5 μm depth. Poly(styrene) particle size is 1.75 μm. Reprinted from Ref. 46.

Jonas et al.\textsuperscript{47} investigated the parameters influencing the templated growth of colloidal particles on chemically-patterned surfaces by vertical deposition. In this case, silanol groups were used to create hydrophilic surface regions, and fluoroalkysilane monolayers were used to create hydrophobic surface patterns. The particles assembled onto the hydrophilic substrate by capillary forces.

Unlike deposition on a non-patterned surface on which the colloid concentration is uniform along the air/solvent/substrate contact line, there is a concentration variation along the contact line when colloids are deposited over a hydrophilic stripe. In
addition to the usual colloid flux from the bulk of the dispersion to the drying zone, there is a lateral particle flux from the hydrophobic region to the hydrophilic region to counter the discontinuous colloidal concentration. In vertical deposition, the liquid in contact with the hydrophilic stripe rises above the dispersion to a certain height, which is defined as the meniscus length, $L$. The liquid in contact with the hydrophobic stripe sinks below the solution. At the two sides where the hydrophilic and the hydrophobic regions meet, there is an abrupt change of the wettability and consequently a strong deformation of the meniscus shape. When the colloids are deposited on a patterned substrate, the pattern dimensions (line widths) have a strong influence on the deposited layer thickness and colloidal crystal quality.

The deformation of the meniscus and the lateral particle flux makes Eq. 1.1 no longer valid, especially on substrates with narrow pattern dimensions. For example, a nonlinear dependence of the film thickness on the colloid concentration and the substrate withdrawal speed was identified for line patterns with widths below 100 μm in Jonas et al.'s work. Control of this particular deposition behaviour is still based on empiricism and more precise work combined with modelling needs to emerge.

![Figure 1.5](image.png)

Figure 1.5 (a) SEM image of a poly(styrene) latex particle array obtained by a floating self-assembly process. Particle size is 10 μm. Reprinted from Ref. 51. (b) SEM image of a close-packed array of polymer colloids obtained by centrifugation. Particle size is 1 μm. Reprinted from Ref. 52.

In addition to substrate patterning, electrostatic, external electric field, floating self-assembly, centrifugation, filtration, and other methods have all been investigated as a means for colloidal particle assembly. For example, in
Figure 1.5 there are examples of three-dimensional structure obtained from floating self-assembly and centrifugation, respectively.  

1.3 Colloidal nanocomposites from latex/carbon nanotube blends

1.3.1 Structures of carbon nanotubes

Carbon nanotubes (CNTs) are well-ordered, all-carbon hollow graphitic nanomaterials with diameters ranging from 1 to 100nm and lengths of microns up to millimeters.\(^5\) Carbon nanotubes can be made by arc discharge\(^5\), catalytical chemical vapour deposition\(^5\) and laser ablation\(^6\). Conceptually, the nanotubes are viewed as "rolled-up" structures of one or multiple sheets of graphene to obtain either a one-atom thick single walled nanotube (SWNT), or a number of concentric tubes called multi walled nanotubes (MWNT).

![Diagram of carbon nanotubes](image.png)

Figure 1.6 a) Schematic representation of a 2D graphite layer with the lattice vectors \(\vec{a}_1\) and \(\vec{a}_2\) and the roll-up vector \(\vec{c}_h = n\vec{a}_1 + m\vec{a}_2\). Idealized defect-free SWNTs with open ends b) a metallic conducting (10, 10) tube ("armchair"), c) a chiral, semi-conducting (12, 7) tube, and d) a zigzag, conducting (15, 0) tube. The images here are produced by Nanotube Modeler© JCrystalSoft.
There are three types of carbon nanotubes, namely zigzag, armchair and chiral, with the graphitic sheets being rolled in different ways.\textsuperscript{61} We can recognize zigzag, armchair, and chiral carbon nanotubes by following the pattern across the diameter of the tubes, and analyzing their atomic structure of the wall.\textsuperscript{62} Figure 6a schematically represented a 2D graphite layer with the lattice unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) and the roll-up chiral vector \( \mathbf{c}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \). The translation vector \( \mathbf{T} \) is parallel to the tube axis. All the \((n, n)\) armchair tubes are metallic. This is also the case with chiral or zigzag tubes if \((n-m)/3\) is a whole number, but otherwise they are semiconductors.

1.3.2 Properties and applications of carbon nanotubes

CNTs can be highly electrically conducting. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter.\textsuperscript{63, 64, 65} Armchair nanotubes are metallic, chiral or zigzag nanotubes can be metallic or semiconductive. An intrinsic electrical conductivity as high as \(10^6\) S/m has been reported.\textsuperscript{66} Conductivity in CNTs enables them as new electrical materials. It has been reported that individual SWNTs may contain defects. Fortunately, these defects allow the SWNTs to act as transistors.\textsuperscript{67, 68} Carbon nanotubes can also be employed for gas sensing, based on the electrical conductance changes of semiconducting nanotubes on exposure to gases.\textsuperscript{69, 70, 71} The incorporation of carbon nanotubes into insulating polymers can impart them electrical conductivity. It is well-established that the higher the aspect ratio of the filler particles, the lower the loading required achieving a given level of conductivity.\textsuperscript{72} A scaling law can be followed by:

\[
\phi_p = \left( \frac{L}{D} \right)^{-1}
\]  

(1.2)

Where \( \phi_p \) is percolation threshold, and \( L/D \) is aspect ratio of the nanotubes.

CNTs are ideal in this sense, since they have the highest aspect ratio of any carbon fiber. This high aspect ratio imparts electrical conductivity at lower loadings, compared to conventional additive materials such as carbon black, chopped carbon
fibre, or stainless steel fibre. This low loading preserves the flexibility of matrix, as well as other key performance properties of the polymers.

Molecular simulations indicate that thermal conductivity of SWNTs can be as high as 6600 W/mK. Experimental measurements also show the values from 1750 to 5850 W/mK for SWNTs. Kim measured more than 3000 W/mK for the thermal conductivity of MWNTs at room temperature. This super high thermal conductivity is due to a high number phonon vibrations within nanotube structure. Thermal conductivity of CNTs depends on their length, aspect ratio and temperature. Carbon nanotubes can enhance thermal conductivity of polymers. Composites with CNTs have been shown to dramatically increase their bulk thermal conductivity, even at very small loadings. Research illustrates that the interfacial thermal conductance has a high effect on the composite’s thermal conductivity. A small interface thermal conductance will highly limit thermal conductivity of nanotube composite materials. Besides interfacial thermal resistance, nanotube diameter, aspect ratio, fraction, space distribution as well as nanotube surface functionalization all influence effective thermal conductivity enhancement.

The carbon atoms of a single sheet of graphite form a planar honeycomb lattice, in which each atom is connected via a strong chemical bond to three neighboring atoms. Because of these strong bonds, the basal plane elastic modulus of graphite is one of the largest of any known material. For this reason, CNTs are expected to be the ultimate high-strength fibers. SWNTs are stiffer than steel, and are very resistant to physical damage. Using atomic force microscopy, the unanchored ends of a freestanding nanotube can be pushed out of their equilibrium position, and the force required to push the nanotube can be measured. MWNTs were tested to have a tensile strength of 63 GPa. The current Young’s modulus value of SWNTs is about 1 Tera Pascal (TPa). Other values have also been reported and the differences probably arise through different experimental measurement techniques and also upon amount of disorder in the nanotube walls. Research also shows that individual SWNT can undergo superplastic deformation, becoming nearly 280% longer and 15 times narrower before breaking at high temperatures as the result of the nucleation and
motion of kinks in the structure. This means that CNT can strengthen and toughen nanocomposites at high temperatures.

The dispersion of CNTs and the interface adhesion are important to the ultimate mechanical properties of polymer nanocomposites. The uniform dispersion of CNTs and their good interfacial bonding with polymers enable the load transfer from the matrix to nanotubes, and thus contribute to mechanical properties. Despite the promise of outstanding mechanical performance, however, this type of nanocomposite (with low nanotube concentrations) often displays mechanical strengths that are far below the idealized theoretical predictions. This failure has been attributed to poor nanotube dispersion in the polymer matrix and to weak interfacial adhesion between the nanotube and matrix, among other factors.\textsuperscript{91} Frequently, it is found that an increase in the elastic modulus and tensile strength is coupled with a reduction in the strain at break.\textsuperscript{92} In such cases, a compromise must be made between high stiffness and high toughness.\textsuperscript{93}

CNTs also have high aspect ratio (more than 1000) and tremendously high surface area, 200-400 m\textsuperscript{2}/g for MWNTs and 400-900 m\textsuperscript{2}/g for SWNTs. Interfacial shear between the nanotube and matrix, although detrimental to high stiffness and strength, could result in very high mechanical damping properties. With careful interface tuning, damping materials can be achieved without sacrificing the mechanical strength and stiffness. Suhr \textit{et al.}\textsuperscript{94} has report strong damping increase properties in polymer/nanotube composites. The damping is related to frictional energy dissipation during interfacial sliding at nanotube-nanotube or polymer-nanotube interface.\textsuperscript{95, 96, 97}

1.3.3 Sterically-stabilized suspensions of carbon nanotubes

Because inorganic nanofillers usually have high surface areas and energies, they tend to aggregate and exhibit poor dispersion ability. Some simple theory explains this effect clearly. The direct interaction force $F_D(r)$ between two bare spherical nanoparticles with a particle diameter $\sigma_c$ separated at a distance $r$ can be described by
an expression for the Lennard-Jones (LJ) potential derived from analytical integration as

\[ F_D(r) = \frac{48}{r} \left( \left( \frac{\sigma_c}{r} \right)^{12} - \frac{1}{2} \left( \frac{\sigma_c}{r} \right)^6 \right) \]  

(1.3)

The attractive (negative) term with the \( r^{-7} \) dependence arises from attractive van der Waals forces. Figure 1.7a shows the calculated direct LJ force profiles for pairs of particles with various diameters, \( \sigma_c \). The minimum in the force profile becomes lower and moves to a closer separation distance as the nanoparticle diameter decreases. Smaller particles are therefore more prone to aggregate and are more difficult to disperse and stabilize.

To describe the interaction between nanotubes, Girifalco et al.\(^9^9\) developed an expression for tube-tube interaction from the Lennard-Jones potential. They also derived an expression for tube-sphere interactions to describe nanotubes blended with nanoparticles. Yerushalmi-Rozen and coworkers\(^1^0^0\) calculated the interaction potential for two parallel single-wall nanotubes (SWNTs) (expressed per unit length) as a function of the tube-tube distance, \( r \), as illustrated in Figure 1.7b. The attraction is a result of the dispersive energy. Several aspects of Figure 1.7b deserve comment. A negative interaction energy here leads to attraction between the particles. The potential is very short ranged, approaching zero at a distance of about 2.5 nm. This potential is in contrast to interaction potentials of most colloidal dispersions, which extend much farther. The potential is also quite steep (varying strongly with \( r \)) and the minimum energy level is quite significant, approaching – 40 kT/nm as \( r \) decreases below 2 nm. Considering that carbon nanotubes can be more than 1 \( \mu \)m in length, the attractive interaction can be 1000s of kT. These very high dispersive interaction energies are the origins of the aggregation of nano-objects. In the case of nanotubes, the result is the formation of "ropes" or "bundles" and the loss of nanomaterial properties.
Figure 1.7 (a) Direct L-J interaction force $F_{\text{D}}(r)$ between two nanoparticles of varying diameter, $\sigma_v$, (as indicated in the legend) as a function of their separation distance, $r$. Simulated using Equation 1.3. (b) Interaction potential of two parallel SWNTs (in vacuum) as a function of the tube-tube distance, $r$, measured from the centres of the tubes ($D$ is assumed here to be 1.1 nm). Reprinted from Ref. 100.

To overcome this fundamental problem of aggregation and poor dispersability, carbon nanotubes can be decorated with a layer of polymers. These molecules impart steric stability to prevent the nanotubes from approaching separation distances in the attractive region. Techniques of steric stabilization have been employed to stabilize various types of colloidal particles, including silica, clay, gold, Fe$_3$O$_4$ and high aspect-ratio carbon nanotubes, through either covalent bonding of the stabilizer onto the inorganic surface or through physisorption onto the surfaces. Stabilization and dispersion of carbon nanotubes is of particular interest in high-strength nanocomposites, and review articles have been written on the use of surfactants and chemical functionalisation. Note that because of the short-ranged and steep interaction potentials between nanotubes, separating nanotubes by just a few nm is highly effective in stabilising them in a dispersion.

As a general rule of thumb, the properties of nanocomposites are usually inferior when the nanophases are not finely dispersed. Aggregates of hard nanoparticles often create a weak point and lead to a loss of optical clarity because of the introduction of heterogeneity in the refractive index at length scales approaching the wavelength of
light.\textsuperscript{110} Hence, effective methods of dispersing nanoparticles to prevent agglomerates or bundles are essential.

Figure 1.8 AFM phase image of isolated multi-wall carbon nanotubes stabilized by physisorbed poly(vinyl pyrrolidone) after being deposited on mica. Image size is 2 μm x 2 μm.

Figure 1.8 shows an example of cylindrical multi-wall carbon nanotubes stabilized by physisorbed poly(vinyl pyrrolidone). To fabricate nanocomposites from waterborne polymer colloids, nanotubes are usually modified with water-soluble molecules, such as polymers and surfactants, to disperse them in water. To disperse nanotubes in a hydrocarbon solvent, suitable hydrophobic polymers can be used. Diblock copolymers have been shown to be more effective than homopolymers as dispersants for nanotubes. One block adsorbs on the surface while the other extends into the solvent to impart steric stability.\textsuperscript{102}

Lessons for the steric stabilisation of nanotubes can be learned from the theory describing the interactions between polymer brushes on flat surfaces developed by Alexander\textsuperscript{111}, de Gennes\textsuperscript{112} and Milner \textit{et al.}\textsuperscript{113} The steric interaction force, $F(r)$, between polymer brush layers of thickness $\delta$, separated by a distance $r$, was proposed by de Gennes\textsuperscript{114} to be:

$$F(r) = \frac{\alpha kT}{s^3} \times \left[ \left( \frac{2\delta}{r} \right)^{\frac{9}{4}} - \left( \frac{r}{2\delta} \right)^{\frac{3}{4}} \right]$$  \hspace{1cm} (1.4)
Here, $k$ is the Boltzmann constant. $T$ is the absolute temperature. $s$ is the distance between the terminally-attached polymer chains, and $\alpha$ is a fitting parameter.

End-anchored polymers on nanotubes can be treated – to a first approximation – as polymer brushes. On a flat surface, the volume available per grafted chain is constant as a function of the distance from a planar grafting surface, whereas the available volume increases with distance for a polymer brush on a highly curved surface. This will affect the extent of confinement on the brushes. The ability to design polymer modifiers on a nano-surface allows precise control of the colloidal suspension for nanocomposite fabrication and will influence the structure and property modulation, through its effect on dispersability and flocculation.

Simulations of the interaction force between end-tethered polymers on cylindrical carbon nanotubes have been developed by self-consistent mean field methods. A steric repulsion is provided by the polymer layer. In this case, the repulsion prevents the nanotubes from moving close together into the attractive regime. The repulsive energy barrier, presented in Figure 1.9 as a positive energy, increases with increasing chain length and prevents nanotube contact. According to the simulation, with sufficiently long polymer chains, the total interaction energy is entirely repulsive.

Figure 1.9 The total interaction energy between two parallel CNTs with end-tethered polymers (chain length $N = 50$ (line) and $N = 100$ (dotted line). Reprinted from Ref. 101.
After the film formation of a colloidal nanocomposite, the polymer dispersant on a nanoparticle will come into contact with the continuous polymer matrix. The interaction between this polymer chain and the matrix is expected to have a profound effect on properties. The dispersant can be used to promote adhesion between the filler and the matrix.

1.3.4 Colloidal nanocomposite assembly

A straightforward way to create nanocomposites is through the blending of polymer particles with carbon nanotubes suspended in a common media (either water or an organic solvent). Film formation from particle blends has the potential to fabricate ordered structures that provide a periodic modulation in the optical, photoluminescent, magnetic, electric and mechanical properties, which cannot be otherwise found in homogeneous structures. This method can essentially be considered a nano-scale version of the processing of pigmented latex films, which contain micrometer-sized particles of inorganic oxides, such as titania, silica or calcite.

After sterical stabilization, carbon nanotubes can coexist in a common media with polymer colloids (e.g. water). An ordered, nanostructured nanocomposite can be created via horizontal or vertical deposition. After deposition on the substrate, the water will evaporate and the polymer particles will assume a close-packed configuration with the nanotubes occupying interstitial void space. Finally, the polymer particles will coalesce to form a coherent film, locking the carbon nanotubes within a so-called segregated network. This method was first demonstrated by Grunlan et al. and has been used increasingly more often by others. Figure 1.10a demonstrates an ordered honeycomb structure achieved from casting a binary blend of polymer colloids and carbon nanotubes. Figure 1.10b gives an example of a carbon nanotube network created by using silica as a colloidal template, fabricated by vertical deposition.
Figure 1.10 (a) Schematic illustration of the horizontal deposition process for polymer colloid/nanotube blends. (b) SEM image of a nanocomposite comprised of a segregated network of carbon nanotubes in silica particles. Reprinted from Ref. 117.

Table 1.1 Examples of Blends of Polymer Colloids with Inorganic Nanoparticles

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Inorganic nanoparticles</th>
<th>Dispersant for the inorganic particles</th>
<th>Film formation method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>SWNT</td>
<td>GA</td>
<td>Horizontal deposition</td>
<td>115, 116</td>
</tr>
<tr>
<td>P(St-BuA)</td>
<td>MWNT</td>
<td>SDS</td>
<td>Horizontal deposition</td>
<td>118</td>
</tr>
<tr>
<td>PS, PMMA</td>
<td>SWNT</td>
<td>SDS, GA</td>
<td>Horizontal deposition</td>
<td>119, 120</td>
</tr>
<tr>
<td>PVAc</td>
<td>Carbon black</td>
<td>---</td>
<td>Horizontal deposition</td>
<td>121</td>
</tr>
<tr>
<td>Sulfate latex</td>
<td>Au</td>
<td>---</td>
<td>Vertical deposition</td>
<td>122, 123</td>
</tr>
<tr>
<td>PS</td>
<td>SiO₂</td>
<td>---</td>
<td>Vertical deposition</td>
<td>12, 13</td>
</tr>
</tbody>
</table>

In this type of nanocomposite, the nanostructures are controlled through the polymer colloid particle size and the relative volume fractions in the blends. Table 1
summarizes the ordered colloidal nanocomposites deposited from various colloidal blends, which have been reported in the literature recently.

1.3.5 Advantages of colloidal nanocomposites

Despite the promise of outstanding mechanical performance, nanocomposites films and bulk materials often display mechanical strengths that are far below the idealized theoretical predictions. This failure has been attributed to poor nanofiller dispersion in the polymer matrix and to weak interfacial adhesion with the matrix, as well as the random and uncontrolled morphology of the nanocomposites.91,124 Polymer nanocomposites by colloidal routes have the potential to resolve these problems by achieving uniform mixing at the colloidal length scale and the 3-D periodically ordered structure. The processing temperature only needs to be slightly higher than the glass transition temperature of the polymer. In comparison to colloidal dispersions, polymer melts have much higher viscosities, so that blending with carbon nanotubes is much less efficient. It is not easy to disperse individual carbon nanotube in the viscous melt. Lower melt viscosities are only obtained at temperatures well-above the polymer $T_g$, and nevertheless, carbon nanotube agglomeration can still be problematic.

As a general rule, low percolation thresholds require particles that are randomly oriented, finely-dispersed (not agglomerated or bundled), and having a high aspect ratio. The colloidal route can satisfy all of these requirements. The 3-D percolating network of a conducting inorganic phase can impart high electrical conductivity, and so measurements of conductivity are a good probe of the structure. For instance, a three-dimensional honeycomb network of SWNTs created around PS colloidal particles has an electrical conductivity on the order of $10^4$ Sm$^{-1}$.125 The percolation threshold for the onset of electrical conductivity in a nanocomposite of colloidal poly(vinyl acetate) latex and SWNTs has been found to be as low as 0.04 wt%.$^{115}$ By comparison, larger filler particles, i.e. micrometer-sized carbon black particles, have a percolation threshold of 2 vol.% in blends with a polymer colloid.$^{121}$ A percolating
network of a conducting polymer in a colloidal nanocomposite achieved a percolation threshold of 0.011, which is a factor of 10 lower than in a conventional blend, accompanied by an electrical conductivity that is several orders of magnitude greater.\textsuperscript{126}

There is also interest in using the assembly of colloidal particles to template inorganic phases in a structure ordered on the nano-scale. The polymer cores in hybrid colloidal particles can be removed by chemical etching or calcination. A porous inorganic structure is left behind, and this inverse opal structure can serve as a template for other nanomaterials or 3D scaffolds for cell or tissue engineering.\textsuperscript{51,127,128,129}

Most existing cell and tissue scaffolds have the drawbacks of having a poorly ordered or even chaotic structure, requiring a complex fabrication process, and using a limited materials selection. The 3D scaffolds fabricated from colloidal nanocomposite networks allow the facile design of porosity, interconnectivity and pore size. The biocompatibility of the inorganic scaffolds can be modified by chemically-selected polymer layers on the inorganic surface. These mechanically strong, biocompatible and well-connected inverse opal structures mimic very well the micro-environment of three-dimensionally native tissues, providing the potential to systematically study cell growth as well as cell-cell and cell-matrix interactions.

