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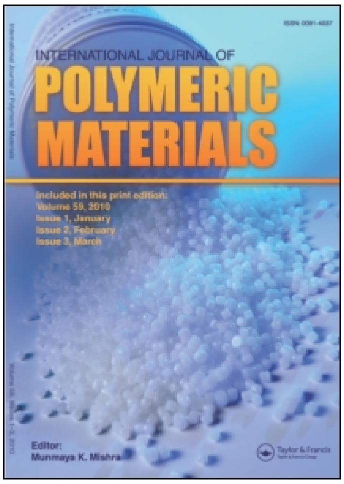

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Time-Dependent Behavior of a Sessile Water Droplet on Various Papers

Cem Aydemir[a]
[a] Department of Printing Education, Faculty of Technical Education, Marmara University, Istanbul, Turkey

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Time-Dependent Behavior of a Sessile Water Droplet on Various Papers

Cem Aydemir

Department of Printing Education, Faculty of Technical Education,
Marmara University, Istanbul, Turkey

In this paper the results of an extensive experimental study on the volume change of a water sessile droplet on various papers such as gloss and matte-coated papers and high-grade papers and boards with certain specifications are reported. The droplet on a paper is observed using a computer-controlled and fully automated instrument. The total volume and the contact angle of the sessile droplet are recorded in short time intervals (as short as 150 milliseconds) for about 6–10 min. The evaporation effect on the change of the volume of the water droplet is controlled by measuring the size change of a droplet on a glass surface. The instruments and the material used in the experiments are introduced in detail and the results are displayed in a series of figures and tables. The effects of possible mechanisms on the behavior of the water droplet are discussed, and directions of future studies are indicated. It is concluded that the relationship between water and a cellulose-based substrate cannot be fully understood if the microstructure of the cellulose-based materials and the three main mechanisms, namely evaporation, absorption and hygroexpansion, are not taken into account simultaneously.

Keywords contact angle, evaporation, hygroexpansion, papers and boards, water absorbency, water-based inks

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Address correspondence to Cem Aydemir, Department of Printing Education, Faculty of Technical Education, Marmara University, Göztepe, Istanbul 34722, Turkey. E-mail: cemaydemir@marmara.edu.tr

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INTRODUCTION

A great portion of any printing process is realized by transferring ink onto the substrate surface. The visual quality of printed matter heavily depends on how good the ink is bonded to the surface of paper and board, especially on the drying and fixing process of the ink. The water content of the ink is absorbed by paper (or board) during the printing process which is one of the main effects on the drying process. As was indicated by Thompson [1], drying is an important characteristic property of the printing process which affects the printing quality most and it should be kept under control. To be able to start the post-printing (for papers) or converting (for boards) processes, such as finishing, folding, and binding, the drying process should be completed. The main components of a typical ink are carrier (binder) and pigments. The carrier is the most dominant component of an ink for the absorbency-based drying process. Depending on printing mechanisms, the function and therefore the desired properties of a carrier can be multifold. The inks are classified into three major groups as far as the carrier is concerned: solvent-based, oil-based, and water-based. Although many carriers have been developed to refine certain properties of inks, water-based inks are increasingly preferred in many printing processes, especially in flexographic and gravure printing when cellulose-based substrates (papers and boards) are used. Water-based inks are preferred over inks containing volatile organic compounds because of environmental and health concerns. A typical water-based printing ink is composed of 60% water, 15% resin (or acrylic-based binders), 20% pigments, and 5% other additives. For a comprehensive account on inks in the printing industry, Thompson [1] can be consulted.

As far as the interaction of a water-based ink with a paper (or board), there are three main mechanisms: absorption, hydroexpansion (swelling), and evaporation. These three mechanisms are closely interconnected with each other and they are affected by the microstructure and the surface properties of the paper (or board). As is well known, one or both sides of most papers (or boards) used in printing industries are coated with various materials. Therefore, the hygroscopic and hygroelastic properties of the coating material dominate the behavior of the paper when a water-based ink is used in the printing process. It is also well-known that papers are composed of cellulose fibers that are attached to each other by various kind of bonds. Although the space between the fibers in papers is filled by various additives, a typical paper is still considered to be a porous medium. The porous structure and the nature of the fibers are the major factors that determine the behavior of water content of the ink in paper. The significance of a detailed knowledge on the behavior of water on paper (or board) for paper/board producers, ink manufacturers, and for the printing industry is beyond any doubt.

