THE APPLICATION OF DIELECTRIC ANALYSIS TO DRYING LATEX FILMS

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Measurements of real and imaginary capacitance (C' and C'') have been made during the drying of a film-forming latex. In one experiment dielectric measurements at frequencies between 1 Hz and 100 kHz were made simultaneously with gravimetric measurements on a microbalance. It was found that both the rate of water evaporation and the a.c. conductance decrease sharply at high polymer volume fraction. These results are discussed qualitatively in terms of a model for the film-forming process. In another experiment C' and C'' were recorded at 10 Hz along with automatic measurements of the build-up of the scratch resistance of the film. It was found that the mechanical response to film-formation appears significantly earlier than the dielectric response. This is also discussed qualitatively in terms of the model.

Keywords: dielectric analysis, latex films, walescence

Introduction

Effective coalescence during film drying is an important requirement for polymer latices used in coatings, in order to achieve good optical, mechanical and barrier properties. An understanding of the film-forming mechanism is, therefore, of great practical importance. This subject, which has received considerable attention in the literature, was recently reviewed by Eckersley and Rudin [1]. Dielectric techniques are well suited to the study of latex film formation because they are potentially sensitive to all the different stages throughout the film-forming process, they can be applied to films drying in-situ on a test panel and they can readily be applied simultaneously with other techniques such as gravimetry.

Dielectric measurements at microwave frequencies have previously been applied to drying latex films by Henry *et al.* [2, 3]. They found that this technique was sensitive to different stages of film-formation such as flocculation and compaction of the latex particles and could distinguish between film-forming and non-film-forming latices. Systematic variations were found for changes to latex

variables such as surface charge density, particle size distribution and ionic strength of the medium. Dielectric measurements at lower frequencies (10^{-5} to 10^7 Hz) are more convenient to apply than microwave techniques, since commercial analysers are available, and have the advantage that measurements across a range of frequencies can be made simply. Hill and co-workers have published a series of papers describing the application to latex film formation of dielectric analysis in this frequency range [4–6]. They noted three regions in the variation of conductance with drying time:

a) an initial induction period, attributable to evaporation of water from the bulk film,

b) a sharp drop, consistent with further solvent loss leading to immobilisation of ionic groups on the surfaces of the latex particles,

c) a power law decay, which can be explained by the presence of a percolation network of conductive pathways which are gradually eliminated by coalescence.

In this preliminary work a similar methodology to that developed by Hill *et al.* was used to obtain the dielectric measurements [4]. Flat cells were employed to allow direct measurement of films without hindering solvent evaporation. Because a cell constant cannot be easily defined for such an electrode arrangement the results are quoted as real and imaginary capacitances (C' and C'') rather than the corresponding permittivities. The real capacitance measures the polarisation of the sample due to motion of bound charges while the imaginary capacitance measures conductance due to the motion of free charges as well as loss processes such as molecular relaxations. Simultaneous experiments were carried out, combining the dielectric technique with gravimetry and with a mechanical technique for following film-formation [7].

Experimental

Dielectric measurements were made using a Schlumberger 1260 Gain-Phase Analyser. A variable gain buffer amplifier circuit (current-to-voltage converter) was used to increase the input impedance. The measurements were computer-controlled using a Tandon PC and software written in GW-BASIC.

Gravimetric measurements were made using a Cahn DCA-312 Dynamic Contact Angle Analyser. The electrodes for the combined dielectric/gravimetric experiments are shown in Fig. 1. They consisted of two strips of pure tin foil (99.999%, 0.025 mm thick, Aldrich) mounted on a glass cover slip. Wet films with a thickness of 150 μm were deposited on the electrodes using a miniature block spreader. The electrodes were suspended in the balance via the device

