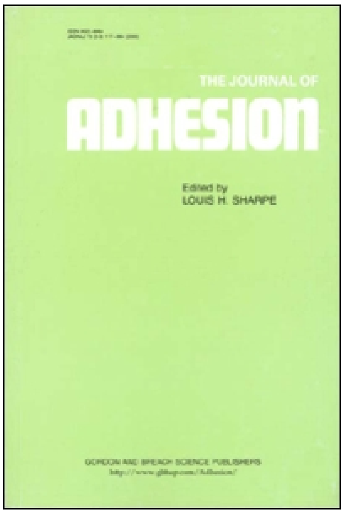

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Granier, V. , Sartre, A. and Joanicot, M.(1993) 'An Atomic Force Microscopy Study of the Wetting of an Inorganic Surface by Latex Particles', The Journal of Adhesion, 42: 4, 255 — 263
To link to this Article: DOI: 10.1080/00218469308026580
URL: http://dx.doi.org/10.1080/00218469308026580

J. Adhesion, 1993, Vol. 42, pp. 255–263
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Printed in the United States of America.

An Atomic Force Microscopy Study of the Wetting of an Inorganic Surface by Latex Particles*

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(Received January 21, 1992; in final form March 31, 1993)

Atomic Force Microscopy is used to investigate the wetting of a calcium carbonate crystal surface by latex particles when dried from dispersion. The measured particle heights are found to depend on the scanning rate and on the force of the probe tip acting on the sample. The analysis of the particle profile shows that the spreading is not governed by capillary forces. Below their glass temperature, the latex particles have weak adhesion to the crystal and are moved easily by the probe tip. This results in tip-induced organization of particles. Above their glass temperature, the particles spread on the surface and they are no longer moved by the probe tip.

KEY WORDS Atomic force microscopy; latex; latex-calcium carbonate adhesion; wetting; spreading of latex particles; latex particle shape; glass transition temperature; capillary forces.

INTRODUCTION

Synthetic latexes consist of colloidally-dispersed polymer particles which can be prepared by a tightly-controlled emulsion polymerization technique. These aqueous dispersions are commonly used in many industrial applications, such as paints, adhesives, paper coating and textile sizing. Most of the applications require the latex to form a continuous film upon drying and also to bind mineral charges within a composite layer. The formation of a continuous film from latex has been a fully-studied topic.[1–4] It results from coalescence of the particles, provided that forces produced during water evaporation are strong enough to overcome both coulombic repulsion forces of the charged particles and particle rigidity. In contrast, the spreading and the ordering of latex particles on an inorganic surface after water evaporation is a poorly-investigated field of research. The interactions between the polymer particles and the surface control the spreading of the particles and also the binding properties required for each application. These individual interactions with

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*Presented at the European Adhesion Conference EURADH '92, September 21–24, 1992, in Karlsruhe, Germany.

the filler surfaces are very difficult to study at the particle scale with conventional techniques such as contact angle measurement and electron microscopy.

Recent progress in surface science and technology has led to a variety of new scanning probe microscopes. Among them, Atomic Force Microscopy (AFM)[5] allows the imaging of insulating surfaces and the description of surface relief at the nanometer scale and, in some cases, down to the atomic level without destroying the surface. AFM is a very fast developing field and most of the studies are devoted to imaging biological molecules (cell surfaces,[6] nucleic acids[7] or proteins,[8] for example) or to demonstrate the atomic resolution of this technique.[9] Recently, AFM was also used to study latex film formation.[10,11]

In this paper, we report on the use of AFM to investigate the wetting of a calcium carbonate crystal surface by latex particles (about 100 nm in diameter). The system chosen consists of a styrene-butyl acrylate copolymer latex. The main variables of concern in this study are the glass temperature of the latex (T_g) and the drying and annealing conditions. It will be shown that these experiments enable us to determine that the capillary forces during water evaporation are not the "driving force" for the fixation of latex particles on the crystal surface.

EXPERIMENTAL SECTION

Latex Particles

Two aqueous dispersions of polymer latex particles were used in this study. The particles are spherical droplets made of a hydrophobic polymer core surrounded by a hydrophilic layer. The core is made of a copolymer of styrene (S) and butyl acrylate (BA). The core of each latex particle is surrounded by a thin hydrophilic layer made of acrylic acid (AA) sequences which are copolymerized with the core polymers. The amount of AA groups at the surface amounts to a monolayer coverage of the particle. These AA groups have been neutralized at pH = 8.0, hence they are charged and generate strong repulsions between the particles, thereby stabilizing the dispersion. After their synthesis, the dispersions were purified in an ultrafiltration cell. The main difference between the two dispersions is the chemical composition of the core polymers which determines the latex glass temperature. The average particle size, measured by electron microscopy, was found to be about 0.120 μm and 0.100 μm, respectively, for the two dispersions, with a narrow width of the corresponding size distribution. The main data concerning the dispersions are given in Table I.

TABLE I
Main features of the synthesized latex particles. The core is made of a copolymer of styrene (S) and butyl acrylate (BA)

Latex	Composition (weight %)	Particle size (nm)	T_g (°C)
A	S:36,7 BA:60	120	0
B	S:60 BA:35,33	100	41

AFM Imaging

The atomic force microscope used was a commercial one (Digital Instruments Nanoscope II system). It operates by scanning a surface with a sharp tip mounted on a cantilever as shown in Figure 1. The tip is triangular and the angle at the end of the probe tip is about 30°. For these experiments, a 25 μm x-y scanner was used, which allows relatively large fields to be imaged. The AFM head includes a focused laser beam which is reflected off the upper apex surface of a gold-coated silicon nitride triangular cantilever to a two-element photodiode detector. The triangular cantilevers were 200 μm in length with a spring constant of 0.12 N/m. The optical beam detection allows for the precise measurement (< 1 nm) in the vertical direction (z axis) of deflections by the cantilever and the attached probe tip. The sample stage mounting includes the x, y, z piezoelectric single tube scanner, which provides the precise x and y raster movement of the sample. The image-processing system converts the variation in voltage signals from the photodetector and z-piezo, as a function of probe position, into a three-dimensional image. AFM images were recorded in the constant force mode, where the applied force was kept constant by using an integral feedback loop and recording the z movement of the sample.

To conduct the AFM experiments, the calcium carbonate crystals were cleaved to obtain very smooth surfaces, with a roughness defined as the maximum displacement less than 2 nm. Samples were prepared by placing a 1 μl droplet of a diluted

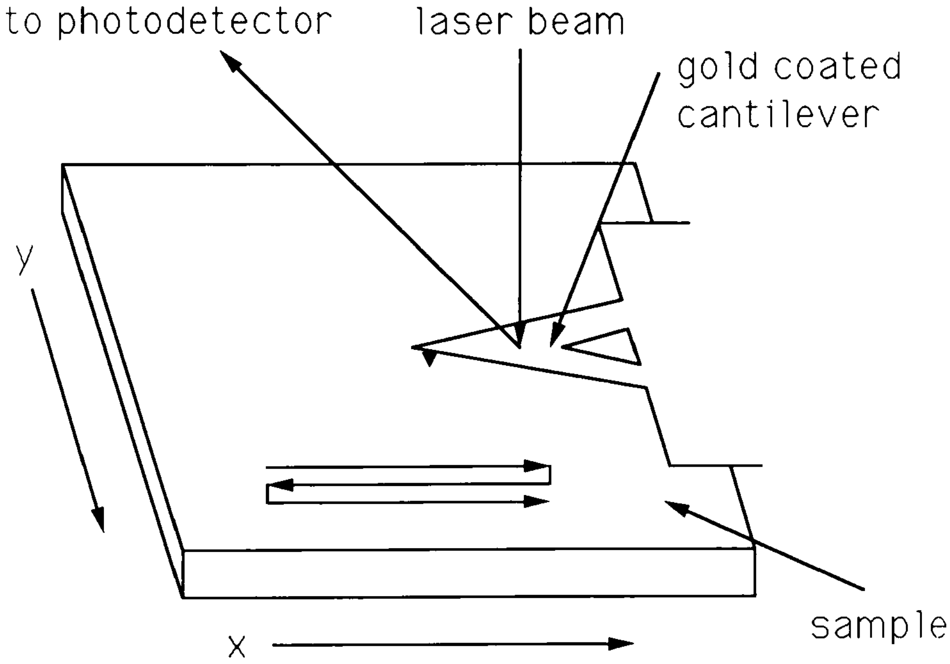


FIGURE 1 Cantilever and AFM scanning. The sample is scanned with a sharp triangular tip mounted on a cantilever. The small deflections of the cantilever are measured using a focused laser beam which is reflected off the gold-coated cantilever to a two-element photodiode detector. The x, y, z piezoelectric single tube scanner, located under the sample, provides the precise raster movement of the sample.

latex solution (0.2×10^{-3} in mass concentration) onto a crystal just after cleavage in order to minimize contamination of the cleaved surfaces. We have not studied the possible effect of any chemical reaction occurring between the aqueous medium and the calcium carbonate. The diluted latex solutions were prepared with ultrapure water and the dispersions were purified in an ultrafiltration cell after their synthesis. In consequence, we think that there are no chemical impurities in the aqueous medium. The only possible reaction which might occur is between water molecules and the calcium carbonate. The effects of such a reaction are independent of the latex specifications and cannot cloud our results concerning the influence of latex parameters on particle spreading. After drying at room temperature, the samples were directly imaged in air without performing a chemical analysis of the covered surfaces. For some experiments, the samples were annealed in an oven at different temperatures before AFM imaging.

RESULTS AND DISCUSSION

A typical AFM image obtained with latex A is shown in Figure 2. This image reveals the ordering of latex particles after water evaporation. The particles are rather well dispersed on the crystal and, for this chosen solution concentration, they do not cover the whole crystal surface. Only a few particles are brought into contact with each other. This means that, upon drying, the latex does not flocculate to form aggregates of tens of particles and that, as the solution evaporates from the surface, the capillary force pulls only a few spheres together. Figure 3 shows a typical particle

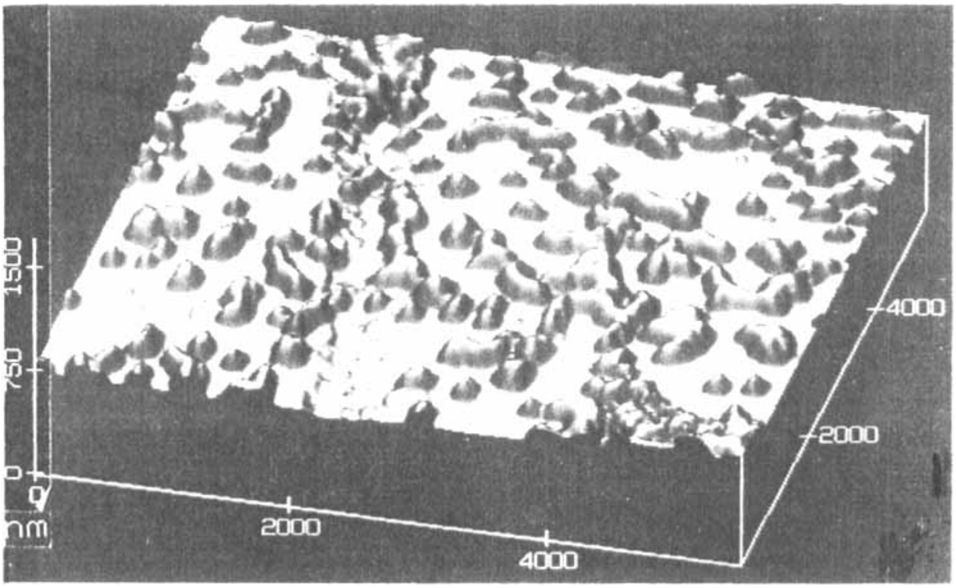
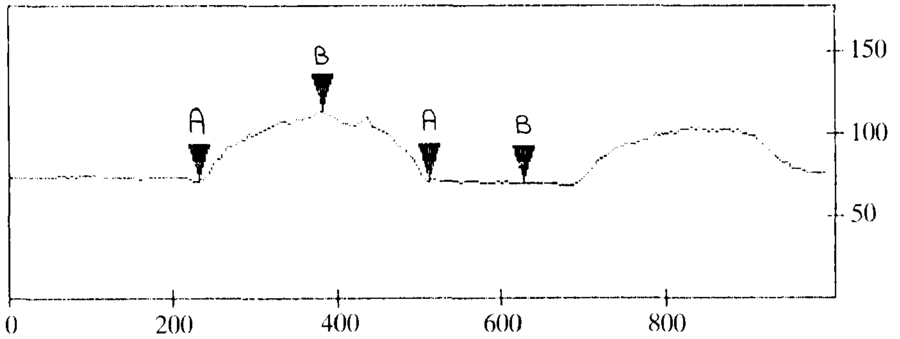


FIGURE 2 A 5000 nm by 5000 nm AFM constant-force image of latex A deposited on a calcium carbonate crystal after water evaporation. The vertical scale is height in nanometers. See Color Plate I.



Horizontal distance A-A (nm) : 270

Vertical distance B-B (nm) : 32

FIGURE 3 A typical particle profile obtained with the image-processing system. The analysis of the particle profiles enable us to determine their diameter and height.

profile obtained with the image processing system. The analysis of the particle profiles enable us to determine their diameter and height. For Figure 2, the analysis of ten profiles gives 260 ± 10 nm in average diameter and 30 ± 2 nm in average height for latex A particle dimensions. The error bars represent the standard deviation. These results indicate that the particles spread on the crystal surface. Thus, with the AFM technique, we can quantify the spreading.

The measured dimensions were found to be dependent on some parameters of the AFM apparatus as shown in Tables II and III. The force of the probe tip acting on the sample is controlled with the setpoint voltage parameter and it increases when the setpoint voltage is varied from -2 to $+1$ V.

TABLE II
Average particle dimensions (latex A) for three setpoint voltage values. The x-scan frequency was set at 5.8 Hz. The force of the tip acting on the sample increases with setpoint voltage

Setpoint voltage (V)	Average particle diameter (nm)	Average particle height (nm)
−2	260	30
0	260	26
1	260	21

TABLE III
Average particle dimensions (latex A) for two x-scan frequencies. The setpoint voltage was set at −2 V

X-scan frequency (Hz)	Particle diameter (nm)	Particle height (nm)
5.8	260	30
19.5	260	41

The force is given in units of a knob set on the AFM and not in units of nanoNewtons because the calibration, which depends on AFM parameters such as the cantilever spring constant, was not made at the time the experiments were performed. However, we can give a relative comparison between the forces. A setpoint of 0 volts means the force is approximately three times that with a setpoint of -2 volts. The results indicate that the measured particle diameter is independent of the force value. In contrast, the height decreases as the force applied by the tip is increased. In our experiments, the lowest attainable force was obtained with a setpoint voltage of -2 V.

The diameter and height values measured for two x-scan frequencies show that the height increases with x-scan frequency when the diameter remains unchanged. The particle diameter value seems to be reproducible and characteristic of the spreading. In contrast, the height value is very sensitive to experimental conditions and its interpretation is difficult. The large variation of the height values may be due to the fact that the latex A particles are soft ($T_g = 0$ °C) and that during the scanning the probe tip might deform the particle. As a consequence, for soft materials like polymers of low T_g, the height measurements have to be taken with caution. In the following experiments, the setpoint voltage was set at -2 V, the x-scan frequency at 5.8 Hz and we focused our attention on the diameter values.

After water evaporation at room temperature, the latex-covered crystals were annealed during 30 minutes at different temperatures and then imaged. The analysis of the profiles of the particles shows that their diameter remains equal to 260 nm even for annealing temperature up to 140 °C. The final particle spreading is attained after drying and it cannot be modified by sample annealing. At this point, we thought that spreading might be governed by capillary forces as is the case for coalescence of latex particles.

During AFM imaging of a crystal covered with latex B particles, we observed an effect of the probe tip, which is to move the particles slowly in the fast (x) scanning direction until the resistance of the particles is sufficient to cause a deflection of the tip. The 1000 nm by 1000 nm area shown in Figure 4a was scanned five times before imaging. The particles, which were initially well dispersed on the crystal surface, were brought into contact with each other by the probe tip. The latex B particles have weak adhesion to the crystal surface since they are moved by the tip. However, we cannot measure their adhesion level because we have no quantitative measure for the forces which are exerted locally by the tip on the latex particles, which are a function of tip geometry as well as the instrumental parameters described previously. We found that the tip interaction decreases with increasing full-scale scanning range, such that the particles could be imaged without being disturbed by the tip but at the cost of a lower resolution. This phenomenon may be attributed to an effect of the increased x and y scanning velocities at the higher scan size. Our attempts to image latex particles over a 1000 nm full scale scan range resulted in important particle distorsions (see Fig. 4a), although the minimum force was used to image the crystal (setpoint voltage $= -2$ V).

The analysis of the particle profiles gives 112 ± 6 nm in average particle height. Unlike for latex A, the latex B particle heights were not found to be dependent on the force of the probe tip acting on the sample. As a consequence, for hard materials

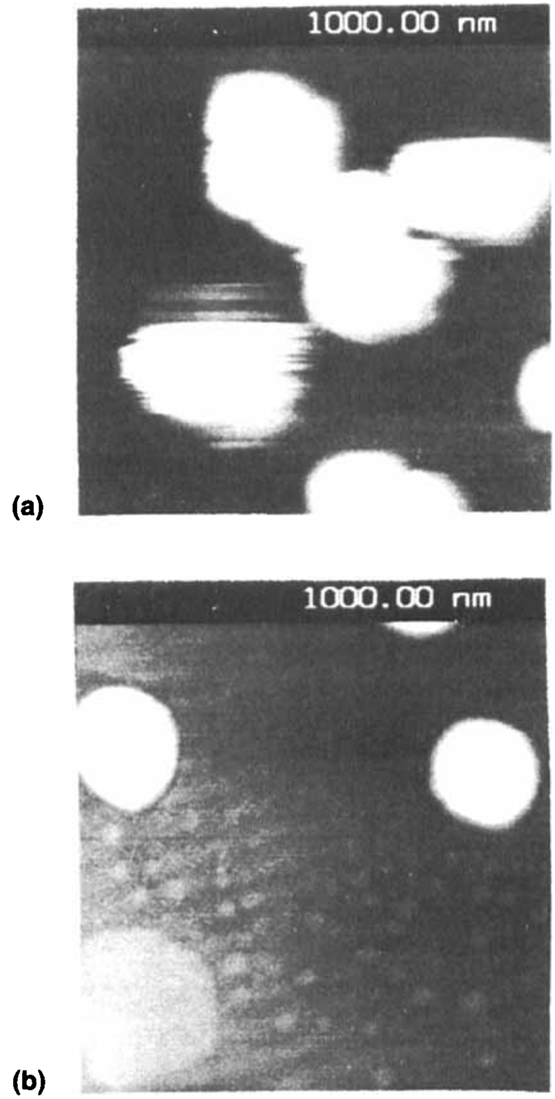


FIGURE 4 A 1000 nm by 1000 nm AFM constant-force image of latex B particles placed on a calcium carbonate crystal: a) after water evaporation at room temperature; b) after annealing (30 minutes at 80 °C). The setpoint voltage was set at -2 V and the x-scan frequency at 5.8 Hz. See Color Plate II.

like polymers of high T_g (T_g above room temperature), we think that the height measurements are reliable. The average height of 112 nm is very close to the latex particle diameter measured by electron microscopy (100 nm), hence the latex B particles remain spherical. The determination of the latex B particle diameter is difficult to perform. The particles are moved by the tip during the scanning due to their weak adhesion to the crystal surface, which induces an error in the measured value.

During water evaporation, capillary forces do not cause any spreading of the particles. After annealing of the same sample at 80 °C during 30 minutes, we noticed a sudden spreading of the particles which were no longer moved by the probe tip as we can see on Figure 4b. The average particle diameter was found to be 250 nm, and it was impossible to increase the particle spreading by a further annealing even during 12 hours at 140 °C. This sudden spreading is not due to capillary forces since the sample is dried before annealing. When the sample is dried at 80 °C for 3 minutes instead of room temperature, the particles are not moved by the probe tip and the measured diameter is also 250 nm.

We have depicted in Figure 5 the profiles of latex B particles recorded as a function of thermal treatment of the sample. By comparing the profiles for the three types of experiments, we can say that capillary forces do not govern particle spreading although these forces are the "driving force" for the formation of a continuous film from latex.[2,12] This spreading phenomenon is attributed to the fact that annealing was performed at a temperature higher than the T_g of the latex. Above T_g, the polymer is in the rubbery state and the molecular chain mobility is greatly increased, compared with the glassy state (below T_g). Particle spreading is not

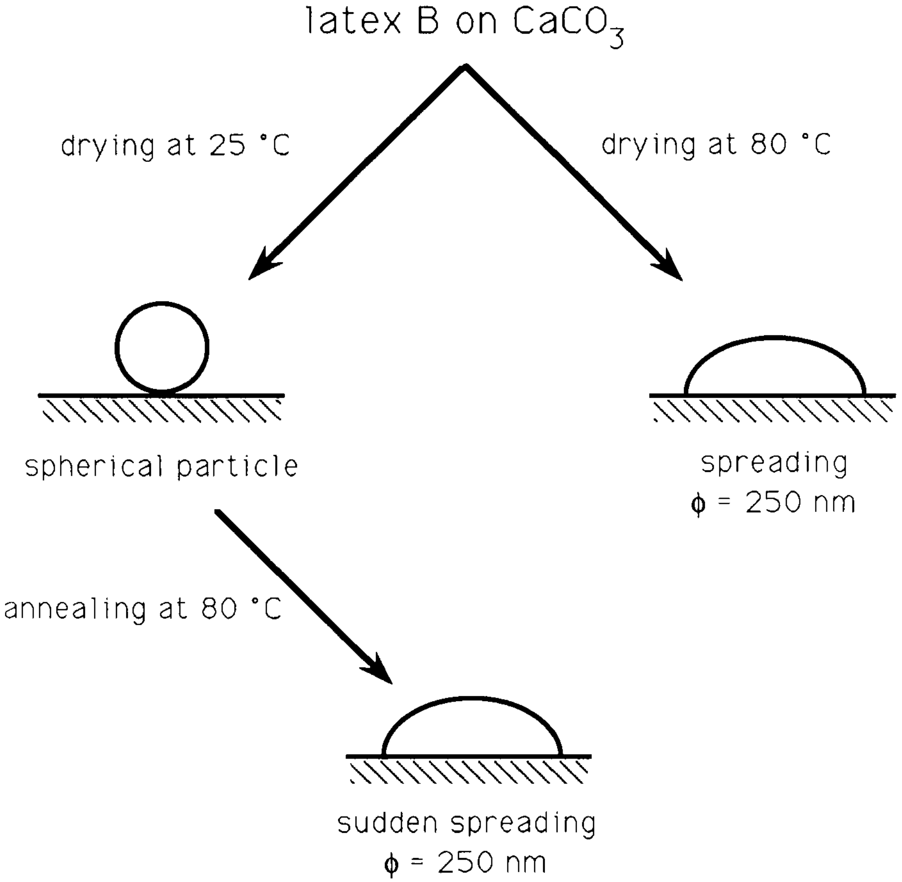


FIGURE 5 Profiles of latex B particles as a function of thermal treatment of the sample.

governed by capillary forces but by the "mechanical properties" of the latex. In other words, a particle can spread on a surface only if the chain mobility is high enough, which was obtained at room temperature for latex A.

CONCLUSIONS

This study shows that AFM can be used at a sub-micron scale to investigate the wetting of an inorganic surface by latex particles at the particle scale. Particle heights measured by AFM were shown to depend on experimental parameters (scanning frequency, tracking force applied). We think that more precise measurements could be done under aqueous conditions using an AFM liquid cell attachment. The particle-diameter measurements showed evidence that particle spreading is not governed by capillary forces. Below their T_g, the particles do not spread on the surface and they are moved by the AFM probe tip. In contrast, above their T_g, they spread suddenly and are no longer moved by the tip. The determination of parameters governing the latex particle diameter after spreading is now under investigation.

Acknowledgements

The latex dispersions were synthesized and characterized by J. F. d'Allest. We also thank Y. Jugnet (ESCA Centre, Lyon University) for her technical assistance during AFM experiments.

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