

SIXTH FRAMEWORK PROGRAMME



Contract No. 505442 (NMP3-CT-2004-505442)

NsHAPe

**Designed Nanoscale Heterogeneities for Controlling
Water-Borne Pressure-Sensitive Adhesive Performance**

SPECIFIC TARGETED RESEARCH PROJECT

Nanotechnologies and Nano-Sciences, Knowledge-Based Multifunctional
Materials and New Production Processes and Devices (Priority 3 - NMP)

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Part 1: Background to the NsHAPe Project and Contractors

1 INTRODUCTION AND GENERAL OBJECTIVES

The NsHAPe project addresses needs of the European pressure-sensitive adhesive (PSA) industry, which makes an important contribution to Europe's economy and encompasses chemical suppliers, polymer producers, coating companies and end-users. Environmental and health restrictions on emission of organic solvents from industrial processes have driven development of water-borne PSAs (wb-PSAs), which are based on colloidally-stable aqueous dispersions (*latexes*) of polymer particles with diameters of 100-400 nanometres (one hundred-thousandth to four hundred-thousandths of a millimetre) and whose composition, internal structure and surfaces can be controlled on dimensions of a few nanometres during synthesis. Due to their socio-economic benefits, there is an increasing demand for wb-PSAs in high performance applications, particularly in the healthcare, aerospace and automotive, construction and assembly, and data tracking industries. A major problem for the PSA industry is that, in comparison to solvent-cast materials, wb-PSAs suffer limitations in adhesive strength and in their ability to bond to non-polar substrates. Thus the overall objective of the project is to establish, through fundamental research, strategies by which the performance of wb-PSAs can be controlled so that these limitations can be overcome. The knowledge gained will inform development of industrial-scale processes and prototypes for high-performance, commercially-viable wb-PSAs and will be transferable to other types of water-borne coatings materials such as paints, lacquers and inks.

2 PROJECT ORGANISATION AND CONTRACTORS

The technical research and development programme was divided into four distinct, but interrelated technical workpackages:

Workpackage 1: Latex Synthesis and Characterisation

Workpackage 2: Adhesive Film Formation and Characterisation

Workpackage 3: Adhesive Testing and Evaluation

Workpackage 4: Evaluation of Technical Feasibility

In addition, there was *fifth workpackage* which concerns Project Management and Assessment.

The academic and industrial participants were drawn from four European countries and provided complementary expertise in polymer synthesis, film characterisation, adhesive testing and industrial processing.

The University of Manchester, United Kingdom

Acronym: UMan

Responsibilities: Project Co-ordinator
Leader of Workpackages 1 and 5
Research on Workpackages 1 and 3

UMan was created on 1 October 2004 by the merger of two leading and long-established UK universities: the Victoria University of Manchester (which originated in 1851) and the University of Manchester Institute of Science and Technology, UMIST (which originated in 1824). The project work was performed in the Materials Science Centre of the School of Materials which achieved the maximum 6* rating for the quality of its research in the most recent (2001) UK Research Assessment Exercise. Peter Lovell, a Professor of Polymer Science, led the research at UMan and also was the overall project coordinator. He has extensive experience of controlled synthesis of polymer latexes by emulsion polymerisation and research into wb-PSAs.

The University of Surrey, United Kingdom

Acronym: UniS

Responsibilities: Leader of Workpackage 2
Research on Workpackage 2

UniS is one of the UK's leading professional, scientific and technological universities and was placed fifth in the UK higher education sector for the quality of its research in the 2001 UK Research Assessment Exercise. The project work was carried out within the Soft Condensed Matter Group of the Department of Physics which has a strong international reputation for its research, as confirmed by its Grade 5 rating in the 2001 UK Research Assessment Exercise and award of the 2001 and 2007 Roon Award for outstanding papers by the Federation of Societies for Coatings Technology. The project research was led by Dr. Joseph Keddie, who is a recognised expert in the study of latex film formation and received the Institute of Physics Paterson Medal and Prize in 2001 for his contributions to this field.

Ecole Supérieure de Physique et Chimie Industrielles, France

Acronym: ESPCI

Responsibilities: Leader of Workpackage 3
Research on Workpackages 2 and 3

ESPCI is a higher education and research institution located in Paris and is part of the French 'Grandes Ecoles'. It has been one of the foremost French research institutions in the fields of physics and chemistry for more than a century, being home to two Nobel prize winners in physics in the last 15 years. The project research took place in the Laboratory of Macromolecular Physics and Chemistry under the direction of Dr. Costantino Creton. He has an international reputation in the area of mechanical properties of polymer interfaces for innovative work in correlating molecular structure at the interface with its mechanical strength, particularly for PSAs.

Cytec Surface Specialties, Belgium

Acronym: Surfs

Responsibilities: Leader of Workpackage 4
Research on Workpackages 1, 3 and 4

Surfs is focused on manufacture of technically-innovative and environmentally-friendly products and solutions for surface applications. The company has manufacturing capabilities and R&D centres for solvent- and water-borne PSAs located throughout the world and is now the world's leading supplier of raw materials for several different categories of eco-friendly coating technologies, such as radiation-cured coatings, water-borne coatings and powder coatings. The R&D centre at Drogenbos in Belgium is one of the major research centres within the company and was the location for the project research which has been led successively by Dr. Steven van Es, Dr. Olivier Dupont and Dr. Keltoum Ouzineb, all of whom have extensive experience of wb-PSAs that spans laboratory synthesis of latexes, adhesive formulation and testing, product development and scale-up in close collaboration with customers.

UPM Raflatac, Finland

Acronym: Raflatac

Responsibilities: Research on Workpackages 3 and 4

Raflatac is one of the world's leading suppliers of paper-based and synthetic self-adhesive labelstock on reels and on sheets with manufacturing facilities in many locations around Europe and the rest of the world. Company R&D is mainly focused into the site at Tampere in Finland which enjoys a good working relationship with Surfs for joint development of PSAs. Raflatac's commitment to finding environmentally-sound solutions has resulted in new proprietary production technology and the replacement of solvent-based adhesives with water-borne alternatives. Environmental management is now a top corporate priority for Raflatac and a benchmark for the whole industry. Work on the project was carried out at Tampere and led by Mr. Ismo Pietari, the R&D Director, who has responsibility for Raflatac's research and long-term development and provides a large skills and knowledge base in the use of water-borne materials and environmentally-benign technologies.

3 PROJECT COORDINATOR CONTACT DETAILS

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4 EXECUTIVE SUMMARY OF PROJECT WORK AND ACHIEVEMENTS

Workpackage 1 Industrial and laboratory benchmark latexes were defined, synthesised and characterised. Methods for controlled synthesis of a range of different types of PSA latex were established and used to prepare a large number of new PSA latexes, the most promising of which were supplied to project partners for evaluation. Some of the original strategies for enhancing pressure-sensitive adhesive performance did not yield useful results and so further work on latex synthesis for these strategies was terminated in Months 16 and 20. As a consequence, latex synthesis work was focused on different types of core-shell latexes and, to a more limited extent, latexes designed for promoting the strength of interfaces with substrates and for investigating water-whitening of adhesive films. Over the duration of the project, more than 100 latexes with systematic variations in key parameters have been prepared, characterised and supplied to partners for further evaluation under one or more of Workpackages 2–4.

Workpackage 2 Optimum conditions for atomic force microscopy (AFM) of wb-PSA films were determined and used to identify the 'fingerprint' morphologies of the benchmark latexes and to provide important information on the morphology of films formed from the new wb-PSAs. Surface and cross-sectional nanostructures, including the distribution of surfactant, were determined for the most promising latex films using AFM and secondary-ion mass spectroscopy surface mapping. Force spectroscopy mapping revealed the extent of nanoscale phase separation within adhesive films. The new insights into segregation of particles and information on heterogeneities in the structure of individual latex particles and in wb-PSA films helped to guide the forward latex synthesis strategy. The latex characteristics required to achieve fast-drying and low water-whitening were established using magnetic resonance imaging combined with measurements of optical transparency.

