

FILM FORMATION FROM AQUEOUS COLLOIDAL NANO - SUSPENSIONS: EFFECTS OF NANOMECHANICAL PROPERTIES

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Abstract:

Evaporation from suspensions of polymer particles at temperatures lower than the glass transition (T_g) generates powder, whereas this same process generates crack free films for $T > T_g$. This has been the subject of research by several groups. Some groups focused on the morphology of crack free films and others locked their efforts on the physics of crack formation of hard colloidal suspensions, thus the passage between the two situations was less investigated. We are focusing film formation process and particularly in the passage from cracked to crack-free film. We studied the evolution of the cracks during the drying of the suspensions in trans- T_g zone. We showed that drying for $T < T_g$ generates parallel, regularly spaced cracks similar to the morphologies observed in the unidirectional drying of hard silica particles. And that the distance between cracks D_c undergoes an abrupt jump in the trans- T_g zone. We exploited these observations to describe the nano-mechanical properties of the nanoparticles and their role in the process of film formation.

Résumé:

Le séchage des suspensions à des températures inférieures à la température de transition vitreuse (T_g) des polymères génère des poudres, alors que ce même procédé engendre des films sans craquelures pour $T > T_g$. Ce problème a été le sujet de recherche de plusieurs groupes; certains ont centrés leur recherche sur les propriétés de films non-craquelés, d'autres ont étudié les mécanismes de formation des fissures pendant le séchage de suspensions colloïdales dures. En revanche, la transition entre les deux a été relativement peu traitée. Nous avons étudié l'évolution des craquelures lors du séchage des suspensions, au dessous et au dessus de T_g . Nous avons montré que le séchage pour $T < T_g$ génère des craquelures parallèles, régulièrement espacées, similaires aux morphologies observées dans le séchage unidirectionnel de colloïdes dures. Et la distance entre craquelures D_c subit une transition brusque dans la zone de T_g du polymère. Nous avons exploité ces observations pour décrire les propriétés nano-mécaniques des nanoparticules et leur rôle dans le procédé de formation de film.

Key-words: Glass Transition, Minimum Film Formation Temperature, Viscoelasticity, Latex.

1 Introduction

Drying aqueous suspensions of polymer particles (latex) yields powder at low temperature and homogeneous crack free film at high temperature. This process is of great importance in many environmental friendly applications: coating, adhesives, paints etc ^[1]. Although water based coatings contain mainly water as the solvent, they still contain Volatile Organic Compound VOC (~15%) to aid the fabrication of crack free films. The Ultimate objective of the coating technology is a Zero-VOC-coating. Numerous studies were dedicated to the different phenomenon involved in this subject: drying phenomenon ^[1-5], the formation of cracked patterns ^[6-11] and morphology of crack-free films ^[12-16]. Film formation from drying colloidal suspensions goes through 3 main stages ^[1] (FIG. 1): a) concentration of the colloidal suspensions and the formation of closed packed array of spherical particles (hexagonal

structure), b) deformation of the particles into a hexagonal form with 12 faces, c) polymer interdiffusion between adjacent particles and formation of tough film^[4, 5]. The fate of cracked or crack free film formation establishes between stage b and c. Brown (1956)^[1] estimated the criterion for film formation by approximating the pressures generated at the surface of the film by the Young-Laplace equation as: ' $P = 12.9\gamma_{wa}/R_0$ ', where P is the resultant required pressure, γ_{wa} is the water-air surface tension and R_0 is the radius of the two particles joining/fusing together. Most recently, Routh and Russel (1999)^[2], considering the shear modulus (G) of the particles, have put forth another criterion for film formation taking into account the closure of the voids by capillary forces during drying as: ' $GR_0/\gamma_{wa} < 309$ '.

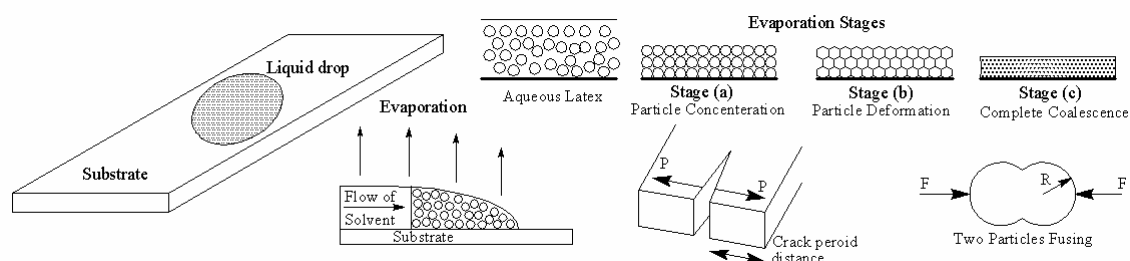


FIG. 1 – The three drying stages and crack generation.