Printing is a complex process that involves placing the ink on the substrate, the wetting of the substrate, the penetration of the carrier in the

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ink into the pores of the substrate, the hygroexpansion of the substrate, the adsorption of the dye molecules or the pigment particles to the surface, and evaporation of the carrier [1]. The liquid uptake that is also termed in printing as “imbibitions” [2] or “wicking” [3] is one of the fundamental issues in printing using water-based inks. The ultimate fate of a droplet on a porous substrate is important not only in printing but also in a wide variety of fields from irrigation in agriculture to environmental issues like the spill of a hazardous material [4]. Three basic mechanisms that control the fate of a sessile droplet on a porous substrate are fluid uptake (also called penetration, permeation, absorption, imbibing, and wicking), evaporation of the fluid, and hygroexpansion (also called swelling) of the substrate. Each of these effects, namely, the capillary and gravity-driven absorption [4], the evaporation of a sessile droplet [5], and the swelling-shrinkage because of the change of the water content in the coatings and/or in the substrate itself [6] are investigated separately. There are not many studies in the literature that investigate all three effects at the same time. The goal of this study is to contribute to the efforts to fill this gap in the literature.

The aim of this paper is to report the findings of an experimental study on the time-dependent behavior of a sessile water droplet on gloss-coated paper, matte-coated paper, and various board surfaces by taking into account absorption, evaporation and hygroexpansion simultaneously. The volume of a sessile droplet is observed with a high speed CCD camera. In order to eliminate the evaporation effect, the time-dependent change of the volume of a sessile droplet is observed also on a glass surface. The experimental tools and the methods used in this study are explained in detail. A comprehensive discussion on this experimental study and a recommendation for further studies are provided.

MATERIALS AND METHODS

Although the main goal of this paper is to report the results of an experimental study on the time-dependent volume change of a water droplet on various paper and board surfaces and not the surface tension or contact angle only, the devices developed for surface tension/contact angle measurements are adequate for the purposes of this study. Among them, the devices based on the sessile droplet method are chosen in this study because the water droplet is directly observed on a surface in this method.

Experimental Tools

The time-dependent behavior of a sessile droplet of water is observed by an optical contact angle device (SCA 20, Version 3.1.4) which is manufactured by DataPhysics Instruments GmbH, 2004, Filderstadt, Germany. The paper is mounted on the measuring stage with special care to make sure that the paper surface is flat. The measuring stage can be accurately positioned in three axes. A water droplet is placed on the paper with a computer-controlled syringe. The water droplet is illuminated by a halogen lamp with continuously adjustable intensity. The droplet is observed with a CCD video camera with a resolution of 752 × 582 pixels and up to 50 images per second. The camera is equipped with a power zoom of 0.7–4.5-fold magnification and with an optical distortion of less than 0.05%. This fully automated device is capable of measuring the volume of a droplet by determining the profile and the baseline of the droplet. The profile of the droplet is approximated by the built-in software of the device as a circle or an ellipse. The profiles are determined by marking at least 3 points on the contour of the droplet for a circle, and at least 5 points for an ellipse. The profiles are also used to measure the contact angle when the appropriate option is chosen for this purpose.

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Specifications and Origin of the Papers and the Boards

In this study, uncoated white paper, gloss-coated paper, matte-coated paper, and board are used. The specifications of the papers and the boards used in this study are given in Table 1.

Properties of the Water Used in the Experiments

Purified water of laboratory quality is used in this experimental study. The properties of this water are given in Table 2.

Table 1: Properties of substrates.

		Substrate Types			
Properties	**Units**	**Gloss-coated paper (wood-free)**	**Matte-coated paper (wood-free)**	**Uncoated white paper**	**Board**
Thickness	μm	103	109	107	370
Gloss (Hunter 75)	%	79	31	6	30
Surface Roughness (PPS method)	μm	0,75	1,33	5,42	2,62
Surface Roughness (Bendtsen)	ml/dk.	1,60	13,20	195,10	64,00
Air Permeance (Bendtsen)	μm/Pa s	0,112	0,103	5,61	0,348
Ash (Total)	%	38,2	46,9	22,9	21,4

Table 2: Physical properties of sessile water droplet.

Density	0,9982 (g/cm^3)
Surface tension	72.8 (mN/m)
Viscosity	1 (MPa s)

RESULTS

The data (volume of the droplet and contact angle) produced by the computer-controlled device (SCA 20) used in the experiments were stored in the computer. The frequency of taking the frames was determined by the software of the device, and differed from one experiment to another. In order to make the results obtained from different experiments comparable with each other the values of one experiment were normalized with respect to time using interpolation. The volume of the droplets was different in each experiment (they were in close proximity with each other), and the volumes in the subsequent moments