Workpackage 3 Standard adhesive test methods were defined and key adhesive test methods established for screening of new wb-PSAs developed at Surfs and UMan. Adhesive testing of the benchmark latexes provided benchmark adhesive performance profiles for the project. Analytical probe test methods in tension and shear were implemented at ESPCI and provided crucial information on the key parameters that need to be controlled in order to optimise adhesive performance. Measurement, modelling and analysis of non-linear deformation led to a full evaluation of the effects of shell crosslinking has provided a better understanding of adhesive properties at the molecular scale and identification of criteria for achieving an optimal balance of cohesion and deformability in the adhesive films. These results guided the forward latex synthesis work throughout the project. Predictive mathematical modelling of the mechanical behaviour of the films formed from the core-shell latexes has been achieved.

Workpackage 4 As planned at the outset, three prototype PSA latexes were developed and evaluated for commercial feasibility, each prototype being produced and coated at pilot scale. The three prototypes showed progressive improvements in adhesive performance. The third prototype latex is far superior in performance as compared to the Industrial Benchmark latex and shows promise for commercialisation in chemical container and drum labelling applications. Labelstock from pilot coatings of this latex have been converted into labels by a Raflatac customer and have been sent for end-user trials.

Workpackage 5 The management structures and processes set up at the beginning of the project proved to be robust, efficient and effective at all levels of the project. The project strategies were reviewed at appropriate times and work on those which were not showing promise was terminated, leading to a focus on promising systems and acceleration towards

attainment of the overall project objectives. This ensured that project resources were used to maximum effect. No changes were needed to the deliverables and milestones planned for achievement within the project and all were completed successfully. All project objectives were achieved.

Dissemination: A patent application has been made to cover the most novel of the new wb-PSAs. New techniques developed in the project and results defining effective principles for design of wb-PSAs of enhanced performance have begun to be disseminated to the wider scientific community and will continue to be disseminated beyond the project, including dissemination through technical and industrial fora.

5 OVERVIEW OF INTENDED OUTCOMES, APPLICATIONS AND IMPACT

The project encompassed several of the NMP priority areas with fundamental knowledge as the underlying rationale for work designed to provide a level of understanding that would facilitate knowledge-led nanoscale design of society-friendly, high-performance wb-PSAs.

The results from the project have defined principles for strategies that can overcome present limitations of wb-PSAs and assist in achieving their full market potential. Due to the environmentally-benign manufacturing processes, and the safer and healthier transport, storage and application conditions, expansion of the wb-PSA market will bring societal benefits both for the general population and, more directly, for workers in the industry. There also will be cost benefits since wb-PSAs are of low cost compared to solvent-borne PSAs. Additionally, there have been specific benefits for the project participants arising from their interaction, which is continuing post-project, and also in the training of researchers in advanced methodologies. Furthermore, the success of the project is ensuring that, through dissemination of the results, the benefits will spread to others in the academic and industrial communities; again this dissemination is continuing beyond the end of the project. Indeed, it is anticipated that the new knowledge generated for the nanoscale design of high performance materials will be readily transferable to provide technological advances in other coating industries. Hence, the outcomes from the research are expected to have much wider benefits for the knowledge-led design and development of new coating materials.

6 PROJECT'S FINAL RELATION TO THE STATE-OF-THE-ART

The original market screenings for current commercial wb-PSAs for filmic oriented-polypropylene label applications (the main target application for prototypes to be developed in the project) remained valid and there were no major breakthroughs by other researchers or companies during the project. The commercial wb-PSA selected as the Industrial Benchmark at the beginning of the project, remained competitive and representative of the commercial state-of-the-art. Reviews of the scientific literature and patents revealed nothing to change the relevancy of the project objectives and strategies. Good progress was made towards achieving the challenging property targets which were set at the beginning of the project. The development latexes prepared within the project out-perform the Industrial Benchmark and the third prototype latex, which is undergoing customer trials, looks promising for commercialisation. A patent application was made to protect the intellectual property, developed in the project, which formed the basis for the second and third prototype latexes.

Part 2: Philosophy of the NsHAPe Project and Summary of Results and Achievements

7 OVERVIEW OF GENERAL PROJECT OBJECTIVES

As stated earlier, in comparison to solvent-borne PSAs, wb-PSAs suffer limitations in adhesive strength and in their ability to bond to non-polar substrates. *The overall objective of the NsHAPe research programme was:*

Objective 1: to design, produce, characterise and evaluate the film formation, deformation mechanisms and adhesive performance of wb-PSAs of controlled nanoscale heterogeneity with the aim of enhancing PSA performance and developing PSAs with novel properties through fundamental research.

The specific scientific objectives were:

Objective 2: to develop strategies for introducing nanoscale heterogeneities in the bulk of PSA films and to assess the effects of such heterogeneities on adhesive properties;

Objective 3: to develop strategies to obtain preferential segregation of specific latex particles to interfaces and to assess the effects of such segregation on adhesive properties; and

Objective 4: to correlate PSA design and synthesis to the nanoscale morphology of PSA films and to cavity nucleation and growth during film deformation in relation to adhesive properties.

The specific technological objectives were:

Objective 5: to develop strategies for developing a new generation of high-performance, commercially-viable wb-PSAs with particular emphasis on high-strength applications and bonding to non-polar substrates; and

Objective 6: to establish technical feasibility through development and industrial-scale evaluation of prototypes.

These objectives remained unchanged throughout the project. Thus the overall aims of the NsHAPe project are embodied in Objective 1, whereas Objectives 2-6 define more specifically the main areas of study. Objectives 5 and 6 were dependent upon successful development of promising strategies in the studies directed towards achieving Objectives 2-4. Thus, the strategies for delivering Objectives 2-4 were key to the overall success of the project.

The following section provides an overview of the crucial background information necessary for understanding the scientific philosophy that underpinned the project strategies, which are then outlined in Section 9. The research and outcomes for each of the technical Workpackages are then described in Sections 10–13. The project management structures and processes and a summary of the key achievements are given in Section 14.

8 BACKGROUND INFORMATION AND PROJECT PHILOSOPHY

Latexes most commonly are prepared by *emulsion polymerisation*. The particles can be grown in sequential stages to form *multi-layer*, onion-like, particles, the simplest of which have a *core-shell* morphology (see Figure 1). Some examples of latex particle morphologies that can be synthesised by sequential emulsion polymerisation are shown in Figure 2. The dimensions and chemical composition of each layer in the particles can be controlled at the nanometre scale during synthesis, including the nature and reactivity of the particle surfaces. Such control has been central to the NsHAPe project.

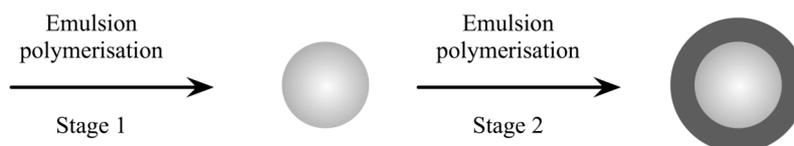


Figure 1. Schematic diagrams of particle cross-sections showing formation of core-shell latex particles by sequential emulsion polymerisation. Particle diameters are typically in the range 100-400 nanometres (one hundred-thousandth to four hundred-thousandths of a millimetre or about one thousandth of the thickness of a human hair).

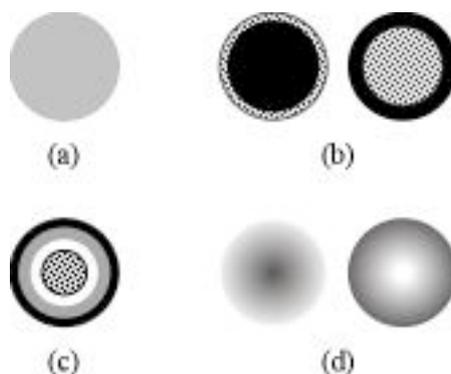


Figure 2. Schematic diagrams of particle cross-sections showing examples of latex particle morphologies that can be synthesised by emulsion polymerisation: (a) homogeneous, (b) core-shell, (c) multi-layer, and (d) radially-varying composition.

One limitation of emulsion polymerisation is that it requires transfer of molecules through water to the water-insoluble latex particles during synthesis, *i.e.*, the molecules must be at least sparingly-soluble in water. Miniemulsion polymerisation is a newer development in which all the molecules needed to form the latex particles are present in preformed droplets dispersed in water (the *miniemulsion*); the miniemulsion droplets are then converted directly into latex particles. Thus, in miniemulsion polymerisation, transport of molecules through water is not required and, unlike emulsion polymerisation, miniemulsion polymerisation can be used to make latex particles from completely water-insoluble molecules. This feature of miniemulsion polymerisation has been used to advantage in the NsHAPe project.