Colloidal nanocomposites with structures tailored on the nano-scale also have applications in printed flexible electronics,\textsuperscript{130} photonic bandgaps,\textsuperscript{131,132} sensors,\textsuperscript{133} data storage,\textsuperscript{134} and displays.\textsuperscript{135} Of course, one of the oldest applications of waterborne polymer colloids is for architectural coatings. Colloidal nanocomposites of polyacrylates and silica have been developed by BASF\textsuperscript{136} for commercial applications as a transparent, flame-retardant, scratch-resistant coating.\textsuperscript{137}
1.4 Mechanical and adhesive properties of soft polymer materials

1.4.1 Mechanical properties of soft polymer materials

The mechanical response of a material to an external force includes elastic, plastic and viscoelastic deformation. In elastic deformation, the force is proportional to the displacement. The material will return to its original dimensions when the stress is removed, as illustrated in Figure 1.11a. This ability is referred to as elasticity and dissipates no energy. The force-distance relation of elastic deformation obeys Hooke's law of $\sigma = E\varepsilon$. The force per unit area, $\sigma$, is called the stress and $\sigma = \frac{F}{A_0}$. The stretch $\lambda$ is the ratio of deformed to initial length and defined as $\lambda = \frac{L}{L_0}$. $\varepsilon$ is called the strain and defined as the ratio of the change in length to original length, $\varepsilon = \frac{L - L_0}{L_0} = \lambda - 1$. Young's modulus, a measure of the intrinsic resistance of a solid to a stress, can be obtained from the linear regime as $Y = \frac{\Delta\sigma}{\Delta\varepsilon}$.\(^{139}\)

The elasticity is independent of loading rate. For most materials, elastic deformation is restricted to a small deformation region and strains instantaneously. When the deformation continues to increase, plastic deformation may operate. Plasticity describes a material undergoing non-reversible deformation in response to applied forces. Plastic deformation dissipates energy, which is proportional to the shaded area in Figure 1.11b.\(^{140,141}\)

The mechanical response of viscous materials, like honey or oil, is time dependent. Polymers exhibit viscoelastic behavior, i.e. both viscous and elastic characteristics, upon application of an external force. Hysteresis is observed in the force-displacement curve of viscoelastic polymers, with the area of the loop being equal to the energy dissipation after a loading-unloading cycle, as illustrated in Figure
1.11c. The viscous component can be described by Newton’s law with a low strain rate, $\sigma = \eta \frac{d\varepsilon}{dt}$, with $\eta$ being the viscosity and $d\varepsilon/dt$ the strain rate. The mechanical behavior of viscoelastic materials is modeled by various combinations of spring and dashpots, e.g. Maxwell model, Kelvin-Voigt model, with the spring obeying Hooke’s law and the dashpot obeying Newton’s law. Stress relaxation and creep are also typical mechanical behavior of viscoelastic polymers.¹⁴⁰, ¹⁴¹

![Force-displacement curves](image)

Figure 1.11 Force-displacement curves of the loading-unloading circle of a) elastic materials, b) plastic materials and c) viscoelastic materials.

The elasticity origins of polymer materials include interatomic forces and entropic resistance. The interatomic force is only valid within a small deformation. Entropic resistance is valid for larger deformation in rubber-like polymers. Polymer molecules are large and loosely connected. When a stress is applied to a polymer material, parts of the long polymer chain reconfigure to accompany the stress, which will create a back stress in the materials to return to its original form. This is termed as entropic resistance.
Viscoelasticity is often studied using dynamic mechanical analysis, when the polymer is subjected to a small oscillatory strain at certain frequency and the resulting stress is measured. Elastic materials have stress and strain in phase, as the response is immediate. Viscous materials usually have a 90 degree phase lag between strain and the responding stress. Viscoelastic materials exhibit a phase lag of strain less than 90 degrees but greater than 0. A complex dynamic modulus, $E^*$, can be used to represent the relations between the oscillating stress and strain:

$$E^* = E' + iE''$$  \hspace{1cm} (1.6)

where $i = (-1)^{1/2}$; $E'$ is the storage modulus and $E''$ is the loss modulus:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$  \hspace{1cm} (1.7)

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$  \hspace{1cm} (1.8)

where $\sigma_0$ and $\varepsilon_0$ are the amplitudes of stress and strain and $\delta$ is the phase lag between them.

The energy dissipation factor (damping) in dynamic mechanical analysis is $\tan \delta$ and is determined as:

$$\tan \delta = \frac{E''}{E'}$$  \hspace{1cm} (1.9)

Figure 1.12 is a tensile stress-strain curve of soft polymer materials. The curve can be divided to four regimes: linear elastic regime (I), transitory regime (II), nonlinear elastic regime (III) and breaking regime (IV). Polymer materials demonstrate a linear elasticity only in the small strain region. In large strains, the force changes with displacement, but varies in a nonlinear way. This region is called the nonlinear elastic regime and demonstrates nonlinear elasticity. The yield stress is defined as the stress at the intersection of the tangents to linear elastic regime and
nonlinear elastic regime. The failure stress is defined from the breaking regime. The area under this curve represents the toughness, or in other words, energy dissipation of the tensile failure. Unlike rigid inorganics or high glass transition temperature materials, the strain of soft materials with a glass transition temperature far below room temperature (e.g. -50 °C) can demonstrate an elongation of 1000%, more or less.

![Figure 1.12 Typical soft material tensile stress-strain curve.](image)

Depending on the physical entanglements and the extent of chemical cross-linking, polymers can demonstrate strain-softening or strain-hardening behaviours in the nonlinear elastic regime. However, there are no universally accepted methods to quantify strain-softening and strain-hardening. One way to define strain-softening and strain-hardening is through a comparison of the force with the forces predicted from the neoHookean model:

\[
\sigma = G(\lambda - \frac{1}{\lambda^2})
\]

where \(\sigma\) is the nominal stress, \(\lambda\) is the uniaxial extension ratio in the direction of the applied stress and \(G = kNT\), with \(k\) the Boltzmann's constant, \(N\) the number of chains per unit volume and \(T\) the absolute temperature.
Figure 1.13 illustrates the strain-softening and strain-hardening defined from the neoHookean model. When less force is required to achieve the same deformation compared with the force predicted from the neoHookean model, the material demonstrates strain-softening behaviour. Strain-softening has been related to the relaxation of the physical entanglements during stretching. Strain-hardening is defined when a larger force is required to achieve the same deformation compared with the force predicted from the neoHookean model. Strain-hardening is normally because of a high density of chemical cross-linking of the materials. The chains are extended to their maximum amount in this extension region, and so the stress rises.

### 1.4.2 Pressure-sensitive adhesive property of soft colloidal materials

Polymer colloids with their glass transition far below room temperature, e.g. -50 °C, are the main building blocks of pressure-sensitive adhesives (PSAs) and demonstrate adhesive properties. PSAs are tacky at room temperature and adhere instantly and firmly to nearly any surface under the application of light pressure, without covalent bonding or activation.\textsuperscript{144} PSAs are usually used in tapes, labels, and bonding applications. Classes of PSAs include natural rubber, acrylics, styrenic block copolymers and silicone PSAs.\textsuperscript{145} Besides made from water-borne polymer colloids,
PSAs can also be made from solvent-based polymer and hot melting. Tighter environmental regulations in the production of PSAs have led to a shift away from solvent-based formulations to aqueous dispersions of polymer colloids, i.e. latex and use of transparent adhesives for labels and displays.

However, the adhesion properties and water resistance of water based PSAs are inferior compared to its solvent counterpart. There remains a need to develop advanced materials for water based PSAs that can overcome these limitations. Besides, functional properties like electrical and thermal conductivity are more and more needed to connect electronic assemblies. Traditional conductive adhesives are made by adding metals such as aluminium, silver, nickel or copper to adhesives. When metals, like silver flake, are incorporated into adhesives to enable them electrical conductivity, the viscosities become very high. These result in a decrease in normal PSA performance, such as shear, peel and adhesion. To develop advanced functional PSAs, traditional metal fillers have vital limitations.

1.4.3 Probe-tack analysis of PSAs

The adhesion energy of a PSA is determined by its debonding process during testing. A first view of the debonding process of PSA films will help us to better understand the energy dissipation of PSAs. When the debonding of a PSA film begins, an internal stress will appear in the bulk of the film (Figure 1.14a). When the internal stress reaches a critical stress, cavities will form either in the bulk of PSA film, or at the interface of the probe and film (Figure 1.14b). As the internal stress continues to increase, more cavities will appear (Figure 1.14c). At the same time, the existing cavities will expand. Basically, they have two ways to expand, i.e. vertical expansion and lateral expansion (Figure 1.15). If either of the expansions dominates cavity growth, it will give a different stress-strain debonding curve. When cavities have spread laterally and the intercavity distance becomes of the order of the initial thickness of the films, the walls (Figure 1.14d) between them extend in the vertical direction, thereby dissipating energy and yielding high tack properties.
A PSA material with viscoelasticity which can promote cavitation and fibrillation development is vital for high performance PSAs.

Figure 1.14 Cavitation and fibrillation development in PSAs debonding process.

Figure 1.15 Vertical and lateral expansion of cavities.
Figure 1.16 shows experimental data obtained from probe tack measurement, which has been normalized from a force-distance curve to a stress-strain curve with stress \( \sigma = \frac{F}{A_0} \) (\( A_0 \) is probe contact area, around 2 mm is this study), and strain \( \varepsilon = \frac{h - h_0}{h_0} \) (\( h \) is distance and \( h_0 \) is the initial film thickness).\textsuperscript{162,163}

In a probe-tack curve, the point when most cavities are initiated is indicated by the maximum in the stress, \( \sigma_{\text{max}} \). The plateau stress referred to as \( \sigma_p \) is related to the stress required to draw the fibrils. The end of the deformation is defined as the maximum strain (\( \varepsilon_{\text{max}} \)), or failure strain (\( \varepsilon_f \)). The area under a tack curve is proportional to the energy dissipated during the debonding process, \( E_a \), which is defined as:

\[
E_a = h_0 \int_{0}^{\varepsilon_f} \sigma(\varepsilon) d\varepsilon \tag{1.10}
\]
There are two types of adhesive failure mechanisms: cohesive failure and adhesive failure (or interface failure).\textsuperscript{164} Cohesion refers to the intermolecular attraction between like-molecules, and adhesion refers to the attraction between unlike molecules. Cohesive failure refers to the failure at either side of the probe-adhesive interface, including failure in the bulk of the substrate or in the bulk of the PSA adhesive. In the probe tack measurement, a cohesive failure usually means that the failure happens within the PSA materials, and hence the adherent surface is covered by the fractured adhesive. Adhesive failure, or interface failure, means that the failure is at the interface of the adherent and the adhesive. As a result, there are no adhesive residues on the adherent surface after the debonding process. One can determine the failure mechanism from the stress-strain curve of the probe-tack measurement. The stress fails to zero sharply at the end of the plateau if an adhesive failure mechanism is operative, whereas the stress fails gradually with a long tail until the stress is close to zero if a cohesive failure mechanism is operative. The cohesive failure is more like to operate when the viscoelasticity of the adhesive material is liquid-like, and adhesive failure will operate when the viscoelasticity of the adhesive materials is more solid-like.

1.4.4 Strategies to increase adhesion

The shape of the growing cavity and its interaction with the neighboring cavities are the most difficult aspects of the experiment to model and yet are the most relevant for practical application.\textsuperscript{158} If the cavities initially form on defects, coalesce and form a crack, the interfacial debonding of the PSA will be rapid and the practical work of adhesion will be low. On the other hand, if the coalescence of neighboring cavities does not occur, the walls between cavities will be extended as polymer fibrils and a very large work of adhesion will be achieved.

The length scale defined by $G_c/E'$ plays an important role in determining the overall behavior of PSA debonding. $G_c$ is the critical energy release rate between probe and adhesive to initiate a interfacial crack deformation.\textsuperscript{163} $E'$ is the storage modulus of the
adhesive. The parameters that determine $G_c$ are complex and include the linear and nonlinear viscoelastic properties of the adhesive film and the frictional properties of the probe-film interface.\textsuperscript{158} For a given probe-film interface, the values of $G_c/E'$ will vary with different viscoelastic properties of PSAs.

![Stress-strain curves corresponding to different $G_c/E'$ values of PSAs.](image)

Figure 1.17 summarizes different stress-strain curves depending on different viscoelastic properties of PSA materials for a given probe-film interface. Curve I is for a low $G_c/E'$. During the debonding, an interface crack propagates and the crack will not expand into the bulk of the PSAs. These PSAs display a very low value of adhesion. Curve II has an intermediate $G_c/E'$. During the debonding, cavitation propagates but fibrils do not form or detach prematurely. The overall work of adhesion is also relatively low. Curve III represents a high $G_c/E'$. During debonding, cavities form and then develop into fibrils which also extend to very large distances before adhesive detachment from the substrate. As a result, a high adhesion energy is obtained. It is apparent that adhesion energy ($E_a$) is proportional to $G_c/E'$.

Providing the same interfacial conditions, there is a reasonable approximation between $G_c$ and $\tan \delta$ (i.e. the energy dissipation factor of the bulk adhesive film)\textsuperscript{(165)}, therefore $E_a$ is proportional to $\tan \delta E'$. Ideally, we need a weakly crosslinked (avoiding high $E'$) but highly dissipative (high $\tan \delta$) PSA at the debonding frequency to facilitate cavitation and fibrillation evolution during the debonding process. For a
high performance PSA, it is also expected that the fibrils are strong and stable, extending a large distance before failure.

1.5 Aims and layout of present work

Studies of the dispersion of nanotubes in latex films so far has focused on low percolation threshold and high electrical conductivity. According to our literature interview, no research has been done to incorporate carbon nanotubes into soft waterborne polymer colloids (or latex) for pressure sensitive adhesive applications. Undoubtedly, carbon nanotubes will give PSAs electrical and thermal conductivity if the nanotubes have been modified to be water soluble and can be stable in polymer colloids and in the dried soft materials. Polymer colloid methodology can promote uniform nanotube dispersion. The inherent high aspect ratio of nanotube enables a much lower percolation threshold compared with normal metal particles. Since the presence of the nanotubes will be kept at a low level, the shear, peel and adhesion performance of PSAs will be expected to be retained, regardless of mechanical reinforcing and toughening effects of nanotube.

In processing these waterborne nanocomposites, there is a wide choice of water-soluble polymers to disperse CNTs in water. To what extent - or why - the choice of dispersants might influence nanocomposite mechanical properties has not been considered. Without an understanding of the molecular mechanism of interfacial stress transfer and slippage, optimization of the compatibiliser in waterborne nanocomposites is being impeded.

This work will use both chemical functionalization and physical modification of carbon nanotubes to impart water solubility and to fabricate colloidal nanocomposites from polymer colloid/nanotube blends in water through horizontal deposition methods. The effect of the nanotubes in the colloidal nanocomposite on the adhesive properties, electrical and thermal conductivity, optical properties will be investigated in Chapter 2. The effect of the matrix/nanotube interface on adhesive properties will be investigated in Chapter 3. Chapter 4 will discuss the effects of interfacial polymer
chain length and density on the interfacial stress and molecular friction of colloidal nanocomposite films. In Chapter 5, the interfacial interactions of individual polymer colloid particles will be adjusted through the pH value of the colloid dispersion. The effects of the molecular interactions on the macro-scale adhesive properties will be studied. And finally Chapter 6 presents the final conclusions of this work and proposes potential future work.
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Chapter 2

Latex/SWNT colloidal nanocomposite adhesives: high tack energy with electrical, thermal conductivity and optical clarity*

2.1 Introduction

As-produced CNTs tend to bundle together due to their huge surface energy. The intrinsic inert surface property of CNTs makes the CNTs and matrix interface interaction poor. Pre-treatment to unrope the nanotube bundles and improve the solubility, processing, dispersion, and compatibility of CNTs with the polymer matrix is vital. CNTs are not naturally water-soluble, but different emulsifiers - anionic surfactant (e.g. sodium dodecyl sulfate\textsuperscript{1, 2, 3, 4}), cationic surfactant (dodecyl trimethyl ammonium bromide (DTAB)\textsuperscript{4}), nonionic surfactant (Triton X100\textsuperscript{5, 6, 7}) and water-soluble polymers (gum arabic\textsuperscript{8, 9}, poly(vinyl pyrrolidone)\textsuperscript{10}, poly(styrene sulfonate)\textsuperscript{10}, poly(vinyl alcohol)\textsuperscript{11}) have been employed to disperse and stabilize them in water.

These methods can generally be separated into either chemical or physical modification, depending on whether there is a chemical reaction or not. Covalent modification of CNTs by water-soluble polymers includes in-situ polymerization of molecules\textsuperscript{12} or polymer grafting\textsuperscript{11}. Physical modification of carbon nanotubes is usually combined with ultrasonication of nanotube bundles within dispersant solutions. When carbon nanotubes are debundled by ultrasonication, polymeric dispersants or surfactants can either coat or wrap onto the nanotubes. The driving force to polymer coating or wrapping around nanotubes is still not clear. π-π stacking

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interactions between conjugated polymers and the nanotube surface have been suggested to explain the helical wrapping of polymers on nanotubes. In addition, electronic energy contributions and nanotube surface curvature are also suggested to stabilize helical conformation. Baskaran et al. has demonstrated that a long molecule, containing many CH linkages, will form CH-π interactions with a nanotube. They concluded that non-specific molecular interactions between polymers and nanotubes are operative. Molecular dynamics simulations using empirical force fields conclude that the interaction energies are solely due to van der Waals interactions between polymers and CNTs. The energy depends on the temperature and the nanotube diameter.

This Chapter reports how single-walled carbon nanotubes were functionalized with hydrophilic poly(vinyl alcohol) (PVA) via an esterification reaction to render them dispersible and stable in water and used to create a dissipative interface between the latex matrix and the nanotube. The functionalized SWNTs were blended with a poly(butyl acrylate-co-acrylic acid) (P(BuA-co-AA)) latex to form a soft nanocomposite. Microstructure, electrical conductivity, thermal conductivity, pressure-sensitive adhesive property and optical clarity of the nanocomposite films were studied. The viscoelasticity of the latex with the presence of SWNTs and its relation to the adhesive properties will be extensively investigated.
2.2 Materials and Techniques

2.2.1 Latex

A poly(butyl acrylate-co-acrylic acid) (P(BuA-co-AA)) latex was prepared at Institute for Polymer Materials (POLYMAT), the University of the Basque Country (Spain) by semi-continuous emulsion polymerization of n-butyl acrylate and acrylic acid in a 99:1 weight ratio, as described elsewhere. PAA was enriched at the particle surface. Sodium dodecyl sulfate (SDS, 2 wt.% on the monomer) was used as the emulsifier, and potassium persulfate (0.25 wt.%) as the initiator. The average particle size is 122 nm and the solids content is 50 wt.%. The gel content of the resulting PSA is 30%, according to Soxhlet extraction in tetrahydrofuran. Analysis (Zetasizer, Malvern Instruments) of dilute latex found a zeta potential of -50.8 mV. The negative charge at neutral pH is attributed to COO⁻ groups from the PAA. The free surfactant concentration in the latex serum was estimated to be 0.35 gL⁻¹ through Du Nouy ring tensiometry (KSV Sigma 70 Surface Tensiometer, KSV Instruments Ltd.) of the serum that had been separated from the latex through ultracentrifugation.

2.2.2 Chemical functionalization of SWNTs

SWNTs (produced by arc-discharge method) were chemically functionalised with PVA (M₆₅ ~ 100k, 99% hydrolyzed, Alfa Aesar) in a typical carbodiimide-activated esterification reaction between the nanotube defect-bound carboxylic acids and the pendant hydroxyl groups on PVA, as described elsewhere. Briefly, purified SWNT was sonicated in a PVA solution in dimethyl sulfoxide in the presence of carbodiimide reagents for 24 h. Upon centrifugation at 3,000 g, the supernatant was obtained as the crude product solution. After solvent removal and thorough washing with acetone, the crude product was re-dissolved in water upon moderate heating and subjected to dialysis against fresh water for 3 days to yield a stable solution with a solid content of 1 wt%. Thermogravimetric analysis of the dried PVA-SWNT indicates that SWNTs
constitute approximately 10% of the total mass. Hence, the concentrations by weight of SWNT, rather than PVA-SWNT, are lower by about one order of magnitude.

2.2.3 Nanocomposite PSA preparation

The nanotube dispersion supernatants were blended drop-wise with the poly(butyl acrylate) latex using magnetic stirring. The nanocomposite colloidal dispersions were cast on glass substrates using a cube applicator and dried at 50 °C in oven under flowing air for 30 min prior to analysis. The dried films were 50–60 μm thick.

2.2.4 Atomic force microscopy

Latex, nanotube suspension or latex/nanotube blends were spin coated on mica. Images of the latex particles and latex/nanotube blends were obtained with an atomic force microscope (NTEGRA, NT-MDT, Moscow, Russia) in the intermittent contact mode. All scans used a silicon cantilever (OMCL-AC160TN, Atomic Force, Germany). The nominal resonant frequency of the cantilevers is about 280 kHz and the average spring constant is 42 N/m. A high tapping amplitude and high spring constant yield the best results on soft adhesive surfaces.