Apart from the description of the stresses, Minimum Film Formation Temperature (MFFT) has its unique importance in the process of film formation, as it is a characteristic temperature where a crack-free film forms. The MFFT value is traditionally measured using temperature gradient ruler^[12]. MFFT of a polymer is affected by the elastic Modulus ' G ' and to a lesser extent by the viscosity ' η '^[1-3]. It is dependent on particle size, the drying time, the rate of water evaporation and on the nature and mainly on the glass transition temperature^[3]. Many papers have reported interesting morphologies of crack patterns during drying of colloidal suspension of silica hard latex^[6-8, 16]. C. Allain et al. (1995)^[6, 7] researched on crack patterns in forced unidirectional drying and found the well spaced ordered array of cracks and proposed the dependence of crack spacing on the film thickness. Weitz et al. (2003)^[8] studied the dynamic of crack propagation in unidirectional drying. Recently, Routh et al (2006)^[12-13] and Russel et al. (2005)^[14-15] reported experiments on the crack patterns in drying from a free surface of circular drops on solid substrate. They proposed that capillary pressure is the cause for the initiation and propagation of the cracks^[14-17]. Routh et al. (2004) proposed a hydrodynamic model for the estimation of the spacing between the cracks^[13]. There are other models; presented by C. Allain et al. (1995)^[6], Sasa et al. (1997)^[11] which take into account the mechanical stress technique for the determination of the crack spacing.

We can divide the literature on the drying of colloidal suspensions into two groups, the first group focused on the physics of crack patterns in hard colloidal particles (Allain, Weitz, etc)^[6-8], and the second group focused mainly on the final morphology of crack-free films (Winnik, Cabane etc)^[4, 5]. We are bridging together these two fields by studying the evolution of the cracks patterns morphology in the transition zone from powder regime to the crack-free film regime. We also study the effect of the nano-mechanical properties of the nanoparticles on the crack patterns in the transition zone. We studies crack formation in radial drying of aqueous polymer suspensions of polybutylmethacrylate colloidal nanoparticles (50nm diameter) with different nanomechanical properties (different cross linking ratios).

2 Materials and Methods

Butyl-Metha-Acrylate (BMA, Aldrich, 99%) was used. Double deionised water was used in the emulsion polymerization. Crosslinker used was ethylene glycol dimethylacrylate

(EGDMA, Aldrich, 99%) The surfactant, sodium dodecyl sulfate (SDS, Aldrich, 99%), initiator, potassium persulfate (KPS, Aldrich, 98%) and sodium bicarbonate were used as received. Polybutylmethacrylate were prepared in batch emulsion polymerisation. The polymerisation was carried out under a nitrogen atmosphere. PBMA particles were prepared using a standard emulsion polymerisation setup in 200 ml three-neck round glass flask, equipped with a mechanical stirrer, a condenser, and a nitrogen inlet. All the ingredients, were mixed and heated to 70°C except the initiator, was added when the temperature reached the desired temperature. The reaction was stopped after 12h. The crosslinker (EGDMA) was added drop wise to the mixture in order to control the crosslinking distribution within the particles to 0, 1, 5 and 10%. Monomer concentration was 10% by wt. Surfactant and free ions were removed from the dispersions by a mixture of anionic and cationic exchange resins (Dowex, Aldrich). Particle diameters (D) were measured using dynamic light scattering (Malvern 5000) and the bulk glass transition was measured by DSC (TA 2000) in modulated mode. The drying was carried out in oven with controlled humidity and temperature. Precision measuring micro balance, METTLER TOLEDO Balance AG245, was placed inside the oven for the insitu measurements of the mass. The morphology of the cracks was observed with WILD HEERBRUGG MAKROSCOP Switzerland, Makro-zoom 1:5, M420 1.25x, equipped with a digital camera. The depth profiles of the films were examined by a profilometer (SM7-ProfilTest, TL70). A 0.10 ± 0.02 g solution drop on glass substrate was dried in an oven set at 20% humidity. Multiple experiments were conducted with varying temperature from room temperature to a limit where a crack free film is formed for each sample (TABLE. 1).