A key advantage of wb-PSAs is that the adhesive films produced from the latexes retain the structure and morphology of the latex particles because the films form by coalescence only of

the outer regions of the particles; see Figure 3 for a schematic illustration. This feature of film formation from latexes has been a key vehicle for enhancing adhesive performance in the NsHAPe project.

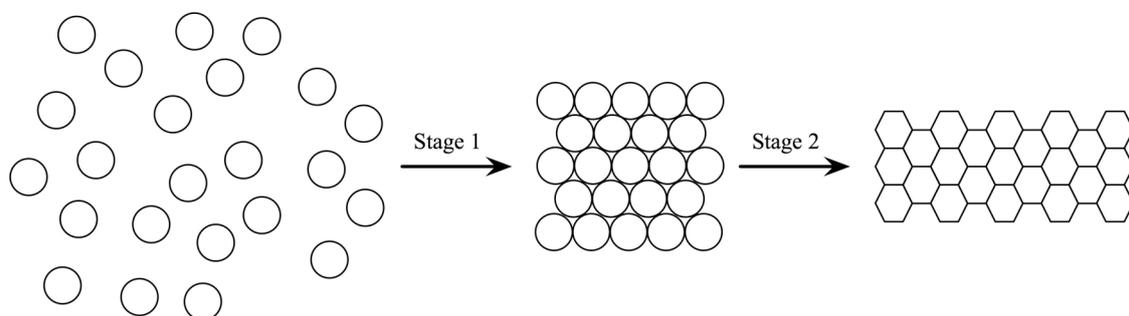


Figure 3. Schematic diagram showing two stages in the formation of films by drying of latexes. During stage 1, evaporation of water concentrates the latex particles to a point where they are packed together in close contact and arranged in a regular array. During stage 2, evaporation of the remaining water leads to particle deformation and formation of a *honeycomb-like* film morphology. Interdiffusion of polymer molecules across the interfaces between the deformed particles then produces a coherent film. Because interdiffusion occurs only near the particle surfaces, the morphology of the latex particles is retained in the final film.

9 KEY PROJECT STRATEGIES

As described in Section 7, the strategies for achieving Objectives 2–4 were key to success in the project, providing the directions for Objectives 5 and 6 and, ultimately, to achieving the overall Objective 1. Therefore, the strategies for achieving Objectives 2–4 are described below. Only through the unique complementarity of expertise provided by the NsHAPe partners was it possible to address all of these strategies efficiently and effectively in a 36-month period.

Strategy for Objective 2

As will be evident from Figure 3, by mixing (*i.e. blending*) different latexes it is possible to produce films that have a distribution of distinct phases corresponding to the different sizes, compositions and morphologies of the particles from each latex. This strategy was to be used in several ways.

A research theme planned at the outset of the project was to use latex blending to produce films containing small proportions of particles that were designed to have weak interfaces with the large proportion of PSA polymer particles, as indicated schematically in Figure 4(a). The concept was that the weak interfaces would be in the form of nanoscale defects within the bulk of the adhesive film and which, during deformation of the adhesive film, could act as sites for nucleation of cavities away from the interfaces, which is highly desirable.

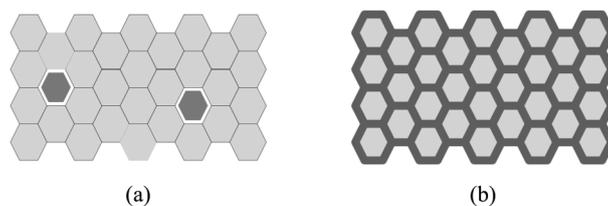


Figure 4. Schematic diagrams depicting the two principal strategies for achieving Objective 2: (a) blending into the PSA latex (light grey particles) a small proportion of a second latex (dark grey particles) whose particles have a weak interface (shown as white regions) with the PSA latex particles in the adhesive film; and (b) use of core-shell latex particles in which the core polymer (light grey) provides the viscoelasticity response and the shell polymer (dark grey) interdiffuses to form a honeycomb-like network that provides the elastic response of the adhesive film.

Latex blends have also been used more simply to balance adhesive performance characteristics and to evaluate possible synergies, whereby films from a blend could outperform films formed from either of the two parent latexes alone.

A further important strategy has been to use film formation of core-shell latex particles to create a honeycomb-like morphology in the adhesive film in which the particle cores provide the dominant viscoelasticity response and the particle shells, which become the continuous matrix in the film, provide the elasticity necessary for good adhesion performance (see Figure 4(b)). This strategy also has been studied in the form of latex blends with different types of core-shell particle.

Strategy for Objective 3

The strategy for this objective was to use latex blending to introduce into a PSA latex, a small amount of quite different latex particles with properties that could cause them to preferentially move to the interface with one or other of the substrates to be bonded and enhance the strength of the interface. This strategy is depicted in Figure 5 and was targeted for enhancing the strength of interfaces with hydrophobic substrates, such as polyethylene and polypropylene.

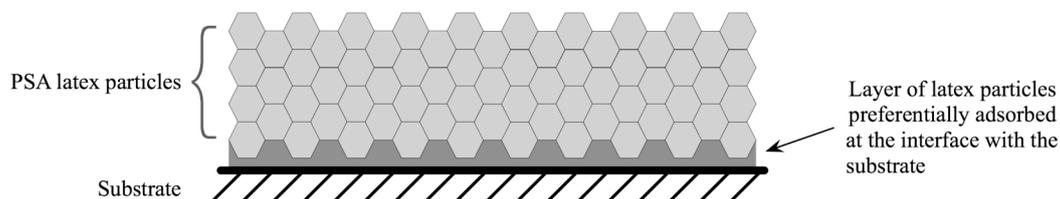


Figure 5. Schematic diagram depicting a strategy for achieving Objective 3 by blending the PSA latex with another latex whose particles move to, and strengthen, the interface with the substrate in the adhesive film.

As indicated, Objective 3 was aimed at improving wb-PSA adhesive performance when bonding to hydrophobic substrates. Core-shell latex particles were also investigated for this purpose.

Strategy for Objective 4

The focus for Objective 4 was to thoroughly evaluate the effects of changes in the design and synthesis of PSA latexes and changes in latex blends. For this purpose there were three principal strategies.

- Firstly, use of standard pressure-sensitive adhesive testing protocols for screening of new latexes and latex blends to identify promising candidates for further investigation.
- Secondly, use of advanced methods of thin film characterisation to monitor film formation and determine the morphology of the films produced from the new PSA latexes and latex blends.
- Thirdly, to use sophisticated, real-time measurements during deformation of adhesive films to provide mechanistic information and insights into molecular and morphological parameters that control the adhesive performance of the new PSA latexes and latex blends.

10 WORKPACKAGE 1: LATEX SYNTHESIS AND CHARACTERISATION

Workpackage 1 Objectives

The overall objectives were as follows.

- To synthesise latexes containing particles with controlled variations in size, internal morphology, chemistry, crosslinking and physical properties for use in latex blends to enhance wb-PSA performance.
- To characterise latexes by measurements of viscosity, particle size, particle size distribution, particle morphology and polymer properties to provide data for interpretation of results from other workpackages.

Workpackage 1 Research and Outcomes

Benchmark latexes and latex characterisation

The first phase of work involved selection of the Industrial Benchmark latex and the definition and synthesis of a Laboratory Benchmark latex. This was done by Surfs in consultation with Raflatac; Surfs then supplied all project partners with these latexes as standards against which to compare the new PSA latexes. The procedure and monomer composition for synthesis of the Laboratory Benchmark latex provided the starting point for synthesis of PSA latexes at UMan.

During this initial period, latex characterisation procedures for measurement of latex solids content, residual monomer, particle size and size distribution, pH and viscosity were established at both Surfs and UMan, and shown to give comparable results. Procedures for cleaning PSA latexes to remove aqueous phase salts and surfactant molecules were established early in the project and used selectively to provide cleaned latexes for study in Workpackages 2 and 3 for systems where testing of the cleaned latex could provide a more complete understanding and interpretation of wb-PSA properties and adhesive performance.

Latexes for promoting cavity nucleation

Three types of latexes were investigated for use as minor components in latex blends to provide weak interfaces in the bulk of the adhesive film (see Figure 4(a)) that could act as sites for controlled nucleation of cavities during deformation of adhesive films, an important factor in achieving good adhesive performance.

- Latexes with highly-crosslinked particles which could not interdiffuse with the PSA latex particles.
- Hard poly(methyl methacrylate) latex particles which are completely immiscible with the PSA latex polymer.
- Core-shell latex particles with a polytetrafluorethylene core and a PSA polymer shell in which there would be a weak interface between the core and shell.

In addition, several silica colloids were sourced in order to investigate their ability to nucleate cavitation in adhesive films formed from their blends with a PSA latex.

With few exceptions, adhesive screening tests (carried out under Workpackage 3) showed that inclusion of these second component latexes has a detrimental effect on adhesive performance. Although they undoubtedly introduced weak interfaces that could act as sites for cavity nucleation in the bulk of the adhesive films, this effect was not significant at low levels of inclusion (up to a few percent). At higher levels of inclusion, the greater rigidity of the second component particles led to significant detrimental effects on the overall viscoelastic properties of the adhesive film. In view of these observations, work on this strategy was terminated in Month 16.

Core-shell latexes for enhancing adhesive performance

Core-shell latexes which form a honeycomb-like film structure, as depicted in Figure 4(b), proved to be the most versatile and useful type of latex for enhancing adhesive performance. Three broad classes of core-shell latex have been designed and synthesised. For each class, a large number of core-shell latexes have been prepared and supplied for evaluation under Workpackages 2–4. The objective was to achieve and optimise synergistic effects arising from the nanoscale honeycomb-like film morphology produced from core-shell latex film formation. The dimensions and properties of each phase in the film could be pre-defined by controlling the dimensions, compositions and properties of the core and shell phases of the core-shell latex particles.

- *Core-Shell Latexes synthesised via Sequential Emulsion Polymerisation* An extensive range of core-shell latexes was synthesised by sequential emulsion polymerisation (see Figure 1). In each case, the core comprises a dissipative polymer designed to provide good adhesion and the shell comprises a polymer containing reactive groups designed to undergo crosslinking during film formation to enhance cohesive properties. A range of latexes were also synthesised with different levels and types of hydrogen-bonding groups incorporated in the shell.
- *3-Layer Latexes synthesised via Sequential Emulsion Polymerisation* These latexes were developed as an extension of the core-shell latex synthesis work and differ from the core-shell latexes by having an inter-layer (between the core and shell) of pre-crosslinked dissipative polymer.

- *Core-Shell Latexes with Encapsulated-Tackifier in the Core* Work on the synthesis of these latexes was preceded by an extensive study of the synthesis of encapsulated-tackifier latexes by miniemulsion polymerisation. Use of miniemulsion polymerisation was necessary because the tackifiers (which are widely used in existing PSAs to improve adhesive performance) are highly insoluble in water. The resulting encapsulated-tackifier latex particles were then grown by emulsion polymerisation to produce core-shell particles in which the shell was a lightly-crosslinked or crosslinkable polymer of high cohesion. A patent application covering the synthesis and use of these novel types of core-shell latex was submitted in Month 13 of the project.

For each of these classes of latex, a wide range of parameters have been varied systematically in order to understand and optimise adhesive performance. Confirmation that core-shell particles had been produced was obtained from measurements of the particle diameter of latex samples removed during the polymerisations and from the analyses carried out under Workpackage 2 (Section 11).

Latexes for preferential adsorption at interfaces

The aim of this work was to synthesise latexes whose particles could show preferential adsorption and bond strongly to interfaces with hydrophobic substrates (see Figure 5), for which polyethylene and polypropylene were the chosen reference substrates. Poly(isodecyl acrylate) (PIDA) was selected as the polymer for these latexes because it is highly hydrophobic and highly compliant. Robust emulsion polymerisation protocols were developed for conversion of the highly hydrophobic isodecyl acrylate into PIDA latex particles and facilitated synthesis of a range of PIDA latexes for evaluation in Workpackages 2 and 3.

Additionally, a series of core-shell latexes were prepared comprising a PIDA core and shells of PIDA with variable levels of a hydrophilic component in the shell phase (*i.e.* a series of latexes with progressively reduced particle surface hydrophobicity). These latexes also were used in Workpackage 2 studies of the effects of hydrophobicity on water-whitening of PSA films.

11 WORKPACKAGE 2: ADHESIVE FILM FORMATION AND CHARACTERISATION

Workpackage 2 Objectives

The overall objectives were as follows.

- To determine the morphology of films formed from blends of latex particles, with particular emphasis on interparticle voids and on film heterogeneities that will encourage cavitation during debonding.
- To observe whether certain latex particles can preferentially adsorb at interfaces in a controlled way.
- To identify the optimum film morphology for imparting high adhesion to non-polar substrates, such as polyolefins.

Workpackage 2 Research and Outcomes

Studies of wb-PSA latexes and films

Atomic force microscopy (AFM) provides information on the morphology of surfaces through momentary contacts of the surface with a highly-sensitive probe that is rastered in a 'tapping' mode across the surface and is capable of revealing surface features on a nanometre size scale. PSA films are particularly difficult to study by AFM because they are inherently 'tacky' materials. Hence, the initial work examined the effects of experimental parameters and established protocols for successful imaging of wb-PSA film surfaces by AFM. These procedures were first used to identify the 'fingerprint' morphologies of films from the benchmark wb-PSA latexes and then for study of films formed from the new wb-PSAs synthesised under Workpackage 1. Additionally, in a further significant technique development, procedures were established for cleanly cutting through the adhesive film in a direction perpendicular to the film surface, thus providing specimens that could be studied by AFM to determine the through-thickness (*i.e.*, cross-section) morphology of the films, which was helpful in studies of preferential segregation of particles to interfaces.

The results from these surface and through-thickness studies of PSA films have been essential to understanding the effects of latex parameters on film morphology and adhesive properties. For example, AFM images showing the morphologies of the surfaces of adhesive films formed from some of the new core-shell wb-PSA latexes are presented in Figure 6.

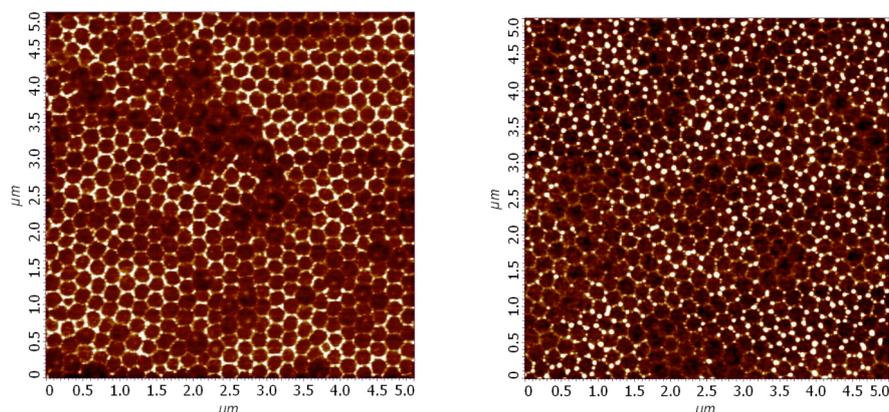


Figure 6 AFM phase images of the surfaces of films formed from some of the new core-shell wb-PSA latexes. In each case, the images are of an area of surface $5\ \mu\text{m} \times 5\ \mu\text{m}$. $\{1\ \mu\text{m} = 0.001\ \text{mm}\}$ Although both the core and shell polymers are 'soft', the core polymer is significantly more dissipative and so appears much darker than the shell polymer phases which appear almost white in colour.

Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) is a well-established technique for probing the chemical composition of surfaces and was used in the project to map the chemical composition of phases present on surfaces and through-thickness sections of PSA films. By correlating the AFM and ToF-SIMS surface maps more detailed information on the nature of the surfaces has been obtained. This was particularly helpful in understanding the accumulation of surfactant molecules at the surfaces of adhesive films, work that benefited greatly from use of cleaned PSA latexes. *{Surfactants are used in the synthesis of*

latexes and in the formulation of PSA latexes prior to coating; accumulation of surfactant at interfaces with substrates is known to have a detrimental effect on adhesive performance.} In some cases, 'puddles' of surfactant were seen on the film surface, which was explained by a new theory that was developed by researchers outside of the NsHAPe project.

In an extension of the AFM studies, force microscopy was used to map the mechanical properties of the adhesive film surfaces. In these experiments, at each point across the surface, the force required to pull the AFM probe away from the surface is monitored simultaneously with the displacement of the probe from the surface. In this way, different phases on the film surface can be identified much more clearly than by conventional AFM. Moreover, any heterogeneities in the mechanical properties across the surface can be identified and measured. Force microscopy was particularly useful in studying the core-shell latexes with encapsulated-tackifier in the core. In this type of film, separate phases are distributed across the film.

The effects of PIDA latex parameters on preferential adsorption at interfaces were studied through a combination of surface and through-thickness AFM imaging (e.g. see Figure 7), and measurements of film surface properties.

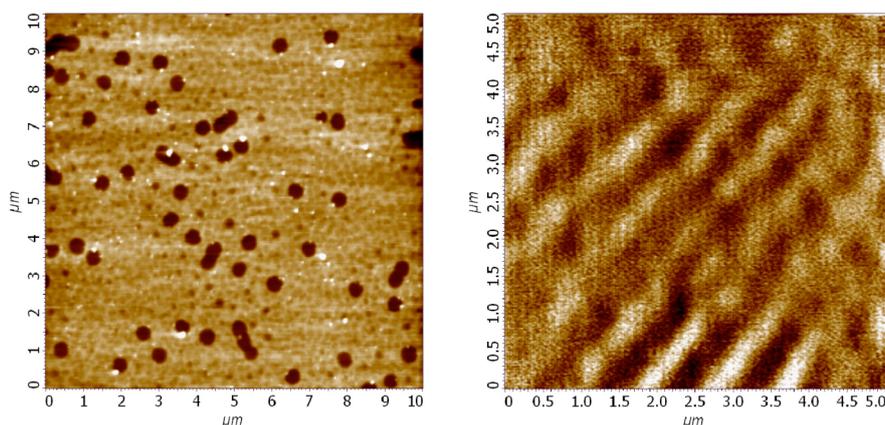


Figure 7 AFM phase images of the surfaces of adhesive films formed from blends of Industrial Benchmark and PIDA latexes. The PIDA phases appear darker because they are more dissipative than the Industrial Benchmark polymer. Discrete PIDA particles can be seen in the image on the left-hand side (10 μm x 10 μm area), whereas the PIDA particles are more numerous and have coalesced in the image on the right-hand side (5 μm x 5 μm area). {1 μm = 0.001 mm.} In this case, the dark and light striations are merely resulting from surface striations.

AFM techniques also were developed to visualise and evaluate the stiffness of individual latex particles deposited from highly-diluted latexes; the results were correlated with the core:shell ratio and the properties of the core and shell polymers.

Studies of film formation from PSA latexes

Film formation from latexes proceeds via loss of water and it is very important to understand the drying process. Key to this understanding is the need to know how the distribution of water through the film changes as drying progresses and how the changes are influenced by

latex parameters and drying conditions. Real-time monitoring of drying has been achieved using magnetic resonance profiling (MRP), in a similar way to the use of magnetic resonance imaging (MRI) for investigation of health problems in humans. In both cases, information is provided on the density and mobility of hydrogen atoms in the subject of investigation. MR profiles of the water content through the thickness of films cast from the PSA latexes have been obtained over time in order to investigate the way in which water is lost from the films. This has enabled the effects of latex parameters to be determined, most significantly for the core-shell latexes with encapsulated-tackifier in the core. Some typical results are shown in Figure 8. The intensity (on the vertical axis) is proportional to the concentration of mobile hydrogen atoms, and hence it gives information on the water content.

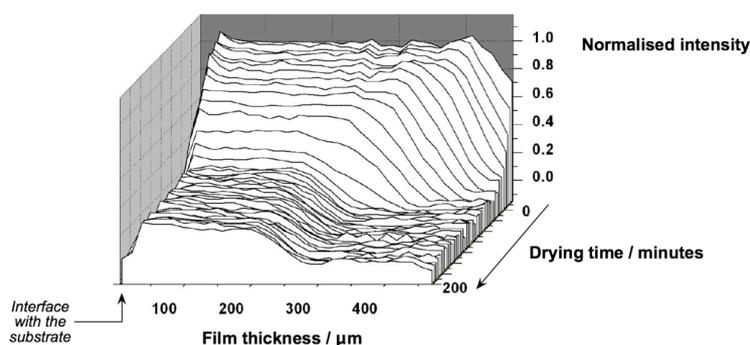


Figure 8 A series of MR profiles obtained non-invasively during the drying of a core-shell PSA latex. The normalised intensity indicates the amount of water at each point away from the interface with the substrate. $\{100 \mu\text{m} = 0.1 \text{ mm}\}$ This latex shows an initial period of rapid drying and development of a non-uniform distribution of water with less water at the surface of the film; the rate of drying then slows down and the non-uniformity reduces, but there is still significant non-uniformity after 500 minutes of drying.

Studies of water-whitening in PSA films

Absorption of water from the atmosphere by PSA films can cause them to become translucent or even opaque (so-called *water-whitening*) and such effects have become a significant issue with growth in the demand for transparent (so-called *filmic*) pressure-sensitive adhesive labels and tapes. Hence, procedures were developed for monitoring the water uptake and water-whitening of films formed from the new wb-PSAs, leading to an understanding of the factors affecting water-whitening and recognition that the extent of whitening was not controlled by the amount of water taken up by the film but more by the domain size of the pockets of water in the film. Of particular significance in establishing this understanding were studies of films formed from the core-shell PIDA-based latexes with different levels of shell polymer hydrophilicity.

In combination with the observations from studies of film formation, the results have led to an understanding of the latex characteristics required to achieve fast drying and low water-whitening.

12 WORKPACKAGE 3: ADHESIVE TESTING AND EVALUATION

Workpackage 3 Objectives

The overall objectives were as follows.

- To gain a detailed understanding of the mechanisms responsible for adhesion of nanostructured wb-PSAs.
- To identify the key synthesis parameters controlling adhesive properties of nanostructured wb-PSAs in order to guide the synthesis and industrialisation of PSAs with improved performance.
- To develop a predictive model of the effect of the nanostructure on the adhesive properties based on inputs from WP1 and WP2.

Workpackage 3 Research and Outcomes

Standard pressure-sensitive adhesive testing

Standard adhesive test methods for use in the project were defined by Surfs and Raflatac, where facilities for these tests were already in place; reference data were produced from testing of the Industrial Benchmark and Laboratory Benchmark latexes. This work also defined the formulation of the PSA latexes for coating, the coating conditions and the coating weight, which corresponds to a film thickness of about 19 μm . $\{1 \mu\text{m} = 0.001 \text{mm}\}$ Two of the tests were implemented at UMan for routine laboratory evaluation and screening of new wb-PSAs: 180° peel adhesion (FINAT Test Method 1); and shear resistance (FINAT Test Method 8). Consistent results were obtained from these tests when testing the same PSA latexes at UMan, Surfs and Raflatac.

The standard adhesive tests were used to characterise and screen the adhesive performance of all new PSA latexes developed in Workpackage 1 so that specific latexes could be identified for more detailed mechanistic studies in Workpackage 3 (see below) and for further study in Workpackages 2 and 4.

Mechanistic studies of pressure-sensitive adhesive deformation behaviour

Mechanistic studies of the deformation behaviour of pressure-sensitive adhesive films were critical to understanding the effects of particle chemical composition, particle morphology, crosslinking and, for core-shell particles, the chemical and physical properties of the core and shell polymers on adhesive performance. These studies were conducted principally at ESPCI, where facilities were established for optical observation and analysis of film deformation during testing. Two analytical probe test methods were developed for measurement of real-time deformation of pressure-sensitive adhesive films in tension and shear, the latter requiring the design and construction of a new apparatus. In each case, the probe is brought into intimate contact with the pressure-sensitive adhesive film and the force on the probe measured together with its displacement as the probe is either moved away from the film at a controlled rate (testing in tension) or oscillated at a controlled frequency (testing in shear). These sophisticated test methods were established and commissioned during Months 1-9 of the project. They have delivered crucial information, identifying the most important parameters to guide the latex synthesis work and helping to accelerate

developments in the design of the new PSA latexes for achievement of the overall project goals.

In addition, conventional tensile testing of pressure-sensitive adhesive films has provided important information on their non-linear viscoelastic response and mechanical properties for correlation with the results from the analytical probe tests. In particular, the non-linear properties obtained from the tensile testing could be analysed with polymer physics models and interpreted in terms of molecular structure, thereby guiding the synthesis work. Figure 9 shows some results from testing of the second prototype PSA latex (see Section 13), which demonstrate very clearly the major improvement in adhesive performance compared to the Industrial Benchmark latex. The tensile test results in Figure 9(b) show that the two adhesives have similar initial moduli, but the prototype softens much more than the industrial benchmark, which is key to the superior performance.

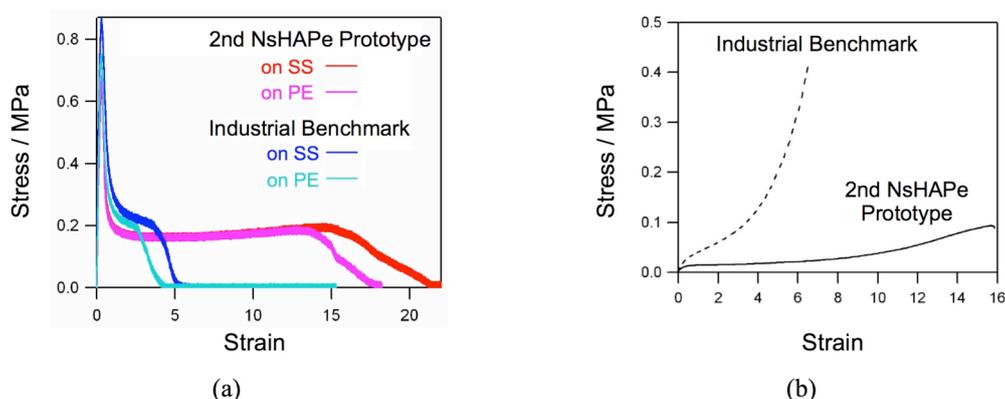


Figure 9 Real-time stress-strain curves obtained from testing of pressure-sensitive adhesive films formed from the Industrial Benchmark latex and the second prototype latex (see Section 13): (a) results from analytical probe testing in tension on stainless steel (SS) and polyethylene (PE) substrates; and (b) results from conventional tensile testing.

The results from the mechanistic studies have shown that the best adhesive performance is achieved by combining a highly viscoelastic majority phase with a more elastic and percolating minority phase, and that this is most effectively implemented using core-shell latexes. (The three-layer latexes with an intermediate pre-crosslinked layer showed no beneficial effects.) For core-shell latexes where both core and shell polymers are similarly soft, the activation of crosslinking at the interfaces between particles during film formation was used to give elasticity to the material, while the viscoelastic properties were mainly controlled by the core. The optimal adhesive performance could be achieved by carefully balancing cohesion and deformability through control of the core:shell ratio, core and shell polymer properties, and the extent of interfacial crosslinking. Similar balances in properties were achieved for the core-shell latexes with encapsulated-tackifier in the core, including optimisation of the type and level of tackifier used, which led to exceptionally high adhesion to polyethylene.

Towards the end of the project, the effect of incorporating of hydrogen-bonding groups in the shell of core-shell particles was investigated. The results showed that this is a strategy worth pursuing in future research because the hydrogen-bonding groups introduce other types of energy dissipation mechanisms.

The concept of introducing a gradient of properties through the thickness of the adhesive film was investigated using bilayer structures where one of the layers is dissipative and the other more elastic. The configuration where the dissipative layer, backed by a more elastic one, is directly in contact with the substrate proved to be particularly effective for adhesion on non-polar substrates. These results validated the strategy for using particle migration to increase adhesion at interfaces and established that the type of structuring required for enhancement in adhesive performance depends on the substrate.

Modelling the mechanical properties of films formed from the new wb-PSAs

The combined results of the analytical probe tests, rheological tests and tensile tests led to the development of a mathematical model for the deformation of films prepared from core-shell particles, which was capable of accurately predicting the tensile properties of the films. The essence of the model was to combine the modelling strategy used for a viscoelastic fluid with that of a strain-hardening rubbery solid. The overall model captures the physics of the deformation with a minimum number of physically-based parameters.

13 WORKPACKAGE 4: EVALUATION OF TECHNICAL FEASIBILITY

Workpackage 4 Objectives

The overall objectives were as follows.

- To develop the most promising approaches for enhancement of adhesive performance into formulated wb-PSA prototypes suitable for technical evaluation.
- To carry out an industrial evaluation of the formulated wb-PSA prototypes by making and testing industrial coatings for label end-use applications.

Workpackage 4 Research and Outcomes

The promising results for bonding to polyethylene observed for the novel core-shell latexes with encapsulated-tackifier in the core led to their selection as the principal type of latex for development as prototypes to be evaluated for commercial feasibility under Workpackage 4. However, the particle cores for these latexes are synthesised by miniemulsion polymerisation, which requires special equipment for preparation of the miniemulsion. Pilot-scale miniemulsion preparation facilities needed to be installed at Surfs in order for these types of latexes to be produced at the scale required for pilot-scale coating and evaluation at Raflatac. Hence, the first prototype had to be based on core-shell latexes synthesised directly by sequential emulsion polymerisation without incorporation of tackifier.

All three prototype latexes were selected using the same sequence of laboratory evaluations. A wide range of candidate latexes were first screened under Workpackage 3. Promising candidate latexes (typically about ten) were then subjected to a full range of adhesive testing at Raflatac, leading to identification of the most promising latex for scale-up. Surfs produced the prototype and Industrial Benchmark latexes at 80 kg scale using pilot-scale plant at Drogenbos. The latexes were shipped to Raflatac in Tampere where they were formulated and pilot-coated, the resulting adhesive labelstock then being subjected to an exhaustive range of tests at Raflatac. Samples were also sent to UniS and ESPCI for more detailed

studies of the pilot coatings and their properties. In each case, the results obtained were used to inform development of the next prototype latex.

First prototype latex

Blends of two different types of core-shell latexes were selected as first prototypes. Each core-shell latex was successfully scaled-up to produce 80 kg pilot batches which showed the same properties as the laboratory batches. The latexes were slightly diluted and formulated prior to pilot coating. The runnability of the prototype latex blends was satisfactory and the pilot machine coating was successful. The resulting labelstock was thoroughly tested at Raflatac and Surfs, and evaluated at both UniS and ESPCI. The first prototype showed improvements in adhesive performance compared to the Industrial Benchmark, notably higher performance on polyethylene, but also had deficiencies, in particular a relatively high latex viscosity and lower than desired shear resistance.

Second prototype latex

The installation and commissioning of pilot-scale facilities for miniemulsion preparation at Surfs facilitated scale-up of core-shell latexes with encapsulated-tackifier in the core. These types of latex then became the focus for the development of the second and third prototype latexes.

The screening process for the second prototype led to identification of two different core-shell latexes with encapsulated-tackifier in the core for closer scrutiny at Raflatac. The most promising of these two latexes was chosen as the second prototype latex and was produced at 80 kg scale by Surfs, yielding a pilot batch with properties equivalent to the latex synthesised in the laboratory. Thus scale-up of this new type of core-shell latex proceeded smoothly and without problems. The batch was shipped to Raflatac where it was formulated and successfully pilot machine coated. Runnability again was satisfactory, though slight foaming was observed. The coatings were investigated as for the first prototype latex, the results from which showed that the second prototype was an improvement over the first. Peel performance was now better than the Industrial Benchmark on both stainless steel and polyethylene. The water resistance of the second prototype was also a distinct improvement compared to the Industrial Benchmark, but shear resistance still needed to be improved.

Third prototype latex

The candidates for the third prototype latex were evolutions of the second prototype latex with changes in the core-shell particles which were designed to improve shear resistance whilst minimising any possible detrimental effects on peel adhesion. Testing of these candidate latexes led to identification of the third prototype latex, which was also successfully scaled-up by Surfs to produce an 80 kg batch that was shipped to Raflatac for formulation and pilot machine coating. Runnability of the third prototype was good and a significant improvement over the previous two prototypes. Peel and tack performance was double that of the Industrial Benchmark and shear performance exceeded the target values defined at the outset of the project. The overall profile of properties shown by the pilot coatings produced from the third prototype latex have identified it as being promising for commercialisation in chemical container and drum labelling applications.

In view of these promising results, labelstock produced from the third prototype was sent by Raflatac to one of their customers, a label converter company, for pilot-scale production of labels and then to an end-user evaluation of the labels. The converter has reported that convertability of the labelstock was satisfactory. Feedback from the end-user also was positive.

14 WORKPACKAGE 5: PROJECT MANAGEMENT AND ASSESSMENT

Workpackage 5 Objectives

The overall management objectives were as follows.

- To ensure that the research programme is carried out efficiently making full use of the resources allocated to the project.
- To ensure that technical and non-technical reports are produced on time.
- To evaluate the results from the research programme and take decisions on the direction of future work, including changes to the original work programme where this is considered to be necessary.
- To ensure that all participants are updated regularly about the progress being made by each participant in each of the technical workpackages.

Workpackage 5 Structures, Processes and Outcomes

Project Management Structures, Processes and Decision-Making

The management structures and processes set up at the beginning of the project were robust, efficient and very effective at all levels of the project throughout its duration and required no modification.

A *Steering Committee*, comprising senior staff from the consortium and which held scheduled meetings every 6 months, had responsibility for reviewing overall project status, for defining the strategic directions for project work and for high-level decision-making, both technical and non-technical. The initial meeting was held in Month 1 to review and refine the initial project objectives and plans. Two extraordinary meetings were held: (i) in Month 16, to refine and focus the Workpackage 1 synthesis work to make best use of the period prior to the Mid-Term Assessment meeting of the Steering Committee; and (ii) slightly ahead of the scheduled Month 31 meeting, to decide upon redistribution of the remaining project funds and resources for the remaining 6 months in order to maximise the output from the project.

Workpackage Leaders were responsible for coordinating and guiding overall work on the respective workpackages and their links with other workpackages. *Local Workpackage Leaders* were responsible for coordinating and guiding work on the respective workpackages at a specific partner under the direction of the respective Workpackage Leaders and the Steering Committee. Work within a given workpackage was discussed, as necessary, through telephone discussions and round-the-table meetings. Also, where necessary, individual researchers visited other partners for training or when this was of benefit to technical work.

In addition to the workpackage-oriented management mechanisms, there has been a cross-cutting parallel series of approximately bi-monthly teleconference discussions which have involved all project workers so that everyone is aware of all progress in the project. The discussions have been based around summary reports of key results obtained in the previous months, which were submitted to the Project Coordinator for collation and distribution ahead of the teleconference. The teleconference discussions have been very successful in helping direct and maintain coordination of the ongoing project work across the four technical workpackages and also were used to discuss project management matters. They also ensured that everyone involved in the project was kept fully aware of, and had opportunity to contribute to, all developments.

The original project strategies were reviewed by the Steering Committee in Month 16 and at the Mid-Term Assessment meeting. This led to termination of work on those strategies which were not showing promise and to a focus on promising systems, decisions that resulted in an acceleration towards attainment of the overall project objectives during Months 17–24. These focused project strategies were further refined in Month 31 to ensure that the final months of the project were used to maximum effect.

Evaluation of Project Achievements in Relation to Project Objectives

The following is a summary of the most important achievements of the NsHAPe project.

- The consortium was highly effective, partly because it comprised *complementary* partners with well-established reputations for competence in their respective fields.
- The management structures and processes set up at the beginning of the project ensured timely communication of results, observations and ideas between the four discipline-focused technical workpackages and the partners. This facilitated focused work on particular aspects of the research and development programme and the refinement and targeting of project strategies and resources to those materials and studies which were most effective in achieving the project objectives.
- No changes were needed to the deliverables and milestones planned for achievement within the project and all have been completed successfully.
- Objectives 1–6 and all of the workpackage objectives have been achieved.
- A very large number of latexes with systematic variations in key parameters have been synthesised, characterised and screened by UMan and Surfs, of which more than 100 latexes have been supplied to partners for further evaluation under one or more of Workpackages 2–4.
- A wide range of concepts for design of wb-PSAs of enhanced performance have been investigated.
- Several effective principles for design of wb-PSAs of enhanced performance have been established, the most novel of which has been covered by a patent application (see Section 16).
- The new knowledge concerning factors affecting film formation, film morphology and adhesive performance of wb-PSA films has begun to be disseminated to the wider scientific community and will continue to be disseminated beyond the project, including dissemination through technical and industrial fora (see Section 16).
- Techniques have been developed for study of film morphology and evaluation of water-whitening in PSA films, which through dissemination activities already are

becoming known and available to the wider scientific community and will continue to be disseminated beyond the project (see Section 16).

- Techniques have been developed for mechanistic studies of the deformation of pressure-sensitive adhesive films, which through dissemination activities already are becoming known and available to the wider scientific community and will continue to be disseminated beyond the project (see Section 16).
- Three prototype wb-PSA latexes have been developed and evaluated, each being successfully produced and coated at pilot scale. The three prototypes showed progressive improvements in adhesive performance.
- The third prototype latex is far superior in peel performance as compared to the Industrial Benchmark latex and shows improvements in other properties; it also exceeds the target value for shear resistance. In view of its balance of properties, the third prototype latex shows promise for commercialisation in chemical container and drum labelling applications. Labelstock from pilot coatings of this latex have been converted into labels by a Raflatac customer and have been sent for end-user trials.
- The NsHAPe project partners have established very good working and personal relationships that will continue beyond the project.

Part 3: Exploitation and Dissemination of the NsHAPe Project Results and Achievements

15 EXPLOITABLE KNOWLEDGE AND ITS USE

A patent application for the tackifier-incorporated core-shell latexes was submitted by Surfs in Month 25 and is progressing through the evaluation process. Maintenance, policing and extension of the patent will continue to be carried out by Surfs beyond the end of the project. The new technology protected by the patent has shown considerable commercial potential and its use in other applications will be pursued by Surfs. The technology will also be disseminated through presentations at technical conferences; for example, K Ouzineb (Surfs) has accepted an invitation to present a talk on these new developments at the 29th FATIPEC, a biennial congress with an industrial focus that is organised by the European Federation of Coatings Scientists, which will be held 9-11 June 2008 in Ghent, Belgium.

The patentability of the core-shell latexes synthesised directly by sequential emulsion polymerisation was evaluated with the decision that the new latexes prepared by this route could not be patented. The knowledge gained in the studies of these materials will, however, provide new directions for future development of wb-PSAs at Surfs and, through public disseminations, will be made available to other researchers and companies for exploitation in wb-PSAs and other water-borne coating materials.

The self-assembly approach in which particles preferentially segregate to specific interfaces is novel, but did not prove sufficiently effective in practice and so was not considered for patenting.

16 DISSEMINATION OF KNOWLEDGE

Dissemination of knowledge resulting from the project has been subject to clearance through the Steering Committee in accordance with an agreement to provide written comments and a decision within 4 weeks from the date of distribution of proposed dissemination materials. With this approval, results from the NsHAPe project have been presented at conferences and are the subject of papers submitted to respected learned journals. Due to the greater sensitivity of the latex synthesis and prototype development work, early dissemination focused on publishable results from Workpackages 2 and 3. The dissemination performed during the project is listed below. At present, the project has generated one patent, which will be published in April 2008, and three papers, two of which have been published, the other being in progress with the journal. It should be noted that results from the NsHAPe project will continue to be disseminated beyond the end of the project through publications in journals and magazines and through oral and poster presentations at conferences. As indicated in the listing, we have plans for at least a further seven journal papers (of which four are currently in progress, with one ready for submission pending approval and another in an advanced stage of preparation). In accord with the Consortium Agreement, the Steering Committee will continue to be active beyond the end of the project to review for approval all future proposed disseminations of NsHAPe project results.

Patent Applications

- "Aqueous Polymer Dispersion and Process", K. Ouzineb and O. Dupont, K. Ouzineb and O. Dupont, EP 06021165.3 filed in October 2006; publication date: 9 April 2008

Papers Submitted to Journals

- "Probing Particle Structure in Waterborne Pressure-Sensitive Adhesives with Atomic Force Microscopy: Explanation of Height Artefacts", C.H. Lei, K. Ouzineb, O. Dupont, and J.L. Keddie, *Journal of Colloid and Interface Science*, **307(1)**, 56-63 (2007)
- "Effect of a Gradient in Viscoelastic Properties on the Debonding Mechanisms of Soft Adhesives", C. Carelli, F. Deplace, L. Boissonet and C. Creton, *Journal of Adhesion*, **83**, 491-505 (2007)
- "Lateral Surface Non-Uniformities in Drying Latex Films", V.R. Gundabala, C.Lei, K. Ouzineb, O. Dupont, J.L. Keddie, and A.F. Routh, *submitted to the Journal of Fluid Mechanics*

Papers Currently in Preparation for Submission to Journals

- "Control of Adhesive Properties through Structured Particle Design of Water-Borne Pressure-Sensitive Adhesives", A.B. Foster, P.A. Lovell and M.A. Rabjohns, *final draft awaiting approval from NsHAPe partners prior to submission to Polymer*
- "Bottom-up Design of Soft-Soft Nanocomposite Adhesives", F. Deplace, C. Carelli, A. Langenfeld, S. Mariot, H. Retsos, A. Chateauminois, O. Dupont, K. Ouzineb, P.A. Lovell, A. Foster, M. Rabjohns, C.H. Lei, J.L. Keddie and C. Creton, *in preparation*
- "Optimizing the Microstructure of a Soft Material made from Latex Particles for Adhesive Properties", F. Deplace, C. Carelli, A. Langenfeld, S. Mariot, H. Retsos, A. Chateauminois, O. Dupont, K. Ouzineb, P. A. Lovell, A. Foster, M. Rabjohns and C. Creton, *in preparation*
- "Adhesive and Mechanical Properties of Model Soft Core-Shell Pressure-Sensitive-Adhesives: Role of Particle Interfaces on the Large Strain Behaviour", F. Deplace, C. Carelli, M. Rabjohns, A. Foster, P. A. Lovell, C. Lei, J. L. Keddie and C. Creton *in preparation*
- "Effects of Hydrogen Bonding Groups on the Adhesive and Mechanical Properties of Model Soft Core-Shell Pressure-Sensitive-Adhesives ", F. Deplace, J. Marchal, M. Rabjohns, A. Foster, P. A. Lovell, C. Lei, J. L. Keddie and C. Creton *in preparation*
- "Adhesive Properties and Nano-scale Structure of Waterborne Tackified Pressure-Sensitive-Adhesives Synthesized by Miniemulsion Polymerization", F. Deplace, J. Marchal, E. Canetta, K Ouzineb, C. Lei, J.L. Keddie and C. Creton, *in preparation*
- "Meeting the Conflicting Requirements for Fast Drying and Water-Whitening Resistance in Waterborne Colloidal Films", C.-H Lei, T.G. Weerakkody, J.L. Keddie, A.B. Foster, P.A. Lovell and M.A. Rabjohns , *in preparation*

Conference Presentations

- "Designed Nanoscale Heterogeneities for controlling Water-Borne Pressure-Sensitive Adhesive Performance (NsHAPe)", poster paper presented by F. Deplace at the Gordon Conference on Science of Adhesion, Tilton, New Hampshire , USA, 6-11 August 2006
- "Lateral Distribution of Surfactants in Waterborne Pressure Sensitive Adhesive Films: Theory and Experiment", poster paper presented by C.H. Lei at the 11th Meeting of the UK Polymer Colloids Forum, Manchester, UK, 11-12 September 2006
- "Debonding Mechanisms in Pressure-Sensitive Adhesives with Composition Gradients", oral paper presented by C. Carelli at the 3rd World Congress on Adhesion and Related Phenomena, Beijing, China, 16-18 October 2006
- "Designed Nanoscale Heterogeneities for Controlling Water-Borne Pressure-Sensitive Adhesive Performance", oral paper presented by F. Deplace at the 3rd World Congress on Adhesion and Related Phenomena, Beijing, China, 16-18 October 2006
- "How to Optimize the Adhesive Properties of Bilayer Pressure-Sensitive-Adhesives", oral paper presented by C. Creton at the Annual Meeting of the Adhesion Society, Tampa, USA, 18-21 February 2007
- "Lateral Distribution of Surfactants in Waterborne Pressure Sensitive Adhesive Films: Theory and Experiment", poster paper presented by C.H. Lei at the 233rd National Meeting of the American Chemical Society, Chicago, USA, 25-29 March 2007
- "Probing the Structure of Waterborne Core-Shell Particles in Pressure-Sensitive Adhesives with Atomic Force Microscopy", oral paper presented by C.H. Lei at the 233rd National Meeting of the American Chemical Society, Chicago, USA, 25-29 March 2007
- "Lateral Distribution of Surfactants in Waterborne Pressure Sensitive Adhesive Films: Theory and Experiment", oral paper presented by C.H. Lei at the 233rd National Meeting of the American Chemical Society, Chicago, USA, 25-29 March 2007
- "How can Tensile Tests be Useful to Design Optimized PSA?", invited oral paper presented by C. Creton at TECH 30 Global Conference VI, PSTC, Orlando, USA, 16-18 May 2007
- "Deformation and Adhesive Properties of Soft Polymer Films made from Core-Shell Particles", oral paper presented by F. Deplace at the Gordon-Kenan Research Seminar on Polymer Colloids, Proctor Academy, New Hampshire, USA, 22-24 June 2007
- "Synthesis of Crosslinkable Structured-Particle Latexes for Use in Water-Borne Pressure-Sensitive Adhesives", poster paper presented by M. Rabjohns at the Gordon Research Conference on Polymer Colloids, Tilton School, New Hampshire, USA, 24-29 June 2007
- "Correlation of Adhesive Performance with Particle Composition and Structure for Structured-Particle Water-Borne Pressure-Sensitive Adhesives", poster paper

presented by A. Foster at the Gordon Research Conference on Polymer Colloids, Tilton School, New Hampshire, USA, 24-29 June 2007

- "Deformation and Adhesive Properties of Soft Polymer Films Made From Core-Shell Particles", poster paper presented by F. Deplace at the Gordon Research Conference on Polymer Colloids, Tilton School, New Hampshire, USA, 24-29 June 2007
- "Lateral Surface Non-Uniformities in Drying Latex Films", oral paper presented by A.F. Routh at the 12th Meeting of UK Polymer Colloids Forum, Warwick, UK, 16-18 September 2007
- "Synthesis of Crosslinkable Core-Shell Latexes for Use as Water-Borne Pressure-Sensitive Adhesives", poster paper presented by M. Rabjohns at the 12th Meeting of UK Polymer Colloids Forum, Warwick, UK, 16-18 September 2007
- "Correlation of Adhesive Performance with Particle Composition and Structure for Core-Shell Water-Borne Pressure-Sensitive Adhesives", poster paper presented by A. Foster at the 12th Meeting of UK Polymer Colloids Forum, Warwick, UK, 16-18 September 2007
- "Proprietes de Deformation et D'adhesion de Films Prepares a Partir de Particules de Latex Coeur-Ecorce", oral paper presented by F. Deplace at 14èmes Journées d'étude sur l'Adhésion, Biarritz, France, 26-28 September 2007
- "Cycles de Traction Uniaxiale de Films Adhesifs Prepares a Partir de Particules de Latex Coeur-Ecorce", oral paper presented by J. Marchal at 14èmes Journées d'étude sur l'Adhésion, Biarritz, France, 26-28 September 2007

Dissemination to the General Public

- "Latex Technology Enhances Adhesive Performance", p. 18, issue 8, European Industrial Research, EC, October 2007 (*invited contribution*)
- "Designed Nanoscale Heterogeneities for Controlling Water-Borne Pressure-Sensitive Adhesive Performance (2004-2007)", *article submitted on request in March 2007 to the EC for inclusion in an EC brochure that is yet to be published*
- Master Class on "Polymer Nanomaterials" for A-Level College Students held at the University of Surrey on 5 July, 2007. A lecture on nanomaterials was given to about 30 students. The lecture was followed by a hands-on activity in which they compared the tack properties of *normal* adhesives to *nanomaterial* adhesives.
- A teaching resource, entitled "Fantastic Plastic," suitable for 12–15 year-old students was prepared using funds from outside of NsHAPe. CD-roms containing the resource were distributed to all schools in England and Wales (more than 4000). The CD-rom contained information on the nanostructure of waterborne PSAs along with a demonstration of polymer viscoelasticity.