2.2.5 Adhesion analysis

Tack measurements of films on glass plates followed the Avery method on a commercial instrument (MicroSystems Texture Analyser, Godalming, UK) using a high energy surface probe (spherical, stainless steel). Photomicrographs were obtained of the PSA surface after debonding.

The probe is brought into contact with a PSA surface, contact the PSA film with settled time and force (1 second and 4.9 N in this study), and then removed from the PSA surface at a constant velocity (10 μm/sec or 100 μm/sec) to form a force-distance curve, which can be normalized to stress-strain curve. The initial strain rate of the probe tack measurement is around 0.17 Hz and 1.7 Hz, responding to 10 μm/sec and
100 μm/sec testing speed, respectively.

2.2.6 Tensile analysis

Large deformation properties of soft polymer materials in tension were studied using strip samples with a sample dimension of 10 mm x 1 mm x 1 mm obtained by casting in Teflon moulds. The testing speed was 5 mm/sec, corresponding to an initial strain rate of 0.5 Hz.

2.2.7 Dynamical mechanical analysis

Dynamical mechanical analysis (Q800, TA Instruments, New Castle, DE, USA) was performed in the tensile mode on strip samples with a sample dimension of 10 mm x 1 mm x 1 mm obtained by casting in Teflon moulds. Temperatures ranged from -100 °C to 60 °C with a strain of 0.25% and a frequency of 1 Hz, which is comparable to the strain rate in the tack measurements. Storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan \delta = E''/E'$) were obtained as the viscoelastic properties of PSA materials.

2.2.8 Electrical conductivity measurement

Latex/SWNT nanocomposite PSAs were cast using a 150 μm cube applicator on ceramic substrate. After drying in oven under 50 °C for 30 min, a clear layer with 50 μm thickness was received. A square area (5 mm x 5 mm) film was coated by a layer of gold with 15 nm thickness via a thermal vapour method. Then two soft gold lines linked the gold on the ceramic substrate and the vapour-coated gold layer, respectively, to form a circuit for current measurement. The room temperature electrical current was measured using Keithley Instruments 487, with voltage varying from -10 V to 10 V. The electrical conductivity $\sigma$ is defined as:

$$\sigma = \frac{h_0}{RA} \quad (2.1)$$
with $R$ as electrical resistance ($1/D$), $h_\theta$ as film thickness (50 μm) and $A$ as cross-sectional area (5mm x 5mm). For non-ohmic I-V curves, electrical resistance is calculated from the linear region at low fields.

### 2.2.9 Thermal conductivity measurement

Modulated DSC (MDSC) (Q1000, TA instruments, New Castle, DE, USA) was employed to measure heat capacity of PSA specimens, from -100 °C to 100 °C with oscillation amplitude of ± 0.5 °C within a period of 80 s. Two kinds of cylinder PSA samples were prepared, thin (<0.5 mm) and thick (>3.0 mm) samples with a diameter around 5 mm. Thin samples were covered by an aluminium pan and thick samples were uncovered, so that the temperature oscillation is applied only to one sample side to produce a temperature gradient across the thick specimen. Thermal conductivity of PSAs were obtained using the equation:

$$k_0 = \frac{8LC^2}{C_pmd^2P} \quad (2.2)$$

where $k_0$ is the observed thermal conductivity, $L$ is the thin sample thickness, $C$ is the apparent heat capacity (thick sample), $C_p$ is the specific heat capacity (thin sample), $m$ is the weight of the thick sample, $d$ is the thin sample diameter and $P$ is the oscillation period.

Effective thermal conductivity $k_e$ for PSAs is obtained according to the equation:

$$k_e = \frac{k_0 - 2D + (k_0^2 - 4Dk_0)^{1/2}}{2} \quad (2.3)$$

where $D$ is a correction factor obtained by thermal conductivity of standard polystyrene (PS). $D$ is defined as:

$$D = (k_{0PS}k_r)^{1/2} - k_r \quad (2.4)$$

where $k_{0PS}$ is the observed thermal conductivity of PS and $k_r$ is 0.14 W mK, the thermal conductivity of PS from the literature.
2.2.10 Optical transmission measurement

Films with a thickness of 50 µm were cast on glass plates and dried at room temperature. Optical transmission of the film was measured with a spectrophotometer (Campsec 350, Cambridge, UK) in the range from 300 to 1100 nm. The transmittance, $T$, is defined as $T = \frac{I}{I_0}$, where $I$ is the transmitted light intensity and $I_0$ the incident light intensity. The absorbance, $A$, is defined as $A = -\log_{10}\left(\frac{I}{I_0}\right)$. The absorption coefficient, $\mu$, is defined as $\mu = -\frac{\ln 10^{-A}}{h_0}$. 
2.3 Results and Discussion

2.3.1 PVA functionalised SWNTs and their interaction with latex

PVA is water soluble polymer. PVA polymer was grafted onto the side-walls of SWNTs by a carbodiimide-activated esterification reaction between the nanotube defect-bound carboxylic acids and the pendant hydroxyl groups on PVA, as illustrated in Figure 2.1. After functionalization, PVA-SWNT dispersions (Figure 2.2) are stable for months and no phase separation occurs. AFM images of PVA-SWNT dispersion spin-coated on mica in Figure 2.3 show that most SWNTs were debundled to individual or very thin bundles, with an average SWNT length of 1~1.5 μm. The content of PVA in PVA-SWNT was ~90% according to TGA measurement.

Figure 2.1 Scheme of PVA grafted onto SWNT surface by carbodiimide reaction.

Figure 2.2 A photograph of PVA grafting modified SWNT water dispersion
Figure 2.3 AFM phase (a) and height (b) images of PVA-SWNT dispersion spin-coated on mica. Image size 3 \( \mu \text{m} \times 3 \mu \text{m} \).

Figure 2.4 AFM phase image of P(BA-co-AA) latex spin-coated on mica. Image size 5 \( \mu \text{m} \times 5 \mu \text{m} \). Latex particles horizontally spread on mica during spin-coating.
Water soluble PVA on external walls of SWNTs give them a hydrophilic property. The compatibility between PVA and P(BuA-co-AA) latex (Figure 2.4) stabilizes SWNT in the matrix. Figure 2.5 is an AFM image of latex particles with one SWNT. Latex particles are sticky to SWNT, illustrating that PVA functionalized SWNTs are compatible with latex.

![Image](image.png)

Figure 2.5 AFM phase image of latex/SWNT spin-coated on mica. Image size 2 μm × 2 μm. Latex particles horizontally spread on mica during spin-coating.

### 2.3.2 Latex/SWNT nanocomposite adhesion

Figure 2.6 reveals adhesion properties of pure PSA and nanocomposite PSAs. P(BuA-co-AA) is a poorly performing adhesive, illustrated particularly by its low values of $\varepsilon_{\text{max}}$ and $E_a$. With the addition of SWNTs, the tack properties are greatly elevated. Specifically, at a concentration of only 0.005 wt%, $\sigma_{\text{max}}$ and $\varepsilon_{\text{max}}$ are both higher. At a concentration of 0.03 wt %, the plateau region is even longer, and $\sigma_p$ is higher, so that $E_a$ is much greater. The same trend is observed with two debonding velocities, 10 μm/sec (Figure 2.6a) and 100 μm/sec (Figure 2.6b). Debonding always occurs at the interface with the probe, indicating adhesive rather than cohesive failure.

Examination of the de-bonded surface after a tack measurement (Figure 2.6 insets) and the stress-strain curves reveal that the addition of SWNTs has a significant impact on both the nucleation of cavities during debonding from the substrate and on the subsequent evolution of fibrils during extension. In the pure latex adhesives, many
small dark spots in Figure 2.6a (insets) are visible indicating the nucleation of cavities (including numerous secondary cavities), but the walls between cavities are not stable and detach prematurely, as can be deduced from the short plateau in the tack curve. The debonded surfaces of PSAs with 0.03 wt % SWNT, however, display traces of fewer initial cavities, but the walls between these cavities are now stabilized by the CNTs and extend much more before detaching. The fibrils give rise to a significantly longer plateau in stress after the initial peak.

Figure 2.6 Tack curves of pure PSA and nanocomposite PSAs at a debonding speed of (a) 10 μm/sec and (b) 100 μm/sec. SWNT concentration are: 0 % (---), 0.005 wt%(—) and 0.03 wt%(—), respectively.
Figure 2.7 Tack properties of (a) $\sigma_p$, (b) $\varepsilon_{\text{max}}$, and (c) $E_a$ as a function of SWNT content. Debonding velocity are 10 $\mu$m/sec(—) and 100 $\mu$m/sec(—), respectively.
Figure 2.7 summarizes key tack properties of $\sigma_p$ (plateau stress), $\varepsilon_{\text{max}}$, and $E_a$, respectively. The key tack properties reach maximum values at SWNT concentrations of 0.03 wt % and decrease again with higher concentrations. At this optimum concentration, $\varepsilon_{\text{max}}$ in the nanocomposite PSA is greater by a factor of two compared to pure PSA, and $E_a$ increases by 85%.

### 2.3.3 Latex/SWNT nanocomposite electrical conductivity

Electrical conductivity percolation threshold, $\phi_p$, is the formation of long-range connectivity of the conductive fillers in the insulated polymer systems where the conductivity increases by several magnitudes. Figure 2.8 illustrates I-V curves of latex/carbon nanotube nanocomposite adhesives. The pristine latex and nanocomposite PSA with 0.005 wt% SWNT show non-ohmic character of the resistivity, in which there is ohmic behavior at low fields and deviation from Ohm’s law at high fields. After incorporating SWNT at 0.01 wt%, the nanocomposites start to show ohmic behavior, illustrating metallic electrical behavior. I-V curves show that a percolation threshold lies between 0.025–0.03 wt%, when the current increase by many orders of magnitude. The electrical conductivity is shown in Figure 2.9. It reaches 1–10 S/m with SWNT at concentration less than 0.1 wt% and is comparable to germanium.

The $\phi_p$ for rods is known to vary inversely with their aspect ratio. Hence, because of the high aspect ratio of SWNTs, a low $\phi_p$ can be achieved if the nanotubes are randomly arranged. The nanotubes and bundles have an average aspect ratio on the order of 100, for which the lowest possible $\phi_p$ is expected to be less than 0.5 wt%, as is observed here. It has been proposed elsewhere that colloidal polymer particles separate the nanotubes and help to achieve a low $\phi_p$. 
Figure 2.8 I-V curves of pristine PSA and nanocomposite PSAs with various nanotube contents. a) I-V curves of pristine PSA and nanocomposite PSA with 0.005 wt% SWNT. b) I-V curves of nanocomposite PSAs with SWNT contents of 0.01 wt%, 0.02 wt% and 0.025 wt%. c) I-V curve of nanocomposite PSA with 0.03 wt% SWNT.
Electrical conductivity in PSAs is conventionally achieved through the use of metallic fillers in the form of flakes and particles. This approach has a detrimental effect on adhesive properties, including shear and peel strengths, because it strongly increases $E'$ and viscosity. Moreover, fillers make an adhesive less transparent or even opaque. These nanocomposite PSAs solves the problem of achieving electrical conductivity via a waterborne process while improving adhesion. The addition of 0.03 wt% SWNT yields the optimum tack properties while offering conductivity (comparable to germanium).

### 2.3.4 Scaling theory discussion

Correlating tack properties and electrical conductivity, it is easy to find that the optimum concentration for tack properties corresponds to the percolation threshold, at which a continuous network of SWNTs is formed. Then tackiness degrades with excess nanotube concentration.

Fibrils develop when the stress in a cavity exceeds the polymer cavitation stress, $\sigma_c$. In this case, much of $E_a$ comes from the extension and then irreversible failure of the nearly elastic fibrils. Thus, $E_a$ for a PSA film with an elastic modulus, $E$, is predicted to scale as $^{25}$.
where $h$ is the film thickness and $\sigma_f$ is failure stress of fibrils.

In the experimental data, pseudo-yield stress, $\sigma_y$, which is indicative of stress level present in the fibrils during extension, can replace $\sigma_f$. Young’s modulus can replace the elastic modulus. Using these experimental value replacements, Eq. 2.5 can be rewritten as:

$$E_a \sim \frac{h\sigma_y^2}{Y}$$  \hspace{1cm} (2.6)

Figure 2.10 illustrates large deformation tensile stress-strain curves of nanocomposite PSAs. Comparison of the large deformation properties of pure PSA and nanocomposite PSAs illustrates that nanocomposite PSAs are stiffer, as deduced by its increased moduli, but also tougher and more energy dissipative, illustrated by the increased area the curve covers. Above 0.05 wt% SWNT, stiffness is more obvious, but toughness (energy dissipation) begins to degrade, possibly because of excess nanotube clustering formed at high concentration.
The changes of $\sigma_y$ and $Y$ in Figure 2.10 are determined following the methods in Figure 1.12 in Chapter 1.4.1 and summarized in Figure 2.11a. Figure 2.11a illustrates that both $Y$ (for $\varepsilon$ up to 0.2) and $\sigma_y$ increase with increasing SWNT concentration. The increase of $Y$ is stronger at SWNT concentrations above $\phi_p$, whereas $\sigma_y$ shows a slightly weaker dependence over this range. Fitting $\sigma_y$ and $Y$ into Eq. 2.6, one can find that a maximum energy dissipation at 0.03 wt% SWNT is predicted (Figure 2.11b), which is consistent with the experimental observations (Figure 2.11c). At higher concentrations, the nanocomposite is too stiff to be an effective PSA, as is qualitatively expected from the so-called Dahlquist criterion.\textsuperscript{26}

![Graph a](image1)

![Graph b](image2)

Figure 2.11 (a) Dependence of Young’s modulus ($Y$) and yield stress ($\sigma_y$) of PSA nanocomposites on SWNT concentration. (b) The predicted trend in adhesion energy ($E_a$) obtained from these experimental values of $Y$ and $\sigma_y$. 

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For optimum tack adhesion, a PSA must not be too stiff and must be able to dissipate energy during deformation, as is apparent in the deformation maps developed by Crosby et al.\textsuperscript{27} An excessively high storage modulus, $E'$, relative to the dissipative character of the adhesive, will induce interfacial crack propagation (in the horizontal direction in our case) so that growth of cavities in the vertical direction is inhibited. The damping factor, $\tan \delta = \frac{E''}{E'}$, where $E''$ is the loss modulus, characterizes the energy dissipation. Hence, the ratio of $\frac{\tan \delta}{E'}$ is a good gauge of expected adhesive performance (also discusses in Chapter 1.4.4), with a high value indicating better adhesion.

Dynamic mechanical analysis (DMA) provides insight into the adhesive characteristics of the nanocomposite. As expected when adding stiff filler to a soft matrix, the storage modulus, $E'$, increases with increasing SWNT concentration (Figure 2.12a). Typically, when a composite's $E'$ increases with the addition of a second phase, its $\tan \delta$ decreases.\textsuperscript{28,29} Remarkably, in the nanocomposite PSA, $E''$ increases significantly as SWNT concentration is increased, so that $\tan \delta$ nearly doubles over the same range (Figure 2.12c). This combination of increased stiffness and energy dissipation has been previously reported for CNTs in a much stiffer epoxy\textsuperscript{30} and poly(carbonate)\textsuperscript{31} matrices at low strains but never in a soft polymer, such as P(BuA-co-AA). The $\tan \delta/E'$ ratio in Figure 2.13b increases strongly with only 0.01 wt% SWNT and reaches a maximum around 0.05 wt%, which is broadly consistent with the tack properties. At higher concentrations, $\tan \delta/E'$ decreases because of the increasing $E'$. 
Figure 2.12 Dynamic mechanical properties of nanocomposite PSAs. (a) Storage modulus, (b) Loss modulus, and (c) Loss factor, tanδ. SWNT concentrations are: 0 % (—), 0.01 wt% (—), 0.03 wt% (—) and 0.07 wt% (—), respectively.
Figure 2.13 (a) Storage and loss moduli (E' and E'') (on left axis) and loss factor (tanδ) (on right axis) and (b) tanδ/E' ratio of Latex/SWNT nanocomposites as a function of SWNT concentration at 22 °C with a strain of 0.25% at a frequency of 1 Hz.

Dynamic mechanical analysis proves that the presence of SWNTs can markedly increase the energy dissipation rate of nanocomposites. Elsewhere, a nanotube/polymer sliding dissipation mechanism was shown to deliver an order of magnitude increase in nanocomposite $E''$ with an addition of 2 wt% SWNT. Interfacial slip at the nanotube/polymer interface is activated by either high strain levels or elevated temperatures. Whereas the strain imposed in DMA was 0.25%, the relevant range of strain levels at the edge of propagating cavities during our probe-tack measurements is certainly higher (~100%). Such high deformation is apparently effective at
activating nanotube/polymer interfacial sliding. High matrix chain mobility will also facilitate filler alignment and interface slippage. For PSAs, the matrix is always in the rubbery or viscoelastic stage, giving the matrix a high chain mobility, facilitating alignment and slippage. Hence energy dissipation is significantly increased in the nanocomposite PSAs.

### 2.3.5 Latex/SWNT nanocomposite thermal conductivity

Figure 2.14 shows thermal conductivity of nanocomposite PSAs as a function of temperature. As temperature enhances, thermal conductivity also increases. Near the glass transition temperature (-50 °C) of the latex matrix, thermal conductivity increases sharply, and then the increase is negligible. This means that the polymer chain mobility has a big effect on thermal conductivity, and raising the matrix chain mobility will increase the thermal conductivity.

Thermal conductivity effects of SWNT on nanocomposite PSAs at different temperatures are illustrated in Figure 2.15. At 20 °C, thermal conductivity of nanocomposite PSA reaches 0.74 W/mK with 0.1 wt % SWNT, an 80 % increase from 0.41 W/mK of pure PSA. A similar improvement is likewise seen at other temperatures of -60 °C and 60 °C.

![Thermal conductivity graph](image)

Figure 2.14 Effect of temperature on thermal conductivity of nanocomposite PSAs with SWNT content of 0 %(--), 0.03 wt%(---) and 0.1 wt%(——), respectively.
Figure 2.15 Thermal conductivity of nanocomposite PSAs as a function of SWNT concentration at different temperatures: -60 °C (—), 20 °C (—), 60 °C (—).

For polymer/CNTs composites, the interface thermal conductance demonstrates a high effect on the composite’s thermal conductivity. A small interface thermal conductance will highly limit thermal conductivity of nanotube composite materials. Different models have been developed to estimate the effects of interfacial thermal resistance, nanotube diameter, aspect ratio, fraction, space distribution, as well as the relationship with nanotube surface functionalization. We compare our results with the model developed by Nan et al. The effective thermal conductivity $k_e$ of a nanocomposite with carbon nanotubes randomly dispersed in a polymer matrix (whose thermal conductivity is $k_m$) can be derived as:

$$\frac{k_e}{k_m} = \frac{3 + f (\beta_x + \beta_z)}{3 - f \beta_x}$$

with $\beta_x = \frac{2(k_{11}^c - k_m)}{k_{11}^c + k_m}$, $\beta_z = \frac{k_{33}^c}{k_m} - 1$

where $f$ is the volume fraction of the nanotubes; $k_{11}^c$ and $k_{33}^c$ are the equivalent thermal conductivities along transverse and longitudinal axes of a composite unit cell, i.e., a nanotube coated with a very thin interfacial thermal barrier layer, and can be expressed as:
where \( d \) and \( l \) are the diameter and length of the nanotube, respectively; and \( a_k \) is a so-called Kapitza radius defined by \( a_k = R_k k_m \). \( R_k \) is the interface thermal resistance. \( k_c \) is the thermal conductivity of nanotubes and taken as 6000 W/MK, and \( k_m \) is 0.41 W/mK for poly(butyl acrylate) as measured by MDSC.

The volume fraction of nanotube in each PSA was calculated from the mass fraction using the density \( \rho = 1500 \text{ kg/m}^3 \) for SWNT. Cross section analysis from AFM images shows that the diameter of nanotube \( d = 20 \text{ nm} \) and \( p = 100 \). These values are used in the model analysis. A typical value of \( 8 \times 10^{-8} \text{ m}^2 \text{ K/W} \) for the interface thermal resistance \( R_k \), was suggested by the model simulation, as well as direct measurement by laser pump-probe for typical polymer-nanotube composites. Fitting of the above parameters into Eq. 2.7 illustrates that \( 8 \times 10^{-7} \text{ m}^2 \text{ K/W} \) is a more reasonable value for \( R_k \) as the fitting curve is more close to our experimental data in Figure 2.16. We suppose this relatively high interface thermal conductivity is achieved by covalent bonding between PVA and SWNTs, resulting in a more effective path for phonon transport. Thus this interfacial thermal resistance is one or two orders of magnitude lower than nanotube interfaces modified by surfactants.

Predictions from the model in Figure 2.17 show that the thermal conductivity of the nanotube, \( k_c \), has a negligible effect on thermal conductivity improvement, since the enhancement \( k_c/k_m \) is within the same order region with higher \( k_c \). This further supports the idea that interface thermal resistance is the main resistance for effective thermal conductivity improvement.
Figure 2.16 Effect of the interface thermal resistance on the thermal conductivity enhancement in nanocomposite PSAs.

Figure 2.17 Effect of $k_e$ on thermal conductivity enhancement in nanocomposite PSAs.