Specimens	PBMA-0	PBMA-1	PBMA-5	PBMA-10
Cross-linking percentage	0%	1%	5%	10%
Particle size (Diameter) nm	68	50	46	52
Glass Transition (°C)	28	35.8	45	49.6

TABLE. 1 – Properties of the samples used.

3 Results and Discussion

3.1 Crack Patterns in the Glassy Regime

Water evaporation from the 20mm circular drop on glass substrate takes about 110mins. At the end of the evaporation process, circular film of dried polymer of with 40-100 μ m thickness was obtained. When the polymer suspensions were dried below the glass transition of the polymer, we observed an interesting morphology of crack patterns (FIG. 2). The cracks were well organized, longitudinal, periodic and parallel. They seem always to emerge from the edge and propagate towards the central region.



FIG. 2 – Sequence wise Pictures of PBMA dried samples at 27°C.

The case of formation of periodic crack patterns was observed in the forced unidirectional drying of hard colloidal suspension by C. Allain et al. (1995) ^[6, 7] and recently by the group of

Weitz et al. (2003)^[8]. The drying in these experiments was performed on suspensions between two glass plates open from one side only; hence the unidirectional drying was forced by the geometry of the set-up. Although our films were dried in open air in circular geometry, we found well comparable crack patterns to the forced unidirectional drying experiments. Recently Routh et al (2006)^[12, 13] and Russel et al. (2005)^[14, 15] also reported periodic patterns in free surface drying of circular drop of hard colloidal suspensions. It is accepted that free surface drying of small drops of liquid suspensions is heterogeneous, i.e., faster on the edge than in the drop centre^[9]. The drying starts from the edges of the drop and continue towards the centre^[9]. This will yield a unidirectional drying similar to that of the forced unidirectional drying between two plates^[6-8]. Cracks were reported to propagate with the drying front and appear during the passage from the gel to solid state^[8]. The distance between cracks (D_c) was found to range between 80 μm to 160 μm for the various PBMA suspensions investigated here at 27°C. These values fall in the same range of the results reported by C. Alain on unidirectional drying of silica suspensions^[7-8] for the same film thickness of 60 to 120 μm .

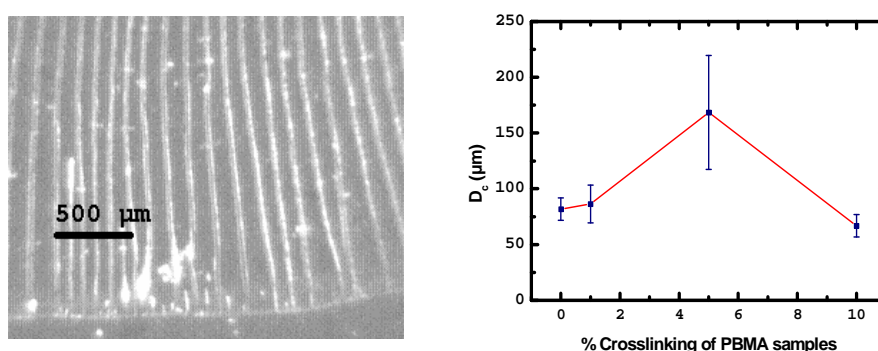


FIG. 3 – (a) PBMA-1% at 27°C, (b). D_c of PBMA samples.

Nanoparticles with different elastic properties i.e., different cross-linking ratios (0, 1, 5 and 10%) exhibit different array of cracks (FIG. 2, 3). The cracked films in the 0% and 1% cross linked particles remained stick to the substrates and formed periodic cracks in three distinct regions: edges, middle and central. The cracks were dense at the periphery, less dense at the middle due to merging and they all merged to the center. However, for 5% and 10%, the fibers formed between cracks disengage from the substrate and form flower like pattern (FIG. 2). This flower is more elaborate in the 10% cross-linked PBMA nanoparticles. Bending of films is a signature of non-relaxed stress. Bending of thin films increase with increasing stored stress. The magnitude of bending has been used to evaluate the stored stress with thin film^[9, 10]. Internal stresses are more relaxed in uncross-linked and slightly cross linked particle (1%) via viscous dissipation and therefore fibers between cracks remain stuck to the substrate. Stress is stored in highly cross linked particles in the form of elastic energy, which induces bending of the fibers. The stored elastic energy decreases with decreasing cross linking ratio from 10% to 0%.