shown in Fig. 1. This allowed electrical contact to be made to the electrode without affecting the weight reading, using very fine stainless steel wires (0.063 mm diameter). The combined dielectric/gravimetric experiments were carried out in a controlled atmosphere room at 25°C±0.5°C and 40±2% RH.
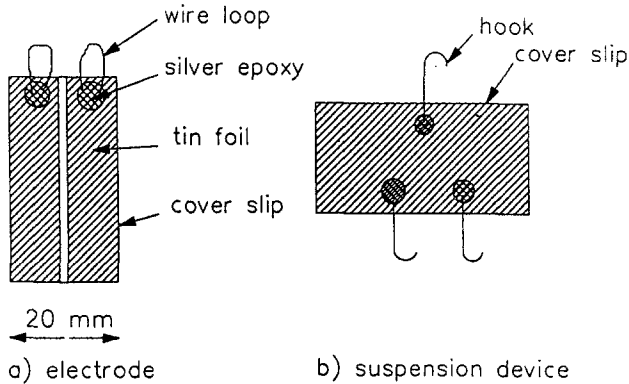

Fig. 1 Electrode used for combined dielectric and gravimetric experiments and the device used to suspend the electrode in the microbalance

The Thin Film Analyser (TFA), developed at ICI Paints, was used to monitor the build-up in scratch resistance of a drying latex film while the dielectric reponses was measured [7]. The instrument is based on an XY recorder in which the pen-holder has been replaced by a force-sensing device, used to measure the force required to drag a needle through a drying coating. The simultaneous dielectric/TFA measurements were made on large area interdigitated electrodes as shown in Fig. 2. Wet films of thickness 200 μm were laid down using a block spreader. These experiments were conducted at ambient temperature in a conventional laboratory at 21°C±2°C.

The latex used for this study is a high MW acrylic co-polymer which readily forms a clear film at ambient temperature. This latex is stabilised by a combination of ionic and steric mechanisms. It contains small quantities of acrylic acid
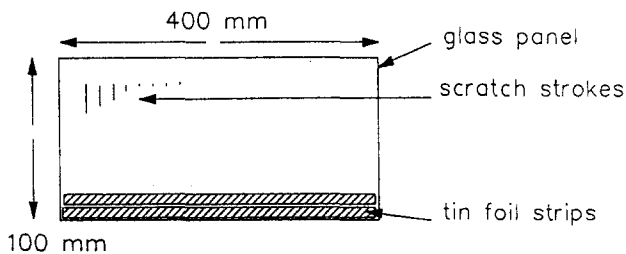

Fig. 2 Large area interdigitated electrodes used for combined dielectric and TFA experiment

which provides charge stabilisation and also solution-phase cellulose-based polymers for steric stabilisation. The T_g was determined by DSC, the specific gravity using an Anton Paar DMA46 densitometer and the average particle size using a Malvern Mastersizer. These physical properties are summarised in Table 1.

Table 1 Summary of the physical properties of the latex

T_g from (DSC)	Volume Averaged Particle Size	Specific Gravity	Calculated Dry Polymer Density
15°C	410 nm	1.046 g/cm^3	1.092 g/cm^3

Results

1) Simultaneous dielectric and gravimetric experiments

The drop in coating weight of the latex due to evaporation of water frorm the film is shown in Fig. 3. It can be seen that the curve is approximately linear up to about 400 s, after which there is a marked decrease in the rate of solvent loss. It has been reported in the literature that this point indicates the transition from the stage of film drying, where evaporation of bulk water occurs, to the stage
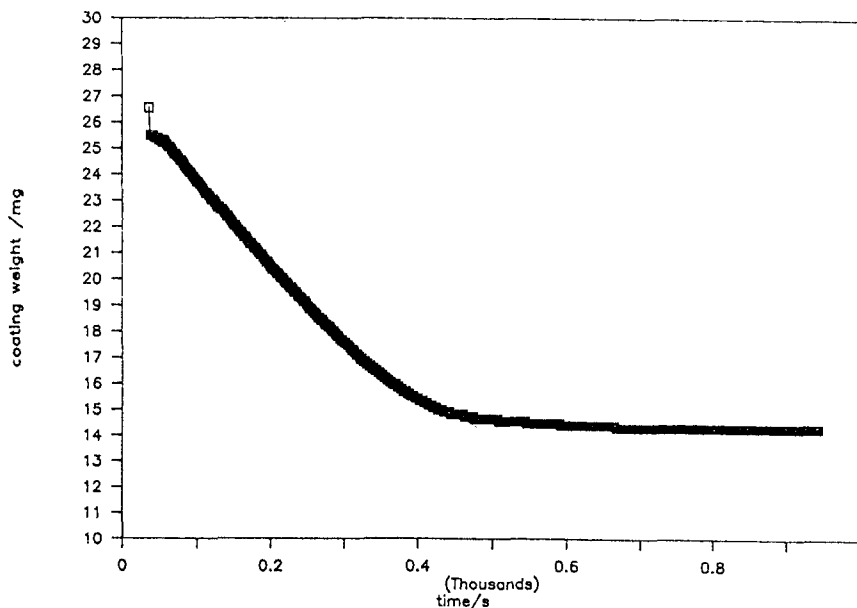

Fig. 3 The variation in the latex coating weight with time

where water is lost from between closely packed polymer particles [3]. Using the known solids content of the latex and the estimated dry polymer density (see Table 1) the weight loss data was used to calculate the polymer volume fraction in the drying film as a function of time. The result is given in Fig. 4. It can be seen that the marked change in the rate of water loss at 400 s corresponds to a polymer volume fraction of about 95%. This is considerably greater than the theoretical closest-packed volume fractions for monodispersed spheres, 74% for cubic closest packing (ccp) and hexagonal closest packing (hcp) or 64% for random ccp and hcp [3]. Although the significant polydispersity in the particle size of the latex used might be expected to increase these theoretical values to some extent it probably does not account for the large discrepancy noted here. A possible explanation for these results is discussed below, in the light of the dielectric data recorded simultaneously.
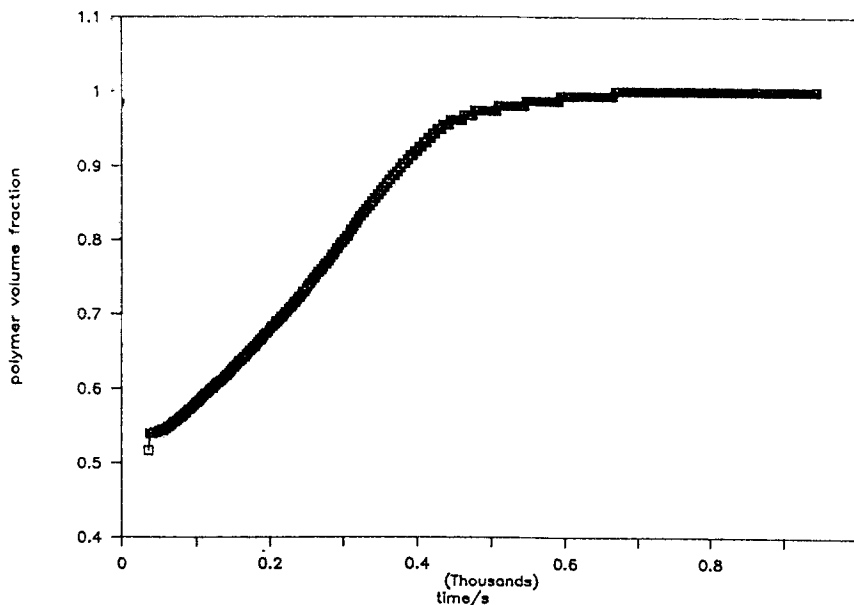

Fig. 4 The calculated polymer volume fraction as a function of drying weight with time

The dielectric analyser was set to continuously perform measurements at ten different frequencies between 1 Hz and 100 kHz. Each frequency scan took 38 seconds. The variations in C' and C'' with drying time at the different frequencies are shown in a three-dimensional form in Fig. 5. The time taken for each scan is ignored in this plot and the scan mid-point is used for each frequency. It can be seen that close to 400 s both C' and C'' undergo step decreases

at all the frequencies studied. The frequency dependence of the complex capaci-
tance components at different drying times is more clearly shown in Fig. 6. In
their general form these curves are similar to those reported for wet and dry
latex films by Hill *et al.* [5] Although a rigorous attempt to quantitatively fit the
data has not yet been attempted, simple investigations with equivalent circuit
models suggest the following qualitative interpretation. The $\log C''/\log$(fre-
quency) curves have slopes close to –1, which is indicative of a d.c. conduction
process, except at low frequencies at short drying times and at high frequencies
at long drying times, where the slopes become less negative. The $\log C'/\log$(fre-
quency) curves exhibit plateaux at high frequencies whose values become
smaller at longer drying times. This is indicative of a non-dispersive capacitance
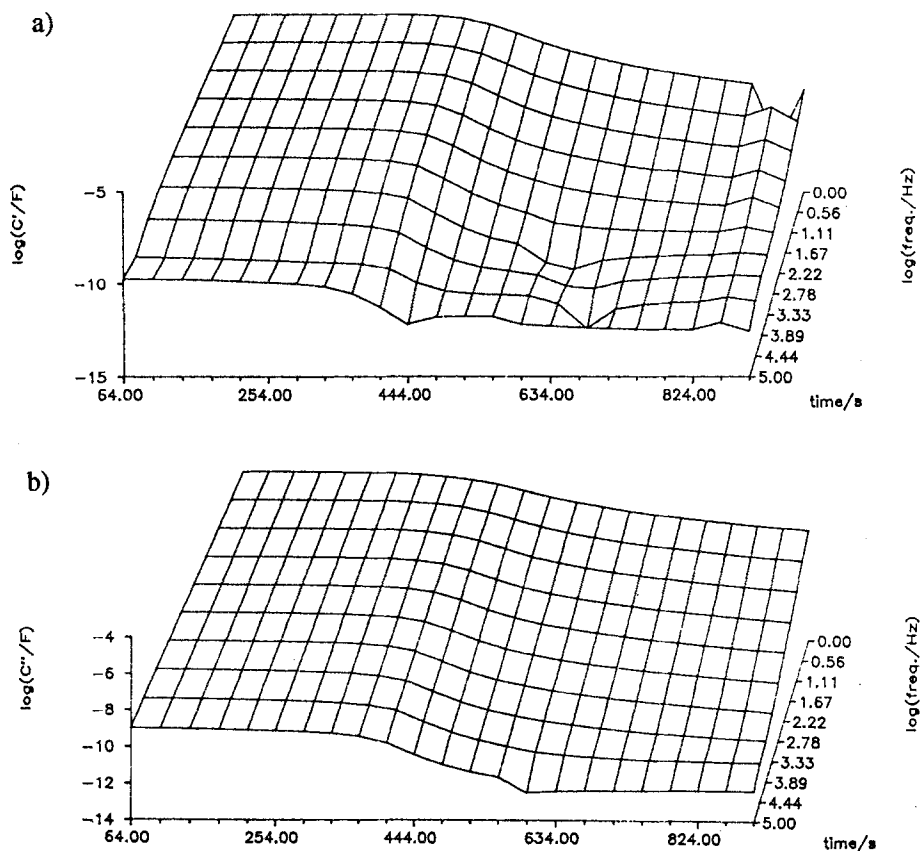element. At high frequencies and intermediate drying times, therefore, the data

Fig. 5 Three dimensional representation of the real and imaginary capacitance of the latex film *vs.*
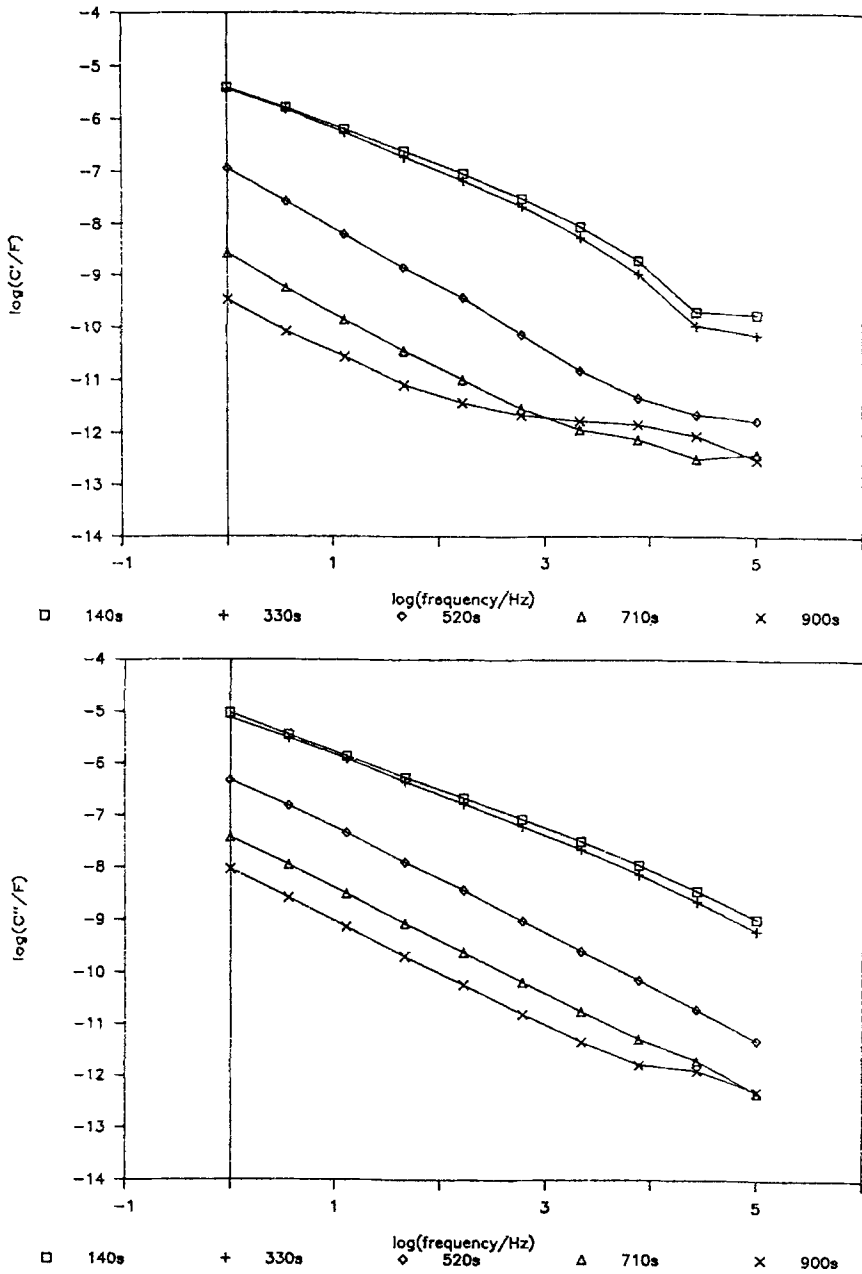frequency and drying time; a) C' b) C''

Fig. 6 The variations in the real and imaginary capacitance of the latex film with frequency at different drying times

can be approximately accounted for in terms of a d.c. conductance in parallel with a non-dispersive capacitance. Both the conductance and the capacitance decrease with the fraction of water in the film and also possibly with the decrease in film thickness. The deviations in the C' and C'' curves at low frequencies and at short drying times are suggestive of contributions fromelectrochemical processes at the electrode surfaces. The deviations at high frequency and long drying times may be artefacts as they appear close the lower limiting capacitance measurable with the instrument.

The imaginary capacitance is related to the real conductance by the equation:

$$G'(w) = w C''(\omega)$$

Recording the dielectric measurements simultaneously with weight loss measurements allows the dielectric parameters to be plotted *vs.* film composition directly. Real conductance *vs.* polymer volume fraction, for different frequencies, is shown in Fig. 7. It can be seen that G' becomes approximately independent of frequency at longer drying times and towards higher frequency, in agreement with the discussion above. Figure 7 is also notable for the sharp drop in G' above a critical polymer volume fraction of around 95%. As was considered
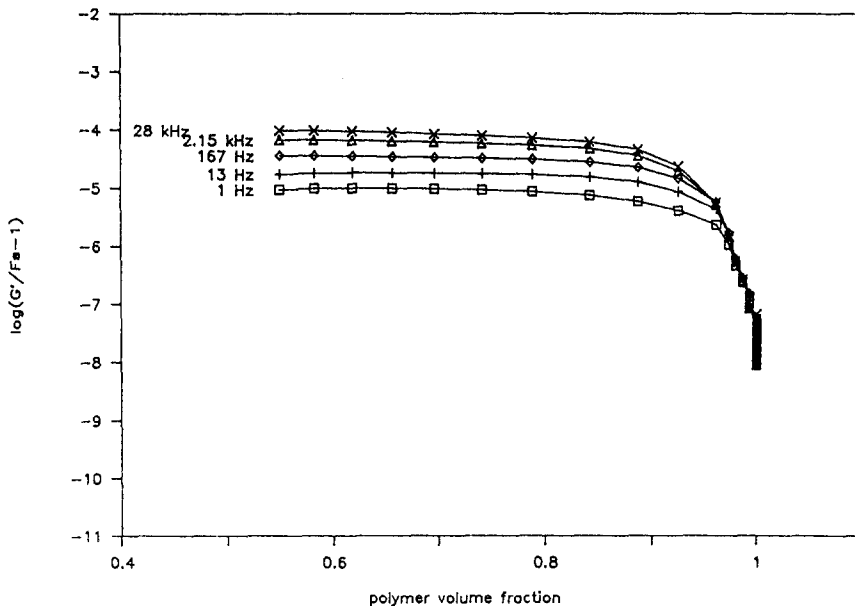

Fig. 7 The variation in the a.c. conductance of the drying latex film as a function of polymer volume fraction

with the gravimetric data above, this is close to where the sharp decline in the rate of water loss occurs.

It is proposed that the weight loss and conductance data are qualitatively consistent with models of latex film formation involving the following stages:

a) loss of bulk water leading to close-packing of polymer spheres.

b) deformation of the spheres to form close-packed polyhedra with channels of water in between.

c) coalescence of polymer particles across the polyhedral faces, so successively cutting of channels of water.

A sharp drop in conductance would be expected when a sufficient number water channels are cut to eliminate continuous pathways through the film. The rate of water loss would also be expected to fall dramatically at this point as the residual water in the channels becomes trapped. Physically this behaviour might be quantitatively treated using a percolation model, as has been suggested by Hill *et al.* [5]

2) Simultaneous dielectric and thin film analyser measurements

Figure 8a) shows the variations in C' and C'', measured at a single frequency of 10 Hz for a film of the latex drying on a large area interdigitated electrode placed on the Thin Film Analyser (TFA). Figure 8b) shows the variation in scratch resistance measured simultaneously by the TFA on the same test panel. It is thought that the TFA is sensitive to the sharp build-up in film viscosity that occurs at a critical stage during the film-forming process [7]. It can be seen that the rise in scratch resistance occurs significantly earlier than the step-like decreases in C' and C''. this suggests that the two techniques are sensitive to different stages of the film-forming process. The viscosity of the latex film is expected to rise sharply when the spherical polymer particles approach their close-packed limit, i.e. during stage b) above. As already discussed, however, the dielectric parameters are expected to change dramatically only when the aqueous phase becomes non-continuous, i.e. during stage c).

Conclusions

It has been observed with a film-forming latex that both the rate of water evaporation and the a.c. conductance of the drying coating decrease dramatically at a critical polymer volume fraction of around 95%. This is significantly larger than the theoretical value for close-packing of spheres. This is qualitatively consistent with a model in which significant deformation of the close-

packed latex particles occurs before coalescence takes place. The form of the conductance changes suggests that coalescence might be described by a percola-
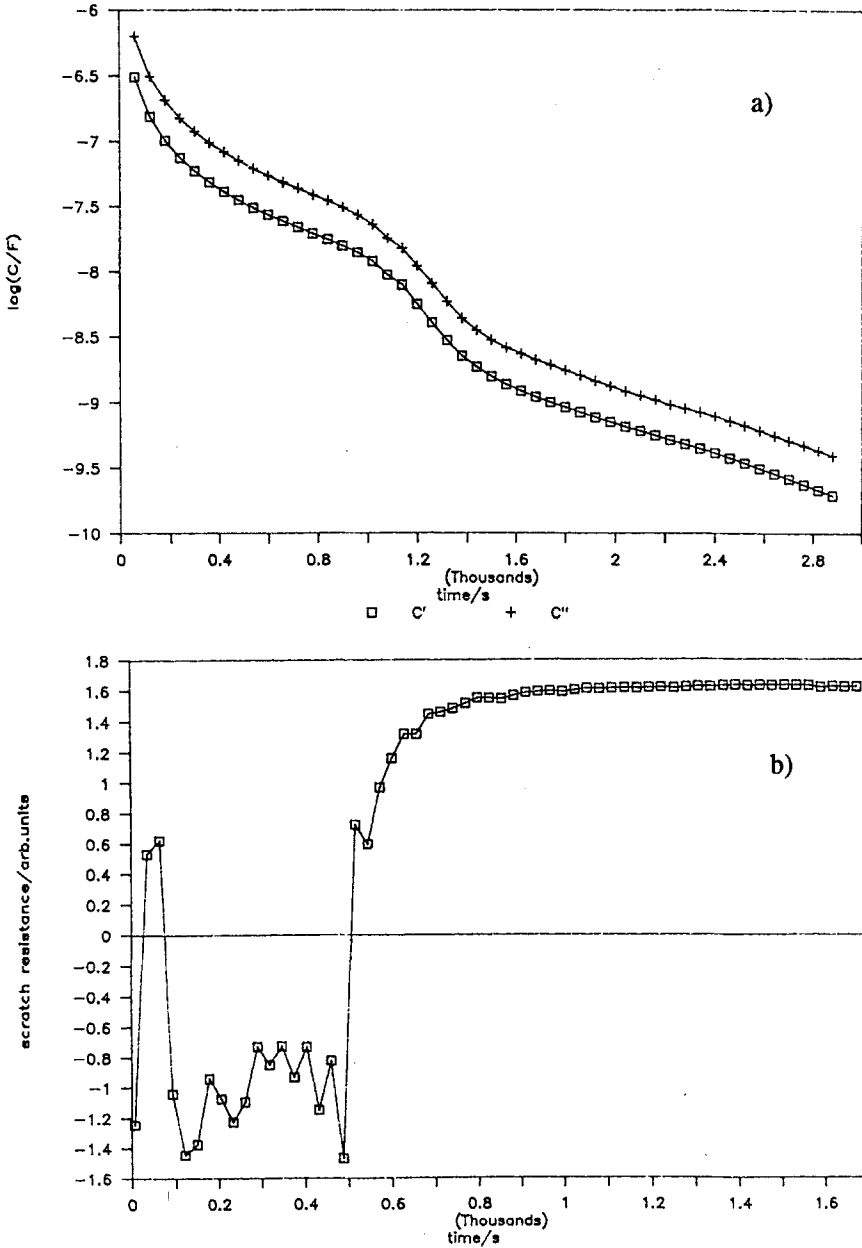

Fig. 8 Results for a drying latex film of a combined experiment with the dielectric analyser and the thin film analyser; a) C' and C'' b) scratch resistance

tion network of conducting channels that are successively eliminated at random by fusion of adjacent particles.

It is hoped that these preliminary results demonstrate the potential of combining dielectric measurements with these other techniques, in contributing to the understanding of the latex film-forming mechanism.

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Zusammenfassung — Beim Trocknen eines filmbildenden Latex wurden Messungen der reellen und imaginären Kapazität (C' und C'') durchgeführt. In einem der Experimente wurden parallel zu den dielektrischen Messungen bei Frequenzen zwischen 1 Hz und 100 kHz simultane gravimetrische Messungen auf einer Mikrowaage durchgeführt. Man fand, daß sowohl die Wasserverdampfungsgeschwindigkeit als auch der Wechselstromwiderstand bei hohen Polymer-Volumenbrüchen steil abfällt. Diese Ergebnisse werden mit Hilfe des Modelles für die Filmbildung diskutiert. In einem anderen Experiment wurden C' und C'' bei 10 Hz registriert, parallel zu Messungen der Entstehung der Kratzfestigkeit. Man fand, daß das Material bei der Filmbildung mechanisch gesehen wesentlich eher reagiert als dielektrisch. Dies wurde ebenfalls anhand des Modelles diskutiert.