Most models predict that the thermal conductivity in carbon nanotube composites obeys a linear concentration dependence. The results here show an obvious increase near the percolation threshold, at which a nanotube network is formed. Nanotubes are isolated before the percolation threshold, after which a network is formed. Thus the nanotube fraction itself is not enough to consider this effect. And nanotube junctions and agglomerates should also be considered when the nanotube fraction is in excess of what is required of the percolation threshold. The modification of the existing models is still needed to describe the experimental data.
2.3.6 Latex/SWNT nanocomposite optical clarity

The optical clarity of nanocomposite PSAs are characterized by UV-visible spectroscopy in Figure 2.18. The decrease in transparency with CNT addition is greatest in the UV region of the spectrum. Although nanotubes have a high absorption cross-section in the visible range, the very low loading of 0.03 wt% at $\phi_p$ yields an absorption coefficient of only 1100 m$^{-1}$ at 600 nm (Figure 2.19). A visual demonstration of the optical transparency of the nanocomposite films in Figure 2.20 shows the optical clarity of this nanocomposite PSA.

![Figure 2.18 Transmission of nanocomposite PSAs at different wavelength with SWNT concentration at 0 % (---), 0.01 wt% (--), 0.03 wt% (---) and 0.07 wt% (---).](image1)

![Figure 2.19 Absorption coefficient of nanocomposite PSAs at 600 nm.](image2)
2.4 Conclusion

The nanocomposite PSAs solve the problem of achieving electrical conductivity via a waterborne process while improving adhesion. The relation of nanocomposite viscoelasticity and adhesive properties were investigated here. Nanocomposites of latex and SWNTs are stiffer but more importantly, more tough compared with pure latex. Consequently, nanocomposite PSAs are stickier with the presence of SWNTs. Nanotubes remarkably double the amount of strain at adhesive failure and increase the adhesion energy by 85%. The addition of 0.03 wt% SWNT yields the optimum tack properties while offering conductivity (comparable to germanium) coupled with optical clarity. A thermal conductivity increase by 80 % is achieved with 0.1 wt % SWNT presence. This combination of properties holds enormous potential for demanding applications in displays and electronics.
References


Chapter 3

Latex/MWNTs colloidal nanocomposite adhesives: interface tuning

3.1 Introduction

Nanotubes have shown a promising ability to reinforce polymer materials. However, the use of nanotubes, as well as other nanofillers, to toughen polymer materials does not always result in significant improvement. A review of either natural or synthetic materials with enhanced toughness, or energy dissipation ability, will help us to properly design the microstructure of polymer/nanotube nanocomposites to achieve desired properties.

There are a few natural and synthetic composite materials that exhibit high toughness. Abalone nacre, a lamellar structured composite of more than 90 percent calcium carbonate and a few percent of proteins, is 1000 times as tough as its constituent phases. Atomic force microscope stretching finds that the proteins elongate in a stepwise manner of unfolding the folded domains. This special molecular mechanism contributes to the high toughness of abalone shell. Further research shows that the building blocks of calcium carbonate in nacre are cobble-like polygonal nanograins. This nanograin rotation and deformation under tension are believed to be another two important factors contributing to the high toughness.

Another example from natural materials is spider silk. The toughness of spider silk can be 165 J/g, which is much higher than steel and most high-performance synthetic fibers. e.g. nylon 6, 6 and Kevlar fibers. Spider silk is a polymer with

* Part of this chapter was published in Advanced Materials, 2008, 20: 90-94.
two distinct alternating regions. a soft elastic region and a hard crystallite region. Orientation of the crystallites in the flexible chain region and the amorphous chain extension under stretching are believed to be the origin of the toughness.\cite{6}

In synthetic materials, super-tough poly(vinyl alcohol)/SWNT fibers have been made by spinning.\cite{6} These fibers can absorb energy of 570 J/g before breaking. After a further treatment of hot-drawing of the as-spun nanotube/PVA fibres, an energy adsorption of 870 J/g can be achieved.\cite{8} The hot-drawing treatment is believed to improve nanotube and PVA alignment and to increase the PVA crystallinity.

A built-in energy dissipation mechanism has been realized in a nanocomposite of a rubbery polymer and hard silicate platelets. The re-orientation and alignment of the platelets in a stress field dissipates energy and leads to greater toughness.\cite{9} Molecular dynamics simulations\cite{10} predicting that the addition of nanoparticles to a rubbery polymer results in greater energy being required for tensile deformation. The simulations reveal a molecular mechanism behind the toughening; it is not simply the result of the high interfacial area between nanoparticles and a matrix, but nanoparticle mobility contributes to energy dissipation.

A simple conclusion from the above examples is that toughening requires mechanisms of energy dissipation. When energy dissipation mechanisms are introduced, the mechanical strength as well as the toughness can be increased. A heterogeneous structure, rather than a homogeneous structure, is needed to incorporate energy dissipation possibilities into materials.

Interfacial modification as a means of altering nanocomposite properties has not been well explored experimentally. In a first attempt, pendant groups were covalently bonded to a carbon nanotube sidewall and used as a compatibilizing agent with an elastomeric matrix to impart strength and toughness to the nanocomposite.\cite{11} Yet, there are no previous experimental investigations of what characteristics are required for good compatibilization, and there have been no reports of a compatibilizer being optimized for adhesive applications.
In adhesive applications, it is noteworthy that a nanostructure of hard particles in a viscoelastic matrix does not necessarily guarantee higher adhesion energy. For instance, the tack adhesion energy and the peel strength of an acrylic adhesive were reduced upon the addition of stiff montmorillonite particles. A nanocomposite of an acrylic and single-wall carbon nanotubes, on the other hand, has demonstrated an adhesion energy that is 85% greater than that of the matrix alone, as reported in Chapter 2.

This chapter will describe the incorporation of physisorption-modified MWNT by various water-soluble polymers and surfactants into latex to fabricate colloidal nanocomposites. The dispersants locate at the interface of the matrix and nanotubes in the nanocomposite. The influence of interface modification on the energy dissipation in adhesive properties will be discussed. This current work shows that a nanocomposite can have a wide range of adhesive and mechanical properties, which can be tuned through the control of the interface between the nanofiller and the matrix.
3.2 Materials and Techniques

3.2.1 Physical modification of MWNTs

The MWNTs (Nanocyl, Belgium) have a purity level of 95% and were used as received. The MWNTs were dispersed in de-ionized water by either sodium dodecyl sulfate (SDS), Triton X-100 (TX), poly(vinyl alcohol) (PVA) or poly(vinyl pyrrolidone) (PVP). Materials are summarized in Table 1. Firstly, aqueous solutions of SDS, TX, PVA and PVP were made by dissolving them in de-ionised water at room temperature at a 1 wt.% (10g/L) concentration. A higher temperature of 100 °C is needed for the PVA dissolution. MWNTs were added to the solutions to obtain a dispersant:MWNT ratio of 9:1. The mixtures were sonicated for a minimum of 5 min. using a sonic tip with output power of 20W (Branson Sonifier 150, Branson Ultrasonics Corp, Danbury, CT) followed by mild sonication for 30 min. in a sonic bath. During both sonications, the dispersions were chilled by immersion in ice water. Then the dispersions were centrifuged for 30 min. at 4400 rpm. and approximately 90% of the dispersion was collected as a supernatant of nanotubes dispersed in water.

Table 3.1 Various MWNT dispersants

<table>
<thead>
<tr>
<th>Materials</th>
<th>Supplier</th>
<th>Average molecular weight $(M_m)$ (kg mol$^{-1}$)</th>
<th>$M_n/M_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX 100</td>
<td>Union Carbide Corp.</td>
<td>0.625</td>
<td>---</td>
</tr>
<tr>
<td>SDS</td>
<td>ACROS Organics</td>
<td>0.288</td>
<td>---</td>
</tr>
<tr>
<td>PVA</td>
<td>Sigma-Aldrich</td>
<td>7.2</td>
<td>1.71</td>
</tr>
<tr>
<td>PVA</td>
<td>Sigma-Aldrich</td>
<td>35</td>
<td>2.11</td>
</tr>
<tr>
<td>PVA</td>
<td>Sigma-Aldrich</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>PVP</td>
<td>Sigma-Aldrich</td>
<td>10</td>
<td>2.7</td>
</tr>
<tr>
<td>PVP</td>
<td>Sigma-Aldrich</td>
<td>29</td>
<td>5.2</td>
</tr>
<tr>
<td>PVP</td>
<td>Sigma-Aldrich</td>
<td>1570</td>
<td>5.3</td>
</tr>
</tbody>
</table>
3.2.2 Thermogravitmetric analysis

Thermogravitmetric analysis (Q500, TA Instruments) in nitrogen was employed to determine the dispersant:nanotube ratios in various dispersions, from room temperature to 700 °C at 10 °C/min.

3.2.3 Transmission electron microscopy

TEM analysis of modified nanotubes was performed on a high resolution transmission electron microscope (Philips CM200, Philips Electron Optics, Eindhoven) operated at 200 kV. Samples were prepared by depositing a drop of a dilute MWNT aqueous dispersion (0.015 wt.%) on holey carbon film grids and wicking the liquid away with a tissue. To increase the wetting, the grids were first coated with a thin film of poly(ethyleneimine). The samples were dried in air and then used for analysis.

3.2.4 Nanocomposite PSA preparation

The MWNT dispersion supernatants were blended drop-wise with the poly(butyl acrylate-co-acrylic acid) latex using magnetic stirring. Material details of the latex were described in Chapter 2.2.1. The nanocomposite colloidal dispersions were cast on glass substrates using a cube applicator and dried at 50 °C in oven under flowing air for 30 min prior to tack measurements. The dried films were 50–60 μm thick.

3.2.5 Atomic force microscopy

Images of the latex particles, modified nanotubes and nanocomposite film surfaces were obtained with an atomic force microscope (NTEGRA, NT-MDT, Moscow, Russia) in the intermittent contact mode. All scans used a silicon cantilever (OMCL-AC160TN, Atomic Force, Germany). The nominal resonant frequency of the cantilevers is about 280 kHz and the average spring constant is 42 N/m. A high tapping amplitude and high spring constant yield the best results on adhesive surfaces.
3.2.6 Adhesion analysis

Tack measurements of films on glass plates followed the Avery method on a commercial instrument (MicroSystems Texture Analyser, Godalming, UK) using a high surface energy probe (spherical, stainless steel) and a low surface energy probe (spherical, polypropylene), and were recorded with a CCD camera from the side view during the tack measurement.

The probe is brought into contact with a PSA surface, contact the PSA film with settled time and force (1 second and 4.9 N in this study), and then removed from the PSA surface at a constant velocity (100 μm/sec) to form a force-distance curve, which can be normalized to stress-strain curve. The initial strain rate of the probe tack measurement is around 1.7 Hz for a 100 μm/sec testing speed.

3.2.7 Tensile analysis

Large deformation properties of soft polymer materials in tension were studied using strip samples with a sample dimension of 10 mm x 1 mm x 1 mm obtained by casting in Teflon moulds. The testing speed was 5 mm/sec, corresponding to an initial strain rate of 0.5 Hz.

3.2.8 Dynamical mechanical analysis

Dynamical mechanical analysis (Q800, TA Instruments, New Castle, DE, USA) was performed in the tensile mode on strip samples with a sample dimension of 10 mm x 1 mm x 1 mm obtained by casting in Teflon moulds. Temperatures ranged from -100 °C to 60 °C with a strain of 0.25% and a frequency of 1 Hz, which is comparable to the strain rate in the tack measurements. Storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan \delta = E''/E'$) were obtained as the viscoelastic properties of PSAs.
3.3 Results and Discussion

3.3.1 MWNT debundling and dispersion in nanocomposites

A wide variety of dispersants has been shown to be capable of dispersing carbon nanotubes in water.\textsuperscript{13} Surfactants are most frequently used, because they are highly effective dispersing agents.\textsuperscript{14,15} De-bundling of the MWNTs was observed with transmission electron microscopy to be achieved with each dispersant in Figure 3.1. TEM microscopy shows that MWNTs have been separated into single tubes. This proves that with either polymers or surfactants, physical modification process under ultrasonication is an effective method to debundle and stabilize MWNTs in water. The MWNT lengths are in the range from 1 to 2 \( \mu \text{m} \) and diameters are around 20 nm, according to TEM analysis.

![Figure 3.1 TEM micrographs of MWNTs modified with either polymer or surfactant: (a) PVP, (b) PVA, and (c) SDS.](image-url)
The dispersant:nanotube ratios in the nanotube dispersion were determined by thermogravimetric analysis as seen in Figure 3.2. Additional TGA on pure SDS, TX, PVA and PVP shows that they degrade completely at 550, 450, 550 and 600 °C, respectively. The results indicate that each dispersion consists of approximately 10 wt.% MWNTs, with the remainder being the dispersant (adsorbed or free). The free dispersants are not removed to retain an adsorption-de-adsorption equilibrium of dispersants on the nanotube surfaces.

![Figure 3.2 TGA analysis used to determine the dispersant:MWNT ratio for (a) SDS and MWNTs, (b) TX and MWNTs, (c) PVA ($M_w = 100$ kg/mol) and MWNTs, and (d) PVP ($M_w = 1,570$ kg/mol) and MWNTs. All analysis was performed in a nitrogen atmosphere, ramping at 10 °C/min. from room temperature to 700 °C.](image)

In nanocomposite films, AFM revealed isolated nanotubes at the surfaces in Figure 3.3. Parts of MWNTs are out of the film surface and parts of MWNTs are
prescreened to be in the bulk film. No differences were observed in the MWNT distribution in the nanocomposite when the four dispersants are compared.

Figure 3.3 Atomic force microscopy phase contrast images of the surfaces of nanocomposite films containing MWNTs (0.015 wt.% on the polymer) with various dispersants: (a) TX; (b) SDS; (c) PVA; (d) PVP. Image size 2 µm x 2 µm.

3.3.2 Nanocomposite adhesion with various interphases

In these experiments, a spherical polypropylene (PP) or steel probe was lifted from the PSA surface at a constant velocity of 100 µm s⁻¹, which imposes a strain rate varying between 0.15 and 1.5 Hz during debonding. The adhesion energy of nanocomposite PSAs as a function of MWNT concentration are summarized in Figure 3.4a and 3.4b. With SDS at the interface, the energy dissipation does not show any convincing improvements on either PP or steel adherent. The nanocomposite PSAs with PVA and PVP at the interface, however, demonstrate increased adhesion energy
with increasing MWNT till an optimum content of 0.015 wt%. Then the adhesion energy begins to decrease with more MWNTs. This is because of the moduli of the nanocomposites with high MWNT content are too stiff for adhesive. The quantitative analysis of the effect of modulus on the adhesive properties has been discussed in Chapter 2 in the SWNT system. The discussion of the relations of the adhesion and modulus of MWNT system is omitted here with an alternative emphasis on the effect of the interface.

Figure 3.4 Adhesion energy of nanocomposite PSAs on a) a low energy PP adherent, and b) a high energy steel adherent as a function of MWNTs concentration. SDS (—); PVA ($M_w = 100$ kg/mole) (—); PVP ($M_w = 1,570$ kg/mole) (—).
Tack measurements are compared in Figure 3.5a and 3.5b for nanocomposite PSAs incorporated with 0.015 wt% MWNT using the four different dispersants on PP and steel probe, respectively. The maximum stress, which is associated with the development of cavities in the PSA, is unaffected by the presence of MWNTs and the type of dispersant.

Figure 3.5 Tack curves obtained with a velocity of 100 μms⁻¹ using a) a PP probe, and b) a steel probe, on pure latex (—) and on nanocomposite PSAs made from pure latex and 0.015 wt.% MWNT with various dispersants: TX (—); SDS (—); PVA (M₆ = 100 kg/mole) (—); PVP (M₆ = 1,570 kg/mole) (—). Nominal stress is plotted as a function of strain, defined as (h−h₀)/h₀, where h₀ is the original PSA thickness.
On a PP probe, the plateau on the tack curve of the pure latex adhesive is narrow, indicating that there is no significant fibrillation. The SDS-MWNT and TX-MWNT nanocomposites show a slightly higher plateau stress, $\sigma_p$, but the strain at failure, $\varepsilon_f$, is around that of the pure latex. The highest $\sigma_p$ and $\varepsilon_f$ are found when the MWNTs are dispersed with PVP. The overall adhesion energy, $E_a$, which is proportional to the area under the tack curve, is likewise highest for the PVP, followed by the PVA, then SDS and TX dispersants.

On a steel probe, the pure latex shows a narrow shoulder rather than a plateau on the tack curve. The SDS-MWNT and TX-MWNT nanocomposites show a slightly longer plateau compared with that of the pure latex. The PVA-MWNT and PVP-MWNT nanocomposites show a higher plateau stress and longer failure strain. The highest $\sigma_p$ and $\varepsilon_f$ are found when the MWNTs are dispersed with PVA, rather than with PVP found on PP probe.

This opposite adhesion energy with PVA or PVP at the MWNT/matrix interface on the low energy PP surface and the high energy steel surface is hard to interpret. As introduced in Chapter 1.4.4 and experimental analysis in Chapter 2.3.4, a simple criterion to predict adhesive performance is the ratio of the critical energy release rate, $G_c$, to the dynamic storage modulus, $E'$. Higher values favor the development of fibrils.\textsuperscript{16, 17} $G_c$ is the energy need for the adhesive film to propagate interfacial crack deformation in a debonding process. $G_c$ is a complex function of both the bulk polymer energy dissipation rate ($\tan \delta$ in dynamic mechanical analysis) as well as the frictional properties and molecular interactions of the probe-film interface.\textsuperscript{18, 19} During the probe-tack measurement, the adhesive simultaneously undergoes an extensional deformation and shrinkage at the probe-adhesive interface.\textsuperscript{20, 21} The shrinkage of the adhesive will induce interfacial slippage and friction.\textsuperscript{21} The interfacial slippage has been found in the literature to increase with increasing chain mobility on the surface, e.g. the adhesive is likely to slip most on a flexible PDMS surface and least on a fluorocarbon surface, as PDMS has a low $T_g$ and high molecular chain mobility.\textsuperscript{21} The interfacial slippage will decrease the interfacial energy dissipation and consequently the adhesion energy.\textsuperscript{21}
Both steel and PP are considered to be hard surfaces without significant mobility at the atomic or molecular level. The different adhesion energy of nanocomposites with PVA or PVP at the interface on the steel and PP probes cannot be explained by differences in chain mobility. The surface energy of steel is around 0.5 J/m$^2$ and PP is around 0.02 J/m$^2$. Since PP has a low surface energy and is chemically inert, the later part of this work will focus on the relation between the viscoelastic properties and the energy of adhesion on PP probe, to minimize the possible effects from the high surface energy of steel probe.

Video images of the de-bonding process aid in the interpretation of the tack curves (Figure 3.6). During the de-bonding of the PP probe from pure latex, only a few rather coarse fibrils are seen to develop (Figure 3.7). The PVP-MWNT nanocomposite shows a high density of fine fibrils developing. The fibrils extend to more than twelve times the film thickness before debonding from the probe. The images show that the addition of MWNTs increases both the adhesive and cohesive strengths of the nanocomposite. Fibrils deform at a higher value of $\sigma_p$ and are more difficult to detach from the PP surface. The MWNTs thus have two key effects. They modify the viscoelasticity of the composite so that fibrillation occurs more easily and fibrils extend farther before debonding. Secondly, they strengthen the fibrils so that they require greater stress for deformation.

To explain the differences observed in the nanocomposites' adhesion, the dynamic mechanical properties of pure latex were obtained from tensile specimens at a frequency of 1 Hz, which lies within the range of strain rates in the tack experiments. As an indicator of the trend in $G'/\varepsilon'$, values of $\tan\delta E'$ obtained from DMA (Figure 3.8) are compared in Table 3.2. As in previous work, the nanocomposites are stiffer and more energy dissipative compared to the pure latex matrix. $\tan\delta E'$ increases in the identical order as the $E_a$ obtained with the four dispersants: TX < SDS < PVA < PVP, in line with theoretical expectations. The addition of the dispersant without MWNTs had a minor effect on adhesion.
Figure 3.6 Videos were obtained from the side view, as illustrated, during tack measurements at a velocity of 100 μm s⁻¹.

Figure 3.7 Video stills are shown for the PVP-MWNT latex nanocomposite and pure latex. Strain is increasing from top to bottom as indicated. The scale bar = 100 μm.
Figure 3.8 Dynamic mechanical analysis of tensile specimens versus temperature at a strain of 0.25% and a strain rate of 1 Hz for pure latex (—) and nanocomposites in which 0.015 wt % MWNTs are dispersed with SDS (—), PVA ($M_w=100$ kg/mole) (—), or PVP ($M_w=1,570$ kg/mole) (—), showing (a) storage modulus, $E'$ and (b) $\tan\delta$.

Table 3.2 Dynamic mechanical analysis and adhesion data of nanocomposites with differing dispersant materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tan\delta/E'$ (MPa⁻¹)</th>
<th>$E_a$ on PP (J/m²)</th>
<th>$\varepsilon_f$ on PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex alone</td>
<td>0.36</td>
<td>79</td>
<td>7.0</td>
</tr>
<tr>
<td>Latex with TX-MWNT</td>
<td>0.23</td>
<td>72</td>
<td>5.5</td>
</tr>
<tr>
<td>Latex with SDS-MWNT</td>
<td>0.26</td>
<td>84</td>
<td>7.5</td>
</tr>
<tr>
<td>Latex with PVA-MWNT</td>
<td>0.47</td>
<td>107</td>
<td>9.4</td>
</tr>
<tr>
<td>Latex with PVP-MWNT</td>
<td>0.56</td>
<td>134</td>
<td>12.6</td>
</tr>
</tbody>
</table>

92
The fact that $\tan\delta$ of the nanocomposites depends on the MWNT dispersant indicates that the interphase between nanotube and matrix influences the energy dissipation during deformation. These results illustrate why this type of nanocomposite is best considered as a three-phase material, consisting of (I) a stiff carbon filler, (II) a viscoelastic matrix, and (III) a dispersant that creates an interphase between the other two phases. Although present in small quantities, the interphase is very influential. In the DMA experiments, the local deformation at the MWNT-matrix interface will be large even though the macroscopic deformation is low. If there is easy interfacial slippage, there will be very little dissipation. On the other hand, if slippage is restricted by the interphase adhering to the MWNT and matrix, the process will be much more dissipative. Ideally, to obtain the greatest energy dissipation without sacrificing strength, there should be a sufficiently strong interface between the filler and the matrix to transfer the imposed stress but not so strong that it prevents any slippage. PVP offers the optimum stress transfer between the nanotube and the matrix, whereas the surfactants are apparently allowing easy slippage. A possible reason for this difference is the interfacial friction differences between the polymer and the matrix. This idea will be further explored in Chapter 4.

For glassy polymers it has been shown with theory and experiment that the strength of the interface can only develop if there is molecular entanglement. However, for interfaces with rubbery matrices (of interest here), the presence of entanglements increases the level of stress transfer while still allowing some interfacial slippage. This controlled interfacial stress transfer is an important mechanism for nanocomposite reinforcement in a rubbery matrix. An entangled interface ensures stress transfer to a filler and subsequent alignment in the stress direction but probably also introduces a dissipative mechanism through interfacial slippage. This idea is supported by molecular dynamics simulations, which predict that increasing the attraction between nanoparticles and a rubbery matrix results in greater energy being dissipated during tensile deformation. A lesson from the simulations is that when energy dissipation mechanisms are introduced, toughness can be increased without sacrificing strength.
3.3.3 Interfacial polymer $M_w$ tuning of nanocomposite adhesion

The polymer dispersants around the nanotubes will locate at the interface between the latex and the nanotubes. The latex particles contain 1 wt.% poly(acrylic acid) (PAA), which is a hydrophilic component that is known to be enriched near the particle surface. Hence, it is relevant to consider the miscibility between a poly(butyl acrylate-co-acrylic acid) copolymer and the MWNT dispersants. PVA and PAA are miscible over the entire range of compositions as a result of hydrogen bond formation. PVP and PAA are likewise miscible because of a combination of hydrogen bonding and ionic–polar interactions.

In experiments to explore the influence of interfacial bonding in the nanocomposites, the MWNTs were dispersed with PVA and PVP having $M_w$ values that approximately bracket the $M_c$. The $M_c$ values of PVA and PVP are ca. 6 kg/mole and 17 kg/mole, respectively. The total weight fraction of the dispersant is the same as in the previous experiments. The tack curves on PP probe in Figure 3.9 illustrate that when the $M_w$ of PVA and PVP are < or $\approx M_c$ (7.2 and 10 kg/mole, respectively), the adhesion characteristics ($\sigma_p$, $\epsilon_t$ and $E_a$) are only slightly greater in the nanocomposite PSAs compared to pure latex. When the PVA and PVP $M_w$ (being 35 and 29 kg/mole, respectively) are greater than $M_c$ by a relatively small margin, the adhesion characteristics of the nanocomposite PSAs are significantly higher and comparable to what was found with much higher $M_w$.

Table 3.3 shows that with increasing $M_w$ of the dispersant, $\tan\delta E'$ likewise increases. As SDS and TX are small molecules, they cannot form molecular entanglements to impart mechanical strength to the interface. Indeed, surfactants have been found to create weak interfaces between waterborne adhesives and adherents. These results support the notion that a high molecular weight polymer dispersant between the interphase and the latex matrix provide an efficient mechanism for greater energy dissipation (indicated by the higher $\tan\delta$).
Figure 3.9 The effect of dispersant molecular weight on PP tack curves is shown for latex (—) and (a) PVP: $M_w = 10$ kg/mole (—), 29 kg/mole (—) and 1,570 kg/mole (—); (b) PVA: $M_w = 7.2$ kg/mole (—), 35 kg/mole (—) and 100 kg/mole (—).

Taking the adhesion energies and $\tan \delta E'$ values from Table 3.2 and 3.3, one can find a correlation between them. As illustrated in Figure 3.10, a high $\tan \delta E'$ value is accompanied with a high adhesion energy, whereas a low $\tan \delta E'$ value is accompanied with a low adhesion energy. The adhesion energies of the nanocomposite adhesives can be adjusted by the extent of chain entanglement and molecular friction at the interface between the filler and the matrix.
Table 3.3 Dynamic mechanical analysis and adhesion data of nanocomposites with different molecular weight polymeric dispersants

<table>
<thead>
<tr>
<th>Material</th>
<th>Dispersant mol. wt. (kg/mole)</th>
<th>Tan δ/E' (MPa⁻¹)</th>
<th>E_a on PP (J/m²)</th>
<th>ε_f on PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex alone</td>
<td>--</td>
<td>0.36</td>
<td>79</td>
<td>7.0</td>
</tr>
<tr>
<td>Latex with PVA-MWNT</td>
<td>7.2</td>
<td>0.18</td>
<td>74</td>
<td>7.5</td>
</tr>
<tr>
<td>Latex with PVA-MWNT</td>
<td>35</td>
<td>0.43</td>
<td>101</td>
<td>8.5</td>
</tr>
<tr>
<td>Latex with PVP-MWNT</td>
<td>10</td>
<td>0.30</td>
<td>85</td>
<td>7.8</td>
</tr>
<tr>
<td>Latex with PVP-MWNT</td>
<td>29</td>
<td>0.44</td>
<td>111</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Figure 3.10 The correlation of the nanocomposite's adhesion energy with tan δE'.

To explain why σ_p is greatest in tack experiments with a high M_w PVP dispersant, the response under tensile deformation must be considered. Nanocomposite bars (10 mm long), with the various MWNT dispersants, were drawn in tension at a velocity of 5 mm s⁻¹, corresponding to an initial strain rate of 0.5 Hz, which is in the range used in the tack measurements. Figures 3.11 and 3.12 show the true stress-true strain (σ_t-ε_t) curves and normalized engineering stress-strain (σ-ε) curves, respectively. The engineering stress-strain has been introduced in Chapter 1.4.1. The true stress is defined as the ratio of the applied load (F) to the instantaneous...
cross-sectional area \(A\): \(\sigma, = \frac{F}{A}\). For incompressible materials, the relation of these two types of curves are \(\sigma, = \sigma(1 + \varepsilon)\) and \(\varepsilon, = \ln(1 + \varepsilon) = \ln \lambda\). During the extension, as the strain becomes large and the cross-sectional area of the specimen decreases, the true stress can be much larger than the engineering stress. A \(\sigma - \varepsilon\) curve is more suitable for elastic materials, while a \(\sigma, - \varepsilon,\) curve is more suitable for liquid-like materials, e.g. honey or oil.

![Figure 3.11 Influence of the dispersant type and molecular weight on the long-range tensile properties of the nanocomposites. True stress is plotted as a function of the true strain for pure latex (−) and MWNT-latex nanocomposites using (a) TX (−) and PVA dispersants with \(M_w\) of 7.2 (−), 35 (−) and 100 (−) kg/mole and using (b) SDS (−) and PVP dispersants with \(M_w\) of 10 (−), 29 (−) and 1,570 (−) kg/mole.](image)
Figure 3.12 Normalized engineering stress-strain curves of the same nanocomposites as in Figure 3.11.

It is observed in both Figures 3.11 and 3.12 that with an increase of the $M_w$ of the PVP and PVA dispersants, the stiffness increases, as seen in the higher gradient either the $\sigma_f - \epsilon_f$ or the $\sigma - \epsilon$ curves. The area under the curve increases with the dispersant $M_w$, meaning that the toughness is likewise increasing. The toughness of PVA-MWNT nanocomposites is two times greater than the latex matrix alone, whereas the PVP-MWNT toughness is greater by a factor of three, as calculated from the normalized engineering stress-strain curves and summarized in Table 3.4. To simplify the calculation and considering that the nanocomposite materials here are less liquid-like, the engineering stress-strain curves will be used to demonstrate the mechanical deformation properties of these soft colloidal nanocomposites.
Table 3.4 Toughness of nanocomposites with different MWNT diepersants

<table>
<thead>
<tr>
<th>MWNT Dispersant</th>
<th>Mol. Wt. (kg mol⁻¹)</th>
<th>Toughness (MJ m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No MWNT</td>
<td>---</td>
<td>1.7</td>
</tr>
<tr>
<td>SDS</td>
<td>0.288</td>
<td>2.2</td>
</tr>
<tr>
<td>TX100</td>
<td>0.625</td>
<td>1.9</td>
</tr>
<tr>
<td>PVA</td>
<td>7.2</td>
<td>2.7</td>
</tr>
<tr>
<td>PVA</td>
<td>35</td>
<td>3.0</td>
</tr>
<tr>
<td>PVA</td>
<td>100</td>
<td>3.5</td>
</tr>
<tr>
<td>PVP</td>
<td>10</td>
<td>2.9</td>
</tr>
<tr>
<td>PVP</td>
<td>29</td>
<td>3.6</td>
</tr>
<tr>
<td>PVP</td>
<td>1570</td>
<td>5.1</td>
</tr>
</tbody>
</table>

With the high-$M_w$ PVP in a 9:1 PVP:MWNT mass ratio, there are an estimated 3000 PVP molecules per nanotube. With lower-$M_w$ PVP, there are more PVP molecules per nanotube (at a fixed mass ratio), and so the grafting density increases. However, if the polymer dispersants are too short, they are ineffective in entangling with the matrix, or imparting enough interfacial stress and energy dissipation through molecular friction along the nanotubes. This idea will be extensively discussed in the following Chapter 4.

Taken together, these results provide an explanation for the adhesion experiments in Figure 3.5 in which the PVP-MWNT nanocomposites exhibit the greatest adhesion. The higher resistance to interfacial fracture (explained by the high $tan \delta E'$) promotes fibrillation. The higher stiffness and toughness of the PVP-MWNT fibrils (demonstrated in Figure 3.12), leads to the formation of fibrils at higher stress levels $\sigma_p$ that detach at a higher $\varepsilon_f$. In adhesives, a high stiffness normally causes fibril detachment at a lower $\varepsilon_f$. In the nanocomposites, the detachment at higher $\varepsilon_f$ can be attributed to the greater dissipation ($tan \delta$) slowing down the interfacial fracture and favoring fibril extension.
3.4 Conclusion

In summary, a colloidal processing method has been employed to disperse MWNTs finely in an acrylic matrix. At a low concentration of 0.015 wt.% MWNTs and with high molecular weight dispersant at the interface, the nanocomposite displays outstanding adhesion characteristics on a PP adherent. The adhesion energy is proportional to the $\tan \delta E'$ value, which is controlled by the dispersants at the matrix/nanotube interface. A high molecular weight polymer dispersant imparts a high $\tan \delta E'$, whereas a low molecular weight polymer dispersant or surfactant imparts a low $\tan \delta E'$.

A high-$M_w$ polymer – not a smaller molecule or surfactant - is required to strengthen the interface between a nano-filler and a soft polymer matrix. A high-$M_w$ polymer above its $M_c$ creates a pseudo-brush structure on the CNT that entangles with the matrix and imparts interfacial friction during stretching. It thereby increases the nanocomposite's stiffness, toughness and energy dissipation during deformation. Surfactants - although commonly used in the processing of waterborne nanocomposites - and low-$M_w$ polymer yield inferior properties because the entanglement or friction mechanism is not operative. In nanocomposites with a soft matrix, the dispersant $M_v$ provides a means to tune the energy dissipation, stiffness and toughness. This general concept can be applied to the design of a range of waterborne nanocomposite coatings, fibers, and adhesives to achieve the desired mechanical properties. The interfacial friction will be intensively studied in the next chapter.
References


Chapter 4

Interfacial strength and molecular friction in a soft polymer colloid/nanotube nanocomposite*

4.1 Introduction

It is well accepted in the literature on polymer composites that the interface between a fiber and the continuous matrix has a profound effect on the macroscopic mechanical performance. The more recent literature on polymer nanocomposites containing high aspect-ratio nanofillers (e.g. platelets, carbon nanotubes, and fibers) has been built upon the models of “classic” uniaxial composites. The models predict that the fracture mechanism and the ultimate strength and toughness of this type of nanocomposite depend on two key parameters: the filler length ($L$) and the interfacial shear strength ($\tau$) between the matrix and the filler (representing the stress at failure). A nanofiller will break during the deformation of the nanocomposite only when the stress transferred to it is larger than its fracture strength, as shown in Figure 4.1a. The stress transferred from the matrix depends on both $L$ and $\tau$. If the transferred stress does not exceed the filler's fracture strength, then the filler will pull out from the matrix when the stress level exceeds $\tau$, as illustrated in Figure 4.1b. The two key parameters can be adjusted by a chemical or physical means to tune the interfacial strength of the nanofillers to induce either a filler fracture mechanism or a filler

* Part of this chapter was published in Macromolecules. 2008, 41: 7656-7661.
pull-out mechanism. They therefore provide a tool for the design of the mechanical performance of nanocomposites.

![Nanofiller failure and Nanofiller pull-out](image)

**Figure 4.1 Nanocomposite failure mechanisms of a) Nanofiller failure and b) Nanofiller pull-out.**

There are a few examples in the literature that illustrate the importance of the interfaces between nanofillers and the matrix. For instance, spherical nanoparticles in glassy polymers are very effective in toughening the nanocomposite when there is high interfacial adhesion, obtained when the testing temperature is above the glass transition temperature \( (T_g) \) of the polymer matrix. In a second example, when polymers are grafted onto multi-walled carbon nanotubes (MWNTs) to impart miscibility with the matrix, the resulting efficient load transfer from the matrix to the nanotubes increases the mechanical properties, such as modulus, strength, ultimate strain and toughness. Additionally, a more effective interfacial stress transfer and a pronounced mechanical reinforcement have been achieved by using carbon nanotubes with a high density of polymer chains grafted onto them.

Although there is a general consensus that carbon nanotubes require surface treatments or chemical functionalisation to achieve good dispersability and compatibility with the matrix, the effects of the interfacial composition and structure on the resultant interfacial strength lack quantitative experimental studies. There has been greater emphasis on chemical modifications of the filler/matrix interfaces (e.g. covalent bonding) rather than on physical mechanisms, as will be presented here. A better understanding of how to control \( \tau \) may enable the bottom-up design of nanocomposites with desired properties.
This present work is partially inspired by previous studies of how polymer chains at interfaces influence fracture, adhesion, and friction. Kramer and co-workers systematically investigated the interfacial fracture strength of glassy polymer interfaces that are reinforced with miscible diblock copolymers. They measured the interfacial fracture toughness using the double cantilever beam method and studied its dependence on the copolymer degree of polymerisation, \( N \), and interfacial chain density, \( \Sigma \) (expressed as chains nm\(^{-2}\)). They found that the interfacial failure occurs by copolymer chain pull-out from the homopolymer when the \( N \) of each block is less than the value at entanglement (\( N_e \)). If \( N \) is above \( N_e \) but with a low \( \Sigma \), the failure is by chain scission, as the entangled chains break under stress rather than pull-out from the matrix.

The adhesion strength at interfaces between elastomers and polymer brushes grafted on solid surfaces is similarly affected by chain entanglements. The energy of adhesion increases with both the \( \Sigma \) and \( N \) of the brush. Furthermore, Brown’s pioneering experiments on the sliding friction between elastomers and grafted polymer chains on solid, planar supports found a strong dependence on the interfacial chain thickness. Later, other systematic studies showed that the friction stress between a tethered brush and an elastomer increases with \( \Sigma \).

Besides the chain density dependence, the friction of a polymer network along the surface of tethered chains also depends on the friction velocity. This velocity dependence comes from the penetration dynamics of the end-tethered chain into the polymer network. Research by Bureau et al. and Casoli et al. have determined the relation between the friction force per chain and the sliding velocity of the polymer network along the tethered chains.

Figure 4.2 shows a scheme for when a polymer network is sliding on a surface covered with penetrating grafted chains (\( N \) monomers of size \( a \) and grafting density \( \Sigma \)). Figure 4.3 illustrates the theoretical dependence of the friction force per chain on sliding velocity and the schematic view of the chain conformation for the different regimes.
Figure 4.2 Scheme of a polymer network slides along the surface with grafted polymer chains.

Figure 4.3 Theoretical dependence of the friction force per chain on sliding velocity and the schematic view of the chain conformation for the different regimes. Redrawn from Ref. 15.

Below a certain velocity $V_r$, the whole chain can relax in the elastomer network.

$$V_r = D_e / \tau_{\text{arm}}(N)$$  \hspace{1cm} (4.1)

with $D_e$ the mesh size of the network $D_e \approx a \sqrt{N_e}$ and $\tau_{\text{arm}}(N)$ the Rouse relaxation time of a chain with $N$ monomers of size $a$. 

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The force acting on a chain, \( F_{\text{frict.}} \), depends on the velocity \( V \) as:

\[
F_{\text{frict.}} = \frac{kT V}{D_e V_r}
\]  

(4.2)

where \( k \) is the Boltzmann’s constant and \( T \) the absolute temperature.

Above \( V_r \), the head of the chain is stretched in a straight tube of diameter \( D_e \) and only a tail of \( q \) monomers has time to relax and form a ball and penetrate into the rubber network. When the velocity increases, the ball will shrink and the stretched chains will grow until \( q \) is less than \( N_e \) (the repeat units between entanglements). The friction force is expressed as:

\[
F_{\text{frict.}} = \frac{kT}{D_e} + [N - q(v)]\xi V
\]  

(4.3)

In Eq. 4.3, the first term of the right-hand side is the force on the relaxed part of the chain, and the second term is the contribution by the Rouse friction of the stretched part. In this regime, the major part of the force comes from the relaxed ball part, and the stretched friction is minimal. While the friction per monomer in the ball increases with increasing velocity, the number of monomers decreases, resulting in an almost constant force per chain. This regime begins at a velocity somewhat smaller than \( V_r \) and finishes at \( V_s \) when the contributions of the friction of the ball and of the stretched part become comparable. \( V_s \) can be written as:

\[
V_s = \frac{D_e}{\tau_m N N_e}
\]  

(4.4)

where \( \tau_m \) is the monomeric relaxation time, and \( \xi_i \) is the monomeric friction coefficient.

In a velocity regime of \( V > V_s \), the whole chain has no time to relax and is mostly stretched, and there is mainly the Rouse friction with the polymer network. The frictional force per chain is linearly proportional to \( V \), such that:

\[
F_{\text{frict.}} = \xi_1 N V
\]  

(4.5)
This present work concerns nanocomposites made from multi-wall carbon nanotubes dispersed in a soft polymer matrix using a waterborne colloidal process.\textsuperscript{16, 17} To make these nanocomposites, the nanotubes are dispersed in water through the physisorption of a hydrophilic poly(vinyl pyrrolidone) (PVP). In the dry nanocomposite, PVP is then located mainly at the interface between the nanotube and the rubbery matrix. Our nanocomposite system can therefore be broadly described as a rubbery polymer in contact with polymer chains adsorbed on a curved surface of solid carbon. The macroscopic properties of the nanocomposite are determined, in part, by $\tau$. We report here a systematic investigation of the effects of the $\Sigma$ and $N$ of the interfacial PVP on the observed macroscopic mechanical properties of the nanocomposites. The results are analyzed through calculations of $\tau$. When interpreting the results lessons are learned and applied from the above work of the friction of rubbers sliding along polymer brushes on solid surfaces.
4.2 Materials and Techniques

4.2.1 MWNT-PVP aqueous dispersions

MWNTs (Nanocyl, Belgium) are reported by the manufacturer to have a purity level of 95% and were used as received. According to TEM image analysis shown in Chapter 3, the average length, $L$, of the MWNTs is 1.500 nm, the average diameter, $D$, is 20 nm, and the average inner diameter, $D_i$, is 8 nm. The MWNTs were dispersed in solutions of poly(vinyl pyrrolidone) (PVP, Sigma-Aldrich) in water. For all experiments, an initial MWNT concentration was fixed at 0.1 wt.% in water; various PVP concentrations were added, as desired, to achieve a range of interfacial chain densities. Various PVP molecular weight, $M_n$, fractions, namely 1 (1.2), 10 (2.7), 29 (5.2), 360 (5.4) and 1570 (5.3) kg mol$^{-1}$ (where the polydispersity index, $M_w/M_n$, is given in parentheses) were used to investigate the effect of chain length. The average degree of polymerization, $\bar{N}$, of the PVP thereby ranged from 9 to 14144. When investigating the effect of chain density on mechanical properties, PVP with a $M_n$ of 1570k was used while the PVP: MWNT ratio was varied.

MWNTs were added to aqueous PVP solutions, and the mixtures were sonicated for 10 min. using a sonic tip with output power of 20W (Branson Sonifier 150, Branson Ultrasonics Corp. Danbury, CT) followed by mild sonication for 30 min. in a sonic bath. During both sonications, the dispersions were chilled by immersion in ice water. Then the dispersions were centrifuged for 30 min. at 4400 rpm, and approximately 90% of the dispersion was collected as a supernatant of nanotubes dispersed in water. The supernatant collected after centrifuging at 4400 rpm contains MWNTs with adsorbed PVP chains on them and with free PVP chains in the solution. TEM analysis shows that MWNTs were, for the most part, homogeneously dispersed and de-bundled in the supernatant.
4.2.2 PVP chain density determination

To determine the amount of PVP adsorbed on the MWNTs, the supernatants were further centrifuged at 50,000 rpm for two hr. The MWNTs with adsorbed PVP chains were isolated at the bottom of the centrifugation tubes, and the free PVP chains in water were isolated at the top. The PVP solution was decanted off, and the MWNTs with adsorbed PVP were collected and dried. The weight ratio, \( w \), of adsorbed PVP to MWNTs was determined with thermogravimetric measurements in nitrogen (Q500, TA Instruments, New Castle, USA). In this analysis, dried solutions of PVP adsorbed on MWNTs were heated to a temperature of 800 °C, which is well above the temperature for the complete decomposition of PVP (600 °C), as reported previously.\(^1\) The mass loss attributed to the PVP decomposition was compared to the total mass and used to find \( w \). The number ratio, \( m \), of PVP:MWNT (i.e. number of PVP chains per nanotube) was then calculated for each dispersion, by modelling the MWNTs as cylinders with a mass density, \( \rho \), of \( 2.15 \times 10^6 \text{ g m}^{-3} \)\(^{18}\) in the expression:

\[
m = \frac{\pi \left( \frac{D}{2} \right)^2 L \rho_w}{M_w} N_A = \frac{\pi D^2 L \rho_w N_A}{4 M_w} \quad (4.6)
\]

where \( N_A \) is Avogadro's number. The areal number density of adsorbed PVP chains, \( \Sigma \) (chains nm\(^{-2} \)), was then found by considering the surface area of the outer wall, \( A_w \), of the MWNTs, expressed as:

\[
\Sigma = \frac{m}{A_w} = \frac{m}{\pi DL} . \quad (4.7)
\]

4.2.3 Nanocomposite preparation and measurement

To prepare nanocomposites, the free PVP was not removed from the dispersion, so as to maintain equilibrium between the adsorption and desorption of the dispersant on the nanotube surface. The MWNT dispersions were blended while stirring into a colloidal dispersion of poly(butyl acrylate-co-acrylic acid) (P(BuA-co-AA)), prepared
by emulsion polymerization, with material details described in Chapter 2.2.1 (Figure 4.4a). The polymer is lightly crosslinked so that there is a gel fraction of 30% The average particle size is 120 nm, and the $T_g$ of the copolymer is -50 °C. The surfaces of the particles are enriched in acrylic acid groups.

In all experiments, the volume fraction of MWNTs, $\phi_{MWNT}$, calculated on the polymer in the dry films, was $7 \times 10^{-5}$. (The volume of the adsorbed PVP is not included in the calculation of the volume of the MWNTs.) To check the mechanical effects of this free PVP which is not removed from the nanocomposite, the same amount of free PVP solution (i.e. the supernatants of the solutions centrifuged at 50,000 rpm for two hr.) were added to the latex to prepare latex/PVP dispersions for control experiments.

All colloidal dispersions were cast in poly(tetrafluoroethylene) molds and allowed to dry at room temperature for seven days. Interdiffusion occurs readily across the P(BuA-co-AA) particle/particle boundaries because of the very low $T_g$ and low level of crosslinking; particle coalescence creates a homogeneous matrix. Tensile specimens (10 mm x 1 mm x 1 mm) were cut from the dried nanocomposite layers. Tensile stress-strain measurements were obtained on an apparatus (Texture Analyzer, Stable Micro Systems Ltd., Goldaming, UK) with a constant strain velocity of 5 mm s$^{-1}$, corresponding to an initial strain rate of ca. 0.5 Hz. Three or more replicate experiments were performed for each $N$ and $\Sigma$ under investigation, and average values are reported here.

4.2.4 Interfacial strength determination

To study the interfacial strength, $\tau$, between a single nanotube and the matrix, a suitable technique must be devised to measure a single interface. AFM-assisted nanomechanics experiments have been employed elsewhere to measure the interfacial adhesion between single nanotubes and the matrix. In this work, $\tau$ is deduced from large-scale deformation of the nanocomposite, using the working hypothesis outlined below.
In classical models of conventional uni-axial fiber-reinforced composites that fail by fiber pull-out,\(^4\) the macroscopic strength is proportional to the interfacial shear strength between the fiber and the matrix. This model has been extended to nano-composites and applied to nano-sized fillers, such as platelets.\(^2\) For nanocomposites filled with nanotubes, Coleman et al.\(^3\) showed how the interfacial stress transferred to the nanotube scales with \(L\). A critical nanotube length, represented as \(L_c\), is predicted at which enough stress is transferred to the nanotube to break it. This length is expressed as:

\[
L_c = \frac{\sigma_{NT}}{2\tau} \left[ \frac{D}{D_i} \right]^2
\]  \hspace{1cm} (4.8)

where \(\sigma_{NT}\) is the nanotube strength (given in the literature as 50 GPa)\(^3\), \(\tau\) is the interfacial strength between the nanotube and matrix, \(D\) and \(D_i\) are the nanotube external and internal diameters, respectively.

When \(L>L_c\), the interfacial stress transferred to the nanotubes is large enough to break the nanotubes, and the composite failed by the failure of the nanotube as illustrated in Figure 4.1a. The relationship of composite strength and interfacial strength are summarized as the following.

If \(\frac{L}{L_c}>10\), the composite strength \(\sigma_c\) can be driven from the rule of mixtures as:

\[
\sigma_c = (\sigma_{NT} - \sigma_m)\phi_{NT} + \sigma_m.
\]  \hspace{1cm} (4.9)

If \(10>\frac{L}{L_c}>1\), the composite strength \(\sigma_c\) can be expressed as:

\[
\sigma_c = (\eta_s \sigma_{NT} - \sigma_m)\phi_{NT} + \sigma_m.
\]  \hspace{1cm} (4.10)

where \(\eta_s\) is the strength efficiency factor given as \(\eta_s = 1 - \frac{L_c}{2L}\).

In the case where \(L<L_c\), the stress transferred to the nanotubes is not sufficient to break them, and the failure of the nanocomposite thus occurs by the nanotube pulling out from the matrix as illustrated in Figure 4.1b. In this pull-out process, the failure is
controlled by \( \tau \). Composite materials with a weak interface have been found to have experimental values of \( \tau \) near 10 MPa.\(^{21}\) However, both computer simulation\(^{22}\) and experimental work\(^{23}\) have reported \( \tau \) values of around 100 MPa when there is strong covalent bonding at the interface. So as \( \tau \) varies between 10 and 100 MPa, \( L_c \) ranges between approximately 4 and 40 \( \mu \text{m} \). Thus, in our experiments in which \( L = 1.5 \mu \text{m} \), it is valid to assume that \( L < L_c \) even if \( \tau \) is considered to have a value at the upper limit. The composite strength \( \sigma_c \) can be obtained from a knowledge of the matrix strength \( \sigma_m \) using the standard expression:\(^3,4\)

\[
\sigma_c = (\tau \frac{L}{D} - \sigma_m) \phi_{XT} + \sigma_m. \tag{4.11}
\]

Measurements of \( \sigma_c \), coupled with measurements of the other parameters, thereby allowed us to calculate \( \tau \) by inversion of Eq. 4.11.

We note that Eq. 4.11 was derived through the extension of a model for uniaxial fiber-reinforced composites. The carbon nanotubes in our nanocomposites are not expected initially to be aligned parallel to each other. However, in the large strain regime, in which our experiments are conducted, nanotubes in a polymer matrix have been shown elsewhere\(^{24,25}\) to align in the direction of a tensile stress. Hence, we proceed in applying Eq. 4.11 after noting the underlying assumption in the analysis and treating it as a working hypothesis.
4.3 Results and Discussion

4.3.1 Effect of interfacial polymer chain density

There are several factors that can influence the mechanical properties of nanocomposites: matrix morphology, the extent of nanotube dispersion (or bundling), the interface type and structure, and the nanotube orientation. The matrix P(BuA-co-AA) here is in a rubbery state and unable to crystallize. Our calorimetry measurements clearly showed that the nanocomposites with the presence of MWNTs have no crystallization and the matrix is still amorphous. As illustrated in our previous work\textsuperscript{17}, MWNTs are de-bundled in the dispersion, and all of the nanocomposites show a similar uniform dispersion of MWNTs, regardless of the PVP chain lengths. The MWNTs in the matrix are randomly dispersed with similar aspect ratios, and there is no preferential orientation.

The effects of the incorporation of the free PVP chains in the preparation procedure were investigated through large-strain tensile deformation measurements. The concentration of the free PVP chains had no significant impact on the strength or toughness of the P(BuA-co-AA) films. The primary differences in the nanocomposites under investigation are the $\bar{N}$ and $\Sigma$ of the PVP dispersant chains, which are primarily localised at the interface between the MWNTs and the P(BuA-co-AA) matrix.

The P(BuA-co-AA) particle surface is enriched in AA, and PVP is miscible with AA.\textsuperscript{26} Plasticisation of the acrylic acid-rich chains by water might facilitate their extension and interpenetration with the PVP chains. The schemes in Figure 4.4c and 4.4d illustrate the PVP chains at the matrix/MWNT interfaces for two different $\bar{N}$ and $\Sigma$ values.
Figure 4.4 Schematic diagram of the preparation of the nanocomposites and the resulting interfaces. a) An illustration of PVP chains adsorbed on MWNTs dispersed in water blended with the colloidal P(BuA-co-AA) particles. b) Interfacial structure for a clean interface, which is not possible to achieve in the colloidal route of processing. c) Illustration of PVP chains with a high $\bar{N}$ at a MWNT/matrix interface at low $\Sigma$. d) Illustration of PVP chains with a low $\bar{N}$ at a MWNT/matrix interface at high $\Sigma$. There is limited miscibility between the PVP chains and the matrix.
Large-strain tensile deformation measurements revealed that the maximum strength of the P(BuA-co-AA) films is 0.14 MPa, which defines the value of $\sigma_m$ for subsequent calculations. This value of $\sigma_m$ was obtained from the maximum stress achieved on the stress-strain curve, as illustrated in Figure 4.5a. This same figure also compares the deformation of the polymer films to that of the nanocomposites having a constant polymer chain length ($\overline{N} = 14,144$) but varying $\Sigma$. The figure illustrates that with a higher $\Sigma$, the nanocomposite strength, $\sigma_c$ (defined as the maximum stress obtained during large-strain deformation) increases, and also greater strains are achieved before failure. Measurements of $\sigma_c$ are used to calculate values of $\tau$ through inversion of Eq. 4.11. The dependence of $\tau$ on $\Sigma$ is shown in Figure 4.5b. A linear relation between $\tau$ and $\Sigma$ is observed up to $\Sigma = 0.0045$ chains/nm$^2$. Thereafter, $\tau$ remains constant at a plateau value of 20 MPa. With more polymer chains at the interface, the interaction with matrix chain is increased and consequently the interfacial strength is raised. Above a critical chain density, however, the effect of $\Sigma$ levels off.

It is worthwhile noting that other studies$^{14,15}$ of macro-scale sliding at planar interfaces found that the friction stress likewise increased linearly with grafting density until reaching a critical value, above which the stress reached a plateau. Bureau and Léger$^{14}$ have proposed that at high $\Sigma$, the sliding friction is set by the rheology of the thin layer of interfacial chains. This idea provides a good explanation for the plateau of $\tau$ found for high $\Sigma$ in Figure 4.5b. We also note that a similar dependence on interfacial chain density was found in the interaction of diblock copolymer brushes at the interfaces in immiscible polymer blends.$^{9,10,11}$ When the $\Sigma$ became sufficiently large, the interfacial strengths were found to level off at a constant value. In Brown's experiments,$^{13}$ sliding friction was increased by thin brush layers (i.e. low $\Sigma$) but liquid-like behavior was found for thicker layers.
Figure 4.5 a) Tensile deformation of pure P(BuA-co-AA) and the nanocomposites with the same average chain length \((\bar{N} = 14,144)\) but different \(\Sigma\) (chains nm\(^{-2}\)) at the interface, as indicated in the legend. The engineering stress is plotted against the strain (change in length over initial length). b) The dependence of \(\tau\) on \(\Sigma\) for these same nanocomposites. The solid line is the best linear fit to the data.

### 4.3.2 Effect of interfacial polymer chain length

Figure 4.6a shows the large-strain tensile deformation of the nanocomposites with varying PVP chain length. Experimentally, it was not possible via the physisorption process to hold \(\Sigma\) perfectly constant while varying \(\bar{N}\), so there is some variation in both parameters. The quantitative dependence of \(\tau\) on \(\bar{N}\) was then
detected experimentally through analysis of the data. $\tau$ was normalized by $\Sigma$ so as to represent the average force provided per individual chain during the pull-out process. Underlying this calculation is an assumption that $\tau$ is negligible when there are no PVP chains at the interface between the nanotube and matrix. Experimentally, it is not possible to create such an interface, because the nanotubes require a dispersant to be suspended in water. However, surfactants are small molecules and hence will not entangle with the matrix nor create a high friction. Previously, we reported that $\sigma_c$ for nanocomposites prepared with surfactants is just slightly higher than $\sigma_m$, showing that $\tau \approx 0$ when the matrix is not sliding along polymer chains adsorbed at the interfaces. Hence, $F_{\text{fric}} \approx \tau \Sigma$.

Figure 4.6b presents experimental measurements of $F_{\text{fric}}$ obtained by varying $\bar{N}$. $F_{\text{fric}}$ is shown here to scale with $\bar{N}$ to a power of 1 (within the experimental uncertainty). On linear axes, the extrapolation of $\tau \Sigma$ to $\bar{N} = 0$ is very small (<2 pN). $F_{\text{fric}}$ is three orders of magnitude higher (on the order of nN) when $\bar{N} = 14.144$. This range of values of $F_{\text{fric}}$ is comparable to those found elsewhere\textsuperscript{9, 27} for the force per chain when the pull-out of diblock copolymer chains occurred at an immiscible polymer/polymer interface. Longer chains, above their $N_c$, were found to create entanglements on either side of the interface, which resist their easy pull-out. In this case, the failure occurs by chain scission. Values in the range of 1 to 3 nN have been reported experimentally\textsuperscript{9, 27, 28} as being required to break a C-C bond in a chain scission process. The range of $F_{\text{fric}}$ values found in the data in Figure 4.6b (except for the largest $N$) is thus lower than what is expected for a chain scission mechanism but is in line with the expected force of friction in a chain sliding mechanism, as will be shown hereafter.
Figure 4.6 a) Tensile deformation of the nanocomposites with various polymer chain lengths (measured through $N^*$) at the nanotube/matrix interface, as indicated in the legend. b) The dependence of the sliding force per interfacial chain on $N^*$. The solid line is the linear fit with a slope of 1.00 ±0.06.

In order for the PVP chains to sustain such relatively high forces, they must be attached strongly to the MWNTs. Molecular dynamics simulations using empirical force fields[29] offer some insight into the expected interaction energies solely due to van der Waals interactions between polymers and CNTs. The energy depends on the temperature and the nanotube diameter. The simulation for poly(styrene) (PS) on a nanotube with a 20 nm diameter (the same size as used in our work) finds an interaction energy of approximately 250 kJ/mole. Note that PS has some structural similarities to PVP. This energy level is below the covalent bond energy of a single
C-C bond, such as is found in the backbone of PVP, with a value of 360 kJ-mole.\textsuperscript{30} Hence, it is expected that the chains can support significant stress without pulling off of the MWNT surface but not enough stress to cause chain scission.

Recall from the introduction that, in the velocity regime where $V > V_s$, the whole chain has no time to relax, and it is mainly stretched. $V_s$ can be calculated using Eq. 4.4. The monomer size, $a$, can be estimated to be 0.5 nm. $N_e$, the number of repeat units between entanglements, is estimated to be 100 for the P(BuA-co-AA) matrix. The monomeric relaxation time $\tau_m$ is expressed as:

$$\tau_m = \xi_i a^2 / (3\pi^2 kT) \quad (4.10)$$

Here, $k$ is the Boltzmann constant, $T$ is the absolute temperature (300 K), and $\xi_i$ is the monomeric friction coefficient, which is the frictional force per monomer unit per unit velocity moving through a medium consisting of other polymer molecules. At the same temperature, $\xi_i$ is a function of both the geometry of the repeat unit and its chemistry.\textsuperscript{31} The $\xi_i$ for rubbery polymers is typically on the order of 50 nNs m\textsuperscript{-1} at room temperature.\textsuperscript{32} The corresponding monomer relaxation time, $\tau_m$, will be on the order of $10^{-7}$ s.

For PVP chains with $N = 3,243$ and 14,144, we estimate, using Eq. 4.4, that $V_s$ is 0.2 and 0.04 µm/sec, respectively. The local sliding velocity $V$ at the nanotube/matrix interface is taken to be 0.75 µm/sec (as estimated from the product of $L$ and the initial strain rate: 1.5 µm × 0.5 Hz). Thus, for $N = 3,243$ and 14,144, the sliding velocity $V$ is found to be larger than $V_s$.

When $V > V_s$, the sliding friction is attributed to the Rouse friction with the rubber network. The frictional force per chain is then linearly proportional to $V$, as in Eq. 4.5. This equation is applicable for the two higher $N$ and can be used to calculate the monomeric friction coefficient of PVP with the P(BuA-co-AA) matrix. We find $\xi_i$ to be on the order of 100 nN s m\textsuperscript{-1} in our nanocomposite. This value is reasonable, when compared to values obtained for other polymers with polar repeat units at a temperature above their $T_g$, such as poly(vinyl chloride) (30 nN sm\textsuperscript{-1} at 125 °C).\textsuperscript{31,32} This broad agreement provides some confidence in the validity of the data analysis.
(Of course, the friction in these experiments is between polar PVP units and units of butyl acrylate and acrylic acid and not between like units.)

Note that our argument presented here does not require the PVP chains to be fully miscible with the matrix. The theory for sliding friction at polymer/elastomer interfaces applies even when the pairs are weakly incompatible because of the intrinsic interpenetration width. Previous experimental work on the sliding friction of polymer melts has used end-grafted brush structures, but we expect friction effects at interfaces to be operative even if there is a loop-and-train structure of chains at the interface and limited miscibility with the continuous matrix. The basic principles are still valid.

The precise conformation of the PVP chains when adsorbed on the MWNTs is not known to us, but there are some recent coarse-grained Monte Carlo simulations that offer some needed insight. The simulation found that flexible chains (such as PVP) are less prone to helical adsorption (i.e. wrapping) in comparison to stiffer chains. Moreover, flexible chains show negligible overlap over the range of concentrations studied. The conformation of flexible chains adsorbed on larger radii was described as "cloud-like". These simulations suggest that there will be some extension of the PVP chains away from the carbon surface, and that they will not lie flat nor wrap.

4.3.3 Interfacial strength and macro-scale mechanics

A low interfacial strength will inhibit effective stress transfer. An improved interfacial strength will help to achieve full stress transfer from the matrix to the nanotube and will result in greater nanocomposite strength. Figure 4.7 shows the interrelationship between the nanocomposite's engineering toughness (which is determined from the area under the stress-strain curve) and the $r$ deduced from the macroscopic strength, as already explained. The toughness enhancement is apparent in these soft nanocomposites. As the matrix macromolecules are in the rubbery state and have high mobility, an increased interfacial strength allows the nanocomposites to
be deformed to a greater extent before fracture. The nanocomposites are therefore able to dissipate more energy, as previous results have revealed. 17 A similar correlation between Young's modulus and $\tau$ is also shown. The nanocomposites exhibit greater stiffness when there is more contribution from the nanotubes as a result of increased stress transfer. Although, in principle, stress transfer can be achieved by covalent bonding between nanofillers and the matrix, 34 our approach relies on a physical mechanism.

![Figure 4.7 a) The correlation of macroscopic nanocomposite toughness with the interfacial strength, $\tau$. b) The correlation of macroscopic nanocomposite Young's modulus with the interfacial strength. The solid line is the best linear fit to the data.](image)

Figure 4.7 a) The correlation of macroscopic nanocomposite toughness with the interfacial strength, $\tau$. b) The correlation of macroscopic nanocomposite Young's modulus with the interfacial strength. The solid line is the best linear fit to the data.
While the improvement of macroscale strength and modulus requires a strong interfacial strength, the toughness increase does not necessarily require a strong interfacial strength. A medium interfacial strength allowing as much as interfacial slippage to dissipate energy before failure is desired to increase toughness, as is the case here. We note that $\bar{N}$ and $\Sigma$ are important parameters in the design of nanocomposites of this type. Their values can be adjusted to increase the macroscopic mechanical properties of the nanocomposite. Even when the molecular weight polydispersity is somewhat broad, as was the case here, $\bar{N}$ has a significant impact on mechanical properties.

Our results also indicate that, in the limit of high velocity, the mechanical strength is a function of $\xi_i$. The value of $\xi_i$ can vary widely depending on the nature of the polymer, and hence the selection of the polymer dispersant on the nanotubes becomes an important design parameter. For instance, at a temperature above their $T_g$ (e.g. 398 K), polymers with bulky and stiff repeat units typically have a $\xi_i$ value on the order of $\mu$Nsm$^{-1}$, whereas others, e.g. polybutadiene, have values as low as a few pNsm$^{-1}$.$^{31}$

4.4 Conclusion

In a systematic study, we have demonstrated that the interfacial strength between carbon nanotubes and a soft polymer matrix increases with the chain length and density of polymer chains adsorbed at the interface. Longer chain lengths and higher chain densities both increase the interfacial strength and hence lead to an increased macroscopic strength (by a factor of two) and toughness (by a factor of three) in the nanocomposite. The observed increase in the interfacial strength is attributed to the sliding friction between the adsorbed dispersant chains and the matrix. These experiments thereby demonstrate a physical approach to improve the mechanical properties of nanocomposites, rather than one that relies on covalent bonding at the interfaces. The effect is quite forgiving of molecular weight...
polydispersity, and drawing from the results here, does not require monodisperse fractions.

The results lead us to propose that the monomer friction coefficient of the interfacial polymers is an important parameter that can be selected to tune the interfacial strength and hence the macroscale properties of nanocomposites of this type.
References


Chapter 5

Effect of pH on nanoscale and macroscale adhesive properties of acrylic colloidal films containing acrylic acid groups*

5.1 Introduction

Latex is an aqueous colloidal dispersion of polymer particles used as the building blocks for coatings and adhesives.1,2 Being waterborne, the materials offer a means of processing that does not emit volatile organic compounds into the atmosphere. Polymer colloids offer a distinct advantage over other classes of materials because they enable the structure to be tailored and controlled at the nano-scale. Particles can contain two or more phases and have a prescribed structure, such as core-shell. Upon the drying of mono-sized latex particles, a dodecahedral (honey-comb) structure3,4 is created in the film formation process5,6. The boundaries between the particles have an enormous area. The properties of the boundary region therefore can have a profound influence on the macroscale properties of latex films. For instance, the boundary region has been tuned by the interparticle crosslinking of the shells of core-shell latexes.7 The molecular interactions at the boundaries between latex particles influence the mechanical and adhesive properties of the resulting films.

In most latex applications, several monomers are incorporated into the polymer by copolymerization, in order to impart the desired properties. Acrylic acid or methacrylic acid is often used in both coating8 and adhesive9,10 formulations. These monomers’ carboxylic acid groups provide colloidal stability through electrosteric stabilization at higher pH values when they are positively charged. Carboxylic acid

* A paper based on this chapter has been submitted for publication.
(COOH) groups are hydrophilic and therefore acidic monomers tend to concentrate at the particle surface during emulsion polymerization, with the more hydrophobic monomers being localized within the particle cores. Upon film formation, the hydrophilic layer around the particle evolves into a continuous phase in which the hydrophobic cores are encapsulated.\textsuperscript{11}

Polymers or copolymers that have carboxylic acid groups are known to be pH responsive. The apparent pK\textsubscript{a} value (defined as the pH with 50\% ionization) of poly(acrylic acid) (PAA), which is of interest here, is ca. 5.8.\textsuperscript{12} When the pH < pK\textsubscript{a}, the carboxylic acid in PAA is undissociated, and it is known to be capable of participating in hydrogen bonding.\textsuperscript{13, 14, 15} When the pH > pK\textsubscript{a}, the groups are de-protonated to create negatively-charged COO\textsuperscript{−} groups. As the pH increases from acidic to basic, the carboxylic acid groups dissociate, leading to the loss of the hydrogen bonds accompanied by an increasing domination of ionic interaction.

The various types of possible interactions involving COOH are illustrated in Figure 1.\textsuperscript{14, 15, 16} At lower pH values, there is H-bonding between the COOH-rich particle surface and water. There can also be H-bonding between two particle surfaces in close contact. At higher pH values, counterions can form bridges between oppositely-facing COO\textsuperscript{−} groups.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.1}
\caption{Molecular interactions of P(BuA-co-AA) drying and dried latex films. (a) Hydrogen bonds between COOH groups and water molecules\textsuperscript{14}; (b) Dimers between COOH groups\textsuperscript{15}; (c) Lateral hydrogen bonds between COOH groups; and (d) Ionic interactions between COO\textsuperscript{−}/Na\textsuperscript{+} groups.}
\end{figure}

Extensive previous research has been carried out on high glass transition temperature ($T_\text{g}$) latex films ($T_\text{g}$ comparable to, or greater than, room temperature)
containing acrylic acid co-monomers for coating applications. The presence of the hydrophilic AA groups imparts colloidal stability in the wet state, and the interactions between the groups have pronounced effects on viscoelasticities of latex films.\textsuperscript{17, 18, 19}

For example, Richard et al.\textsuperscript{17} first investigated the effects of particle-particle interfacial interactions on the dynamic mechanical properties of the core-shell latex films. An ionic interaction between latex particles demonstrated higher modulus than that of hydrogen bonding interaction between particles. Later Rharbi et al.\textsuperscript{18} found that the latex films with their hydrophilic membranes reinforced with cations have high moduli and low deformations, compared with the films with weak membranes in acid states. Kan et al.\textsuperscript{19} also found that carboxylated latex film demonstrated a high modulus at a higher pH than a lower pH value.

Research by Winnik et al.\textsuperscript{20} found that the carboxylic acid groups in a hydrophilic copolymer, poly (butyl methacrylate-co-methacrylic acid (P(BMA-co-MAA)), have a significant effect on the polymer diffusion by affecting the water absorption in the latex films. The presence of 5 wt% of the methacrylic acid groups increases the diffusion coefficient by a factor of 5 at 60 °C, compared with a hydrophobic poly(butyl methacrylate)(PBMA). Upon neutralization of the carboxylic acid groups of P(BMA-co-MAA) with NaOH, the polymer diffusion was much retarded in dry films but greatly enhanced in wet films. Neutralization with NH\textsubscript{3} resulted in intermediate diffusion rates, between those of unneutralized and NaOH-neutralized P(BMA-co-MAA) films.

Acrylic latex films that are employed in pressure-sensitive adhesive applications must have a low $T_g$. Formulations often contain copolymers of AA. In a preliminary study on adhesives,\textsuperscript{21} it was shown that the pH value of a poly(butyl acrylate) latex containing methacrylic acid groups has an effect on the adhesive tack properties of the resulting latex films. However, no extensive studies of how the pH of a low-$T_g$ latex affects the molecular interactions and, in turn, the film drying, mechanical properties and adhesion have been reported. A systematic study of these relations will lead to a design principle for emulsion copolymerization for various applications.

This chapter considers a poly(butyl acrylate-co-acrylic acid) (P(BuA-co-AA)) latex, which is suitable as a model pressure-sensitive adhesive. The particle surfaces are enriched with PAA. We explore how the pH of the wet latex influences the molecular interactions in the dry films and how - in turn - these determine the mechanical and tack properties at both the nano-scale and the macro-scale.
5.2 Materials and Techniques

5.2.1 Materials

The P(BuA-co-AA) latex was prepared by emulsion polymerization, as described in Chapter 2.2.1. The average particle size is 120 nm and the $T_g$ of the copolymer is ca. -50 °C. The final solids content is 50 wt.%, and the gel content is 330%, according to Soxhlet extraction in tetrahydrofuran. The pH of the P(BuA-co-AA) latex dispersions, as-received, was 6.8. The pH was adjusted with the drop-wise addition of 1M HCl, 1M NaOH or 1 M NH₄OH solutions in water.

The fraction of the carboxylic acid groups at the surface of the particle was determined by conductometric titration. Because the latex was neutralized with ammonia just after it was synthesized, the ammonia was removed by devolatilization prior to the titration. In this procedure, the pH of the latex was adjusted to 10 with NaOH to shift the ammonium-ammonia equilibrium towards the ammonia. Once the sample was free of ammonia, HCl was added until a pH lower than 2 was reached. Then the sample was titrated with NaOH, which reacted first with the strong acids and then with the carboxylic acid groups. It was found that the amount of acrylic acid at the particle surface is 20% of the total acrylic acid in the formulation.

5.2.2 FTIR spectroscopy

FTIR spectra of dried free-standing latex thin films were obtained by using an FTIR spectrometer (Perkin Elmer system 2000 FTIR, Waltham, Ma., USA) from 500 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ from an average of 64 scans.

5.2.3 AFM force spectroscopy

Atomic force microscope (AFM) spectroscopy is an AFM based technique to measure, and sometimes control the polarity and strength of the interaction between the AFM tip and the sample.²²

During the last decade, AFM has been extensively employed to study intermolecular interactions between receptor and ligand, and intramolecular interactions forces in biological macromolecules like DNA, proteins and cells, mainly due its precision and sensitivity to probe surfaces in physiological environments with
molecular resolution and with forces down to the pico-Newton range. AFM is also a useful tool to characterize the mechanical properties of soft polymer materials such as: topography, elasticity and adhesive properties. We will employ AFM force spectroscopy to measure the particle deformation at the latex film surface and evaluate the particle interactions in the film cast from dispersions with different pH.

Latex films (ca. 50 μm thick) consisting of more than 400 particle layers were spin-cast onto freshly cleaved mica at 500 rpm. The nanomechanics of the surfaces were investigated by performing force spectroscopy experiments in contact mode using a commercial atomic force microscope (NTEGRA, NT-MDT, Moscow, Russia). The spring constant of the cantilever (NT-MDT, Moscow, Russia) was around 7 N m⁻¹. During the force spectroscopy measurement, the cantilever and the tip are moved in the vertical direction towards the surface using the piezo at a speed of 0.45 μm/sec. The AFM tip indented into the latex film under a normal force of ca. 4 nN and then was retracted away from the film with a constant speed of 0.45 μm sec. All experiments were performed at a room temperature of ca. 25 °C. Independent force spectroscopy measurements at different points along the same surface were obtained. Averages of 25 measurements are reported here.

The deflection of the cantilever (d(z)), the piezoelectric displacement (Z) and other signals, such as the amplitude or phase in dynamic AFM modes, can be recorded during the force spectroscopy measurement. The force spectroscopy result is a force-displacement curve (F-Z curve) with x-axis as the piezoelectric displacement (Z), and the y-axis as the force, F. The force is converted from the cantilever deflection d(z) and the cantilever spring constant k, following Hooke’s law:

\[ F = kd(z) \] (5.1)

The force spectroscopy measurement can be separated into the following stages as illustrated in Figure 5.2 on a latex film surface in air, with typical experimental F-Z curves shown in Figure 5.3.
Figure 5.2 Scheme of the vertical tip movement during the trace and retract parts of an AFM force spectroscopy experiment on latex film surface.

In stage I, the AFM tip is far away from the sample surface. There is no interaction between the tip and the sample surface. This stage finishes when the distance between the tip and the surface reaches a few microns, when there may be long-range electrostatic forces.

In stage II, the AFM tip will jump to contact with the sample when the tip is close to the surface within nanometers to atomic distances. This jump-to-contact, also referred to as “snap-in”, is caused by the short-range forces, e.g. van der Waals, capillary forces, DLVO/screened electrostatics (in aqueous solutions), chemical potential and magnetic forces. When the above attractive forces overcome the cantilever spring constant, the tip jumps into contact with the surface and this normally demonstrates a negative force in the force spectroscopy curve. This negative
force is more often found in ambient conditions rather than aqueous solutions. The force curve on a sample in liquid often shows a gradual increase in force, without the sharp onset of the interactions seen in air.\textsuperscript{33}

In stage III and IV, the separation between the cantilever base and the sample decreases further. The AFM tip indents into the surface with an indentation of $\delta$, and there is also a deflection of the cantilever ($d(z)$). The piezoelectric displacement, $Z$, is a combination of the cantilever deflection $d(z)$ and the indentation of $\delta$: $Z = d(z) - \delta$.\textsuperscript{27} The indentation equals the displacement when the force $F$ is zero, as illustrated in Figure 5.3. The indentation in Figure 5.3 is around 0.9 $\mu$m (i.e. 8 colloidal particles). Typical values of $\delta$ were less than 1 $\mu$m in this work. The maximum cantilever deflection $d(z)$, which can be roughly calculated from Eq. 5.1 by taking an maximum force of 200 nN and a spring constant of 7 N m$^{-1}$, is around 30 nm. Therefore, $d(z) \ll \delta$ in these experiments.

From the trace curve, the viscoelastic properties, e.g. Young’s modulus and stiffness, can be evaluated. The calculation of Young’s modulus is based on the Hertzian model of elastic contacts in Sneddon’s modification.\textsuperscript{34} Several formulas have been developed based on the shapes of the AFM tip to determine the elasticity of materials by AFM nanoindentation.\textsuperscript{35} In this work, the elastic modulus, $E$, of the surface of the latex films was extracted from the trace curves following a reasonable analytical approximation\textsuperscript{35} given as:

$$F = \frac{2 \tan(\alpha) E \delta^2}{\pi (1 - \nu^2)}$$

(5.2)

In Eq. 5.2, $\delta$ is the indentation depth, $\alpha$ is the half-opening angle of the cantilever tip (taken as 11° for tip used in this work), $E$ is the elastic modulus at the sample surface, and $\nu$ is the Poisson’s ratio of the sample, which is assumed here to be 0.5 for an incompressible polymer. In this work, the force at the maximum indentation, and the maximum indentation $\delta$ were used to calculate the modulus of the latex film surface by inversion of Eq. 5.2.

In stage V, the cantilever begins to retract from the surface. When the distance of the tip away from the surface is within atomic distances to nanometers, adhesion forces such as ligand-receptor, protein-protein interactions, DNA hybridization, and cell surface interactions can be measured.\textsuperscript{16}
In stage VI, the cantilever is deflected downwards, and the adhesion forces from the bulk deformation of the samples can be measured. For example, the stretching of single molecules attached between the tip and surface, protein unfolding, and the long-range deformation of soft polymer adhesives have all been studied. The force-distance (F-d) curve, which can represent the real deformation of the adhesive film, can be obtained by left shifting the F-Z curve along the horizontal axis with a distance of the indentation δ. The F-d curve extracted from the F-Z curve (Figure 5.3) is shown in Figure 5.4. The maximum distance until the tip detachment from these μm-scale thick films is identified in Figure 5.4 as \( d_{\text{max}} \), and is on the order of several μm for all samples. The separation force, \( F_s \), is defined as the maximum force obtained during the tip retraction. The trace and retraction curve are not overlapped, but there is a hysteresis. This is because that the deformation of the adhesive films in this work is on the microscale. Consequently when the piezo moves over a relatively large range, nonlinearity and hysteresis will occur.

![Figure 5.4 Force-distance (F-d) curves on an adhesive film in air.](image)

Adhesive analysis at the nano-scale by AFM force spectroscopy allows one to study the adhesion and deformation of single latex particles, particle monolayers, or multilayers. The force spectroscopy curve can also reflect both the tip-particle and the particle-particle interactions. In Figure 5.4, the F-d curve shows a rigid response at small distances (< 1 μm) until reaching a maximum separation force. Then the polymer yields with a continuously decreasing force until the release of the tip from the surface. With a high film thickness (>> 1 μm) in this work, the force curve demonstrates a monotonic shape in the final part of the retraction curve rather than a
step-like shape, as in previous reports in the literature on nano-scale thickness films.\textsuperscript{28, 29} Previous studies of latex deformation with nano-scale thickness showed a displacement of several hundred nanometers before the AFM tip detached from the latex particle surfaces.\textsuperscript{28, 29} Because the thickness of the latex films studied here was on a μm-scale, the AFM tip could deeply indent the films, and thus it was able to probe multiple latex particles during the retraction process and a μm-scale deformation was observed on thick adhesive films.

In stage VII, the AFM tip is far away from the surface and the connections are detached. Based on the deformability and the thickness of the samples, the detachment may occur after a distance from nanometers to a few micrometers.

5.2.4 Probe-tack analysis

Probe-tack adhesive analysis of latex films on glass plates followed the Avery method on a commercial apparatus (MicroSystems Texture Analyser, Godalming, UK) using a spherical, poly(propylene) probe. The latex film thicknesses were around 60 μm and were measured before each experiment. The probe was pressed into contact with the film under a load of 4.9 N for 1 second of contact before being retracted from the film surface at a constant velocity of 100 μm/sec, corresponding to an initial strain rate of 1.7 Hz. Films were cast at room temperature using a cube applicator and allowed to dry at 50 °C in the oven under flowing air for half an hour prior to analysis.

5.2.5 Macro-scale mechanical analysis

The latex dispersions were deposited in Teflon molds and allowed to dry for seven days before removing to obtain a thick (ca. 1mm) free-standing film. Tensile specimens (10 mm x 1 mm x 1 mm) were cut from the dried films. Tensile stress-strain measurements were obtained on a commercial instrument (Stable Micro Systems Ltd., Godalming, UK) with a constant strain velocity of 5 mm s\textsuperscript{1}, corresponding to an initial strain rate of ca. 0.5 Hz. Three replicate experiments were performed. To determine the energy dissipation rate and modulus, similar specimens were used for dynamic mechanical analysis (DMA, Q800, TA Instruments, New Castle, DE, USA) in tensile mode with a strain of 0.25° and a frequency of 1 Hz over
a temperature ranges from -80 °C to 50 °C. The frequency is comparable to the strain rate in the tensile and tack measurements.

5.2.6 Gravimetric analysis of film drying

Wet films were cast onto clean glass cover-slips (18 mm × 18 mm) with an initial wet film thickness of around 200 μm and immediately placed on a digital balance to study the gravimetric analysis of water loss during latex drying. The temperature within the balance was ~25 °C for all experiments, and the air above the sample was static. The room humidity was typically 40%. The weight of the sample was recorded every two minutes over a period of three hours. The room humidity was 40%, and the air above the sample was static.
5.3 Results and Discussion

5.3.1 FTIR of latex films

Figure 5.5 shows the FTIR spectrum of a dried film cast from as-synthesized latex with a pH of 6.8. The wavenumbers for the main bands are identified in the figures. To focus on the topic, only the bands assigned to hydrogen bonding or ionic interactions will be compared and studied for dry latex films cast from different pH dispersions.

![FTIR absorbance spectrum of dried films cast from as-synthesized latex with pH 6.8.]

In IR spectra in the literature for PAA in water, it has been reported that lateral hydrogen bonds between COOH groups, as illustrated in Figure 5.1c, have a characteristic stretching band that ranges between 1669 cm\(^{-1}\) and 1679 cm\(^{-1}\), depending on the concentration and the buffer.\(^{14}\) The stretching band of the COOH dimer (Figure 5.1b) is reported to be at 1712 cm\(^{-1}\), and the stretching band of free C=O is at 1739 cm\(^{-1}\).\(^{14}\) A band centered at 1542 cm\(^{-1}\) is assigned to the antisymmetric \(\nu_a (\text{COO}^-)\) stretching vibration of carboxylate groups.\(^{14}\)

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Figure 5.6 FTIR absorbance spectra of dried latex films cast from dispersions with differing pH as indicated in the legend for three different regions: (a) lateral COOH bond characteristic region; (b) free C=O stretching and COOH dimer regions; and (c) ionic interaction characteristic region. Spectra in 5.6a and 5.6c are shifted vertically for clarity.
Figure 5.6 illustrates the FTIR spectra obtained from dry P(BuA-co-A.A) films cast from dispersions with different pH values. These characteristic bands have several wavenumber shifts due to the different intermolecular interactions between different chemical components. In Figure 5.6a, the latex film cast at a pH of 4 shows a peak centered around 1672 cm\(^{-1}\), which is attributed to lateral H-bonds of COOH groups. This peak is stronger in comparison to the weaker peak in the latex film at pH 9.0, indicating the formation of more lateral hydrogen bonds in the latex film at pH 4.0.

A band centered around 1729 cm\(^{-1}\) is observed in all spectra in Figure 5.6c, and it is assigned to the free C=O stretch. This band is weaker in the film cast at a pH of 4.0, which indicates that the concentration of free C=O groups is lower in this film because parts of the groups participate in hydrogen bonding. Drawing on the literature, one would expect a band for the COOH dimers to appear in the region around 1712 cm\(^{-1}\). The asymmetry in the 1729 cm\(^{-1}\) band could be caused by the convolution with the COOH dimer band. In any case, there is no observable difference with changing pH.

Increasing the pH above the pKa value is expected to lead to the ionization of the carboxylic acid group. We attribute the band at 1542 cm\(^{-1}\) in Figure 5.6c to the presence of negatively-charged COO\(^{-}\) groups. The strength of this band increases as the pH increases from 4 to 9, which is consistent with the presence of more of these groups with their charge balanced by Na\(^{+}\) counterions.

These results reveal that the pH of the latex dispersion has an influence on the final bonding interactions in the dry films, which is consistent with the findings of previous research.\(^{17,18,19}\) At a pH of 4, the data indicate that H-bonding is dominant. At a pH of 9, adjusted by NaOH, there is some evidence for the formation of ionomers, in which the negative charge of the COO\(^{-}\) groups is balanced by the Na\(^{+}\) cations. Hereafter, the influence of the observed H-bonding and ionic interactions on the low \(T_g\) film properties is reported.

5.3.2 AFM force spectroscopy of latex films

Figure 5.7 shows representative \(F-d\) curves obtained from latex films cast at three pH values, and hence with varying levels of H-bonding or ionic interactions between particles. Good reproducibility of the force spectroscopy traces was found, which
indicates that patchiness in the coverage of surfactants at the film surface does not affect the nano-adhesive properties. There is no evidence for contamination of the tips during a series of force spectroscopy measurements.

![Graphs showing force-distance curves](image)

Figure 5.7 AFM force spectroscopy $F$-$d$ curves from latex films cast from different pH dispersions. (a) pH 4.0, (b) pH 6.8, (c) pH 9.0 adjusted with NaOH, and (d) pH 9.0 adjusted with NH$_4$OH.

Table 5.1 summarizes the nano-mechanical properties of the latex films presented in Figure 5.7. The reported values are the average of 25 traces. The elastic modulus ($E$) of the latex films are calculated from the processed $F$-$d$ trace curves using Eq. 5.2. The latex film with hydrogen-bonding interaction (pH of 4) shows an elastic modulus of 1.8 MPa, whereas the latex film with ionic interactions (pH of 9, adjusted by NaOH) exhibits a significantly higher modulus of 3.0 MPa. With hydrogen-bonding interactions between particles, the retraction curve shows an $F_s$ of around 300 nN and a $d_{max}$ of 5.5 μm. The $F$-$d$ curve of the latex film with ionic interactions, on the other hand, shows a higher $F_s$ of 380 nN but a shorter $d_{max}$ of only 2.5 μm. These results indicate that the contribution of the hydrogen-bonding interactions to the film stiffness
and cohesion at the surface is less than the contribution from ionic interactions. Greater extensibility is obtained with hydrogen bonding interactions.

An additional experiment was performed to determine the role of the counter-ion in determining the mechanical properties of the latex films. The pH was adjusted to 9 using NH₄OH. During the drying process, some NH₃ will evaporate, and so it is anticipated that there will be a lower concentration of counter-ions in the dry latex film. The $F_s$ of latex films pH-adjusted with NH₄OH is only 310 nN and is close to the 300 nN of latex films cast from a latex with a pH of 6.8. The ionic interactions are deteriorated and consequently there is depressed film cohesion.

Table 5.1 AFM force spectroscopy data of latex films cast from different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Maximum separation force, $F_s$ (nN)</th>
<th>Maximum distance, $d_{max}$ (µm)</th>
<th>Elastic modulus, $E$ (MPa)</th>
<th>Separation energy, $E_s$ ($10^{-13}$ J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>300±20</td>
<td>5.5±1.0</td>
<td>1.8±0.4</td>
<td>7.8±1.0</td>
</tr>
<tr>
<td>6.8</td>
<td>300±15</td>
<td>3.2±0.3</td>
<td>2.0±0.2</td>
<td>5.8±0.3</td>
</tr>
<tr>
<td>9.0 by NaOH</td>
<td>380±18</td>
<td>2.5±0.2</td>
<td>3.0±0.2</td>
<td>6.7±0.3</td>
</tr>
<tr>
<td>9.0 by NH₄OH</td>
<td>310±20</td>
<td>3.2±0.2</td>
<td>2.6±0.2</td>
<td>6.2±0.3</td>
</tr>
</tbody>
</table>

The separation energy ($E_s$) to retract the AFM tip from the latex film surface is proportional to the area under an $F$-$d$ curve. This energy is a function of the adhesion energy between the tip and the surface coupled with the energy required to deform the polymer. Table 5.1 shows that the film cast at a pH of 4 (dominated by H-bonding interactions) has the highest $E_s$ of around $7.8 \times 10^{-13}$ J. This greater separation energy is associated with a greater deformability (high $d_{max}$). The stiffer (high modulus) latex films obtained at higher pH values are less deformable and show an inferior $E_s$.

5.3.3 Macro-scale adhesion

The macro-scale adhesion of the latex films with different particle interactions was determined from probe-tack measurements. Three representative probe-tack curves are presented in Figure 5.8a for films cast from latex dispersions with a pH of
4.0, 6.8, and 9.0. The stress-strain curve of the latex with hydrogen bonding interactions (pH of 4) shows a much longer plateau compared with the adhesive made from a latex dispersion with ionic interactions (pH of 9). Consequently, the greatest adhesion energy is obtained. The length of the plateau indicates that the polymer has an appropriate viscoelasticity to allow the drawing of fibrils. It is not too stiff, and the stress level indicates that the polymer is not too liquid-like. The adhesive made from latex dispersion at a pH of 9.0, adjusted by NaOH, shows a very narrow shoulder rather than a plateau, and a lower adhesion energy. Fibrils are not drawn very far.

![Stress-strain curve and adhesion energy](image)

Figure 5.8 (a) Probe-tack stress-strain curves of latex films, and (b) Adhesion energy of the latex films as a function of dispersion pH values.

The adhesion energy as a function of the pH of the latex dispersions is summarized in Figure 5.8b. With hydrogen-bonding interactions (in the low pH
range). the adhesion energy is around 110 J m\(^{-2}\). When the latex pH is above the pK\(_a\) of PAA, the adhesion energy begins to drop, as ionic interactions start to contribute to the particle-particle interactions. With a further pH increase, the PAA groups at the latex particle surfaces are further ionized. This leads to a continuous decrease of the adhesion energy. At a pH of 9.0, adjusted by NaOH, the adhesion energy is around 50 J m\(^{-2}\). As a comparison, the adhesion energy of the adhesive films cast from a latex dispersion at a pH of 9.0, adjusted by NH\(_4\)OH, remains around 78 J m\(^{-2}\). An explanation is that the NH\(_4\)OH decomposed to NH\(_3\) and evaporated during the film drying process. Therefore, a counter-ion effect is not active in the film.

The trend in these macro-scale measurements of adhesion tack energy is consistent with the one observed in the AFM separation energy. Elsewhere, AFM nano-mechanical analysis on a soft latex also demonstrated that relatively weak interparticle junctions can improve tackiness.\(^{32}\)

A full explanation of these adhesion results requires further information about the macro-scale mechanical deformation and the viscoelasticity of the latex films. Tensile deformation and dynamic mechanical analysis was performed on films with the different particle interactions adjusted by pH.

The tensile deformation properties of the latex film, which were determined from thick film strips, are compared in Figure 5.9a. The latex film cast at a pH of 4 demonstrates the lowest elastic modulus (measured from the curve’s slope at small strains) and the greatest strain at failure. The latex film cast at a pH of 9 adjusted by NaOH (with dominant ionic interactions), however, has a much higher modulus with a smaller strain at failure. Previous work\(^{17,18,19}\) on the macro-scale deformation properties of high T\(_g\) latex films with different particle interactions also showed that ionic interactions lead to a more rigid response, compared to that of hydrogen-bonding interactions. The stress-strain curve of a pH 9 film adjusted by NaOH demonstrates some strain-hardening, while the pH 4 film demonstrates a strain-softening character after the yield point. Recall that the F-d curves from AFM force spectroscopy showed similar mechanical behavior. During the failure, the force degrades gradually over a long distance in the pH 4 latex, whereas the force falls abruptly at the maximum separation force in the pH 9 latex adjusted by NaOH. Hence, the macro-scale tensile deformation is consistent with the nano-scale deformation properties.
Figure 5.9 (a) Macro-scale tensile deformation of latex films cast at three different pH values as indicated in the legend. Temperature dependence of the (b) storage moduli, $E'$ and (c) tan $\delta$ obtained by dynamic mechanical analysis on the same materials.
As further evidence for the counterion effect, when NH$_4$OH was used to raise the pH, there is a negligible mechanical strengthening effect. The modulus, strength and maximum strain stay around the values for pH 6.8 film. When NH$_3$ evaporates, there is no cation bridge and the particle interactions are weak. Other research$^{38}$ also showed that the counterions in latex/clay nanocomposites had a decisive macro-scale mechanical effect originating from the interionic forces at the latex-clay interface.

The dynamic mechanical analysis of the various latex films is shown in Figure 5.9b and 5.9c. Table 5.2 summarizes the key dynamic mechanical parameters. The latex film with hydrogen-bonding interactions (pH of 4) has a low modulus (0.28 MPa) but a high tan δ. The pH 9 (NaOH) latex films, on the other hand, show the highest modulus (0.52 MPa) but an intermediate tan δ value. The modulus has a pronounced effect on the adhesive properties. As stated in the Dahlquist criterion$^{39}$, and demonstrated in experiments$^{40}$, a pressure-sensitive adhesive must have a modulus that is not too high. A modulus of 0.52 MPa, as reported above, is higher than the acceptable range and the materials are too stiff as pressure-sensitive adhesives.

Table 5.2 Correlation of the modulus of latex films from dynamic mechanical analysis and the macroscopic adhesion energies

<table>
<thead>
<tr>
<th>Latex pH</th>
<th>Storage modulus, E' (MPa)</th>
<th>Tan δ</th>
<th>Tan δ/E' (MPa$^{-1}$)</th>
<th>Probe-tack adhesion Energy (J m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.28</td>
<td>0.24</td>
<td>0.85</td>
<td>115</td>
</tr>
<tr>
<td>6.8</td>
<td>0.28</td>
<td>0.10</td>
<td>0.36</td>
<td>79</td>
</tr>
<tr>
<td>9.0 by NaOH</td>
<td>0.52</td>
<td>0.21</td>
<td>0.40</td>
<td>48</td>
</tr>
<tr>
<td>9.0 by NH$_4$OH</td>
<td>0.39</td>
<td>0.18</td>
<td>0.45</td>
<td>77</td>
</tr>
</tbody>
</table>

*Note*: Tan δ and E' were obtained at 20 °C.

The ratio of the tan δ over the storage modulus (E') of an adhesive can be used as a gauge of the adhesion energy. In general, the tan δ/E' value is proportional to adhesion energy of a pressure-sensitive adhesives.$^{40}$,$^{41}$,$^{42}$ The experimental ratio can be used to explain the adhesive results. The tan δ/E' ratio at room temperature of the pH 4 latex has the highest value (0.85), and it likewise has the highest adhesion
energy (110 J m$^{-2}$). The tan $\delta/E'$ value is higher when the pH is adjusted by NH$_4$OH in comparison to NaOH, which is consistent with the observed trend in adhesion energy.

The absolute values of the modulus from AFM nanoindentation and macroscale dynamical mechanical analysis are different, but they are on the same order of magnitude and demonstrate the same trend caused by the different interactions. Eq. 5.2 applies to the indentation experiments performed with a conical tip. If the shape of the tip is less sharp, for example, a parabolic or hyperbolic shape, different formulae should be applied to calculate the elastic modulus.\textsuperscript{35}

### 5.3.4 Rate of water loss

Both AFM nanomechanics and macroscale probe-tack measurements show that a low pH with hydrogen-bonding gives the highest debonding energy (as indicated by the separation energy and the tack adhesion energy, respectively). It is necessary to evaluate the film formation process of the latex at various pH values to determine the feasibility of using the low pH latex in an application.

![Figure 5.10 Gravimetric analysis of water loss from latex films at different pH values](image)

Figure 5.10 shows the water fraction as a function of the normalized drying time for the dispersions of the P(BuA-co-AA) from pH 4, 6.8, 9 by NaOH and 9 by NH$_4$OH. To take into account small variations in the film thicknesses, the drying time has been normalised by the initial film thickness. Until a normalized time of 0.1, each of the four latex loses water at the same rate. During this early stage of drying, there is the free evaporation of water. At longer times, when there is less than 20 wt.% water
and the polymer particles are in close contact, the rate of water loss slows in the latex at a pH of 4. A possible explanation is the predominance of H-bonding interactions (as illustrated in Figure 5.1a) that bind with the water at the particle boundaries. These restricted water molecules evaporate much more slowly, and the latex film therefore takes a longer time to reach the dry stage.

These results on drying can also be considered in the light of previous research on water uptake by high-$T_g$ latex films that contain carboxylic groups. Dry latex films that contain methacrylic acid$^{20}$ or acrylic acid$^{18}$ have been shown to absorb a larger amount of water (from vapour or liquid) when neutralized with NaOH rather than when in the acid state containing COOH. These results were attributed to the greater hydrophilicity imparted by ion clusters between COO$^-$ and Na$^+$. These observations suggest that the boundaries between particles in neutralized latex films remain intact and create a pathway for water transport. As such, in the drying process observed here, water loss is not impeded. Greater hydrophilicity at the particle boundaries is thereby expected to aid drying.

5.4 Conclusion

The effects of pH on the film drying, mechanical and adhesive properties of a poly(butyl acrylate-co-acrylic acid) latex film have been investigated. FTIR spectroscopy confirms that hydrogen bonds are formed by PAA carboxylic acid groups in the dried films cast at pH values lower than the pKa of PAA, whereas ionized carboxylic acid groups are present in films cast at a pH above the pKa.

Macro-scale tensile deformation and nano-scale AFM force spectroscopy show that hydrogen bonds in the dried latex film do not affect the elastic modulus but increase the extension before failure. On the other hand, ionic interactions impart a higher modulus and lower deformability in the dry films. The trends in the nano-mechanical properties are consistent with the observed macro-scale adhesive properties.

Probe-tack measurements illustrate that latex films from low-pH dispersions are more deformable and have a higher adhesion energy compared to films cast from high pH dispersions. The adhesion energies of films cast at the various pH values can be explained by the bulk dynamic mechanical properties, using $\tan \delta E'$ as a criterion.
Latex films cast at a pH of 4 have a lower $E'$ but a higher tan $\delta$, whereas latex films cast at a pH of 9 have a higher modulus but an intermediate tan $\delta$.

Although a low pH of the latex leads to a higher adhesion energy, it is relevant to note that the drying rate is slower, probably because water is trapped by hydrogen bonding with the acrylic acid groups. If fast drying is required for manufacturing, then a compromise might be found by raising the pH closer to the $pK_a$. 
References

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Chapter 6

Summary and potential future work

6.1 Summary

The current work has fabricated various soft colloidal nanomaterials from polymer colloids, or colloidal blends with carbon nanotubes, via horizontal deposition of the colloidal dispersions. A specific interest here is employing these soft colloidal nanomaterials as pressure-sensitive adhesives. The microstructures and various properties, e.g. viscoelasticity, mechanical properties, electrical conductivity, thermal conductivity and optical transparency, were investigated. The various properties are correlated with the microstructures and the interactions between colloid-nanotube and colloid-colloid interfaces. Various models were employed to interpret the results.

The nanotube bundles, resulting from short range van der Waals attraction forces, were overcome by steric-stabilization of various surfactants and water-soluble polymers on the nanotube surfaces, via either chemical-functionalization or physisorption methods. Various stable nanotube aqueous solutions were obtained with debundled nanotube structures determined by AFM and TEM. These well-debundled nanotubes provide the necessary uniform dispersion of nanotubes in the matrix, which is the first step to fabricate polymer nanocomposites with improved properties.

In Chapter 2, the colloidal polymer nanocomposites made of single-walled carbon nanotubes (SWNTs) and soft latex were shown to achieve high adhesion energy, electrical and thermal conductivity while retaining optical clarity. The viscoelasticity and large-deformation properties of the colloidal nanocomposite in the presence of the SWNTs were determined by DMA and tensile testing. Their
influences on the adhesive properties were discussed using $E_a \sim \frac{h\sigma^2}{Y}$ and $E_a \sim \frac{\tan \delta}{E'}$. The electrical percolation threshold was found to be between $0.02-0.03$ wt% SWNTs, with conductivity comparable to germanium on the order of $1$ S/m after the percolation threshold. The thermal conductivity likewise increases with increasing SWNTs, with an $80\%$ increase with the presence of $0.1$ wt % SWNT. Model fitting illustrates that the bulk thermal conductivity of the nanotubes has a negligible effect, whereas the interfacial thermal resistance and volume fraction of the SWNT have a bigger influence on the thermal conductivity improvement.

As various water-soluble nanotube aqueous solutions can be fabricated with various dispersants to impart steric-stabilization, there is a wide choice of the interface between the nanotube and the matrix. In Chapter 3, these differences in the interface were found to have a big influence on the viscoelasticity and mechanical properties of the colloid/MWNT nanocomposites and the consequent adhesive properties. A high-$M_w$ polymer — not a smaller molecule or surfactant — is required to strengthen the interface between a MWNT and a soft polymer matrix. A higher value of $\tan \delta E'$ was obtained for the nanocomposite with a high-$M_w$ polymer at the nanotube/matrix interface. The adhesion energies were found to be proportional to the $\tan \delta E'$ values, consistent with the scaling theory prediction of $E_a \sim \frac{\tan \delta}{E'}$.

The importance of the interface at a soft polymer/nanotube interface on the interface strength and macro-scale properties was extensively discussed in Chapter 4. The interfacial strength, $\tau$, was deduced from a nanofiller pull-out model for uniaxial fiber-reinforced composites. The interface strength as a function of interfacial polymer (PVP) chain density ($\Sigma$) and chain length ($\bar{N}$) was systematically investigated. The friction force contributed by individual polymer chain was obtained by the interface strength normalized by polymer chain density, $\tau\Sigma$. It was found that the interfacial strength $\tau$ increased with $\Sigma$, but then leveled off above a critical value. The interfacial friction force provided by individual polymer chain increased with
increasing chain length. The interfacial friction discussion drew upon the molecular friction of the adsorbed polymer chains sliding along the rubbery polymer matrix. The monomeric friction coefficient of PVP with the latex matrix, $\xi$, was found to be on the order of 100 nN s m$^{-1}$ in these nanocomposites. The macro-scale material strength and toughness increased with increasing interfacial strength. The results can be used to guide the interfacial design of polymer nanocomposites to obtain ultimate macroscopic mechanical control.

In Chapter 5, another colloidal nanomaterial system without the presence of the carbon nanotubes was investigated. The colloidal nanomaterial’s molecular interactions were tuned by pH values of the latex dispersions, with 1 wt% pH-responsive PAA groups enriched around the latex particle surface. The molecular interaction between individual particles were confirmed by FTIR, with hydrogen-bonding interactions in the dried film cast from acidic latex suspensions, and ionic interactions in the dried film cast from basic latex dispersions. AFM force spectroscopy, which can perform nano-indentation, illustrated that the colloidal nanomaterials are soft and more deformable with hydrogen bonding interactions between the colloidal particles, whereas the nanomaterials are stiff and less deformable with ionic interactions among the colloidal particles. These nano-scale deformation characteristics are consistent with the macro-scale probe-tack analysis, which showed that colloidal nanomaterials with hydrogen bonding interactions are soft and more deformable, and dissipate more energy. Colloidal nanomaterials with ionic interactions are too stiff to be used as high-performance adhesives.

This work concludes that the interfacial control of the building blocks of the colloidal nanomaterials play an important role in determining the macro-scale properties. With careful control, nanomaterials with the presence of different phases can work together as multifunctional materials.
6.2 Potential future work

In Chapter 4, it has been deduced that the friction between the matrix molecules and the polymers physisorbed on the carbon nanotube surface contributes to the interfacial strength. The friction depends on the polymer chain length $N$, friction velocity, $V$, and monomeric friction coefficient $\xi_1$. At the same temperature above the $T_g$, the monomeric friction coefficient is a function of both the geometry of the repeat unit and its chemistry. Molecules such as PS and PMMA, which possess stiff, bulky repeat units, have high monomeric friction coefficients of 2900 and 53000 nN sm$^{-1}$ respectively, at 125 °C. On the other hand, molecules such as PDMS and polybutadiene made up of flexible, less bulky repeat units, possess quite low monomeric friction coefficients of 2.2 pN sm$^{-1}$ and 16 pN sm$^{-1}$, respectively, at 125 °C. Molecules such as poly(vinyl chloride) and poly(vinyl acetate), which possess compact polar repeat units that can interact via strong dipole-dipole secondary bonds, are typically intermediate between these two, with PVC of 27 nN sm$^{-1}$ and PVAc 1.1 nN sm$^{-1}$, at 125 °C. Polymers with different molecular weight and monomeric friction coefficient can be chosen to design the nanocomposite interface to adjust the interfacial strength, where a low interfacial strength for damping or high interfacial strength for strengthening is desired.

By introducing an energy dissipation mechanism into the colloidal nanocomposite system, the nanotubes have been found to increase the macro-scale energy dissipation, $\tan \delta$. However, it has been demonstrated that the incorporation of the nanotubes also increases the elastic moduli of these soft colloidal nanomaterials. As a result of high elastic modulus at high nanotube content, the materials become stiff and out of the range to be effective adhesives. The wetting ability of the nanocomposite film on an adherent is deteriorated as a result of the enhanced stiffness, and finally the adhesion energy is decreased at very high nanotube concentrations. For a further increase of the adhesive adhesion energy at high nanofiller concentration, a colloidal nanomaterial system which can increase the energy dissipation rate but does not increase the elastic modulus of the materials needs to be found. Soft core-hard shell
hybrid colloidal particles show some potential in this direction. These soft hybrids are constituted of low $T_g$ polymer colloids armored by well-dispersed nanofillers in the shell, e.g. nanotubes or nanoclays. One method to prepare these soft hybrids is by Pickering polymerization, with the monomers forming emulsion droplets stabilized by the nanotubes or nanoclays, and then polymerized to form polymer core-inorganic shell hybrids.\textsuperscript{2, 3} Another method is by hetero-flocculation of various nanofillers onto soft polymer colloids by opposite charges, hydrogen bonding and other interactions or reactions.\textsuperscript{4} The deformation ability of the soft polymer core upon mechanical stretching can increase the nanofiller mobility and alignment, consequently increase the energy dissipation rate.\textsuperscript{5, 6} While the mixing effect of soft polymer colloids and the hard nanofillers could make the elastic moduli of these hybrids low. The incorporation of this type of soft hybrids might be able to overcome the elastic modulus increase at high nanofiller concentration. It shows promise for high-performance nanocomposite adhesives and deserves future investigation.
References