3.2 Crack Patterns in the Glassy Regime

As the drying temperature increases the number of cracks diminish, yet they retained their regular periodic patterns (FIG. 4). The distance between cracks increase slowly about 2-5 $\mu\text{m}/^\circ\text{C}$ in the glassy region for all the PBMA suspensions investigated here (FIG. 5). This is different from that reported on unidirectional drying experiments^[6, 7]. They observed a decrease in the D_c with increasing drying rate. As the temperature increase the drying rate increase and therefore one could expect D_c to decrease. The increase of D_c with temperature (FIG. 5) could be the result of drying the PBMA suspensions in the glass transition zone. Increasing temperature in glass transition zone would affect the nanomechanical properties of the particles and therefore

relax part of the stress in the film, making the cracks more spaced. The spectacular result is that D_c underwent an abrupt increase in the proximity of glass transition (5 to 6 times) within a short temperature variation of 2-6°C for all PBMA samples (FIG. 5). The jump temperature was found close to T_g for 20% humidity during drying.

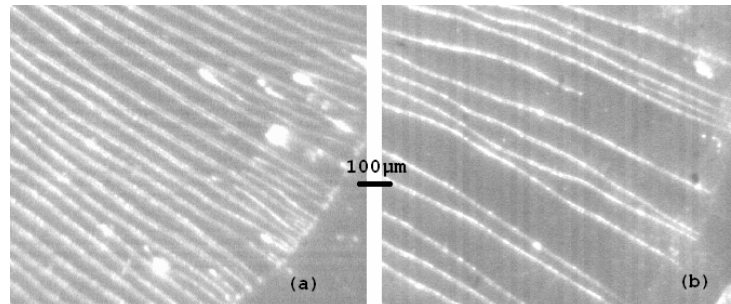


FIG. 4 – PBMA-0%, a) 23°C b) 31°C, depicting change in D_c .

One attractive model to describe the periodicity of crack patterns is that a crack relaxes the stress locally and therefore no other crack could appear within a distance D_c from it. The film will cumulate enough stress at a distance D_c from the first crack and, which would generate a new crack^[6, 7]. This describes the periodic array of cracks with a period D_c . Two types of models were proposed to describe the driving forces for crack patterns. The first one is a mechanical model^[6, 7] and the second is hydrodynamic model^[12, 13]. The mechanical model treats the colloidal gel as an elastic medium and predicts the cracks to appear if the elastic stress exceeds a critical value σ_c . They could predict the dependence of D_c on the film thickness. The second model is a purely hydrodynamic^[12, 13]. They attributed the cracks to a capillary pressure on the colloidal gel and the energy dissipation around the crack to a diffusion of water in the gel. These two models are mesoscopic models and do not take into consideration the nanomechanical properties of the nanoparticles. The rapid jump of D_c in trans- T_g region can not be well explained except by a rapid change in the nanomechanical properties of the particles. In this transition the particles go from glassy to rubbery state. As the particle goes deep into the rubbery regime, part of the capillary stress dissipates through viscous relaxation which yields a decrease of D_c . The results of FIG. 5, question also the definition of the MFFT, which is described as the passage from cracked to crack-free film. Highly elastic particles go from stages of narrower cracks to more spaced cracks, without reaching the crack-free film regime. These prove that the physics behind a MFFT and the Jump zone is different.

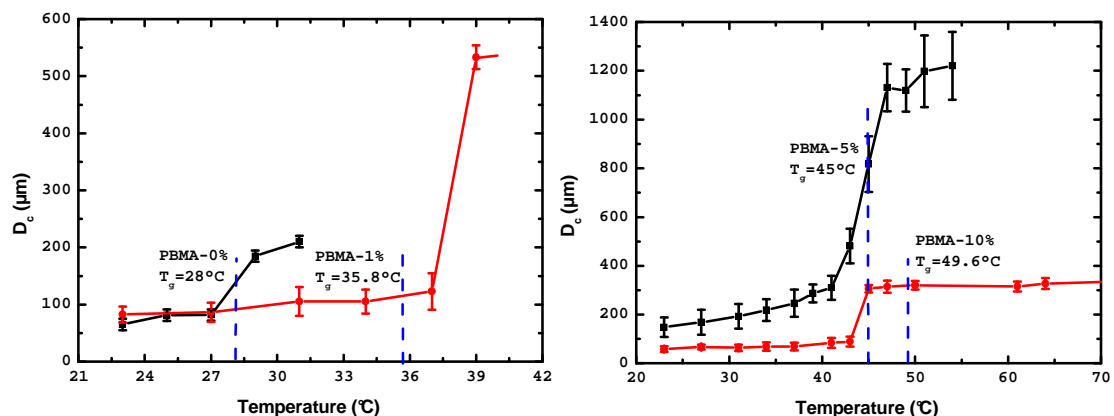


FIG. 5 – Superimposed curves of (a) PBMA 0% and 1%, (b) PBMA 5% and 10% samples.

4 Conclusions

In this work we have elaborated the diversity of cracks formed by drying of the well controlled polymer suspensions. The morphology of cracks goes through various stages: First the distance between cracks increases slightly below the glass transition temperature, after that the crack patterns become less dense. Close to T_g the relaxation spectrum and consequently the nano-mechanical properties of the individual particles experience abrupt changes, which influences the stress concentration in the film and hence the crack patterns. These findings have opened new field in the understanding of the nano-mechanical behavior of the nanoparticles in the proximity of T_g . From this, we may say that the debate on the physical meaning of MFFT is not closed and indeed our results have revived it. We are in a process to relate MFFT to the nano-mechanical properties and relaxation spectrum of the polymer nanoparticles. This area also needs further investigation with respect to the jump zone in distance between cracks.

References

1. Steward, P. A.; Hearn, J.; Wilkinsom, W. C. 2000. An Overview of Polymer Latex Film Formation and Properties. *Advances in Colloid and Interface Science* **86**, pp. 195-267.
2. Russel, W. B.; Routh, A. F. 1999. A process Model for Latex Film Formation. *Langmuir* **15**, pp. 7762-7773.
3. Toussaint, A.; Wilde, M. D. 1997. A comprehensive model of sintering and coalescence of unpigmented latexes. *Progress in Organic coatings* **30**, pp. 113-126.
4. Feng, J.; Winnik, M. A.; Shivers, R. R.; Clubb, B. 1995. Polymer Blend Latex Films: Morphology and Transparency. *Macromolecules* **28**, pp. 7671-7682.
5. Cabane, B.; Chevalier, Y.; Pichot, C.; Graillal, C.; Joanicot, M.; Wong, K.; Maquet, J.; Lindcer, P. 1992. Film formation with Latex particles. *Colloid & Polymer science* **270**, pp. 806-821.
6. Allain, C.; Limat, L. 1995. Regular Patterns of cracks formed by directional drying of a colloidal suspension. *Physical Review Letters* **74** (15), pp. 2981-2985.
7. Pauchard, L.; Adda-Bedia, M.; Allain, C.; Couder, Y. 2003. Morphologies resulting from the directional propagation of fractures. *Physical Review E* **67**, pp. 027103-1 to 027103-4.
8. Dufresne, E. R.; Crowin, E. I.; Greenblatt, N. A.; Ashmore, J.; Wang, D. Y.; Dinsmore, A. D.; Cheng, J. X.; Xie, X. S.; Hutchinson, J. W.; Weitz, D. A. 2003. Flow and fracture in drying nanoparticle suspensions. *Physical Review Letters* **91** (22), pp. 224501-1 to 224501-4.
9. Chen, K.; Taflove, A.; Kim, Y. L.; Backman, V. 2005. Self-assembled patterns of nanospheres with symmetries from submicron to centimetres. *Appl. Phys. Letters* **86**, 033101-1 to 033101-3.
10. Kitsunozaki, S. 1999. Fracture patterns induced by desiccation in a thin layer. *Phys. Rev. E* **60** (6), 6449-6464.
11. Komatsu, T. S.; Sasa, S. 1997. Pattern selection of cracks in directionally drying fracture. *Japanese Journal of Applied Physics* **36**, pp. 391-395.
12. Lee, Wai Peng; Routh, A. F. 2006. Time Evolution of transition points in drying latex films. *JCT Research* **3** (4), pp. 301-306.
13. Lee, Wai Peng; Routh, A. F. 2004. Why Do Drying Films Crack? *Langmuir* **20** (23), 9885-9888.
14. Tirumkudulu, M.S.; Russel, W.B. 2005. Cracking in Drying Latex Films. *Langmuir* **21**, 4938-4948.
15. Tirumkudulu, M. S.; Russel, W. B. 2004. Role of Capillary Stresses in Film Formation. *Langmuir* **20**, 2947-2961.
16. Martinez, C. J.; Lewis, J. A. 2002. Shape evolution and stress development during Latex-Silica Formation. *Langmuir* **18**, pp. 4689-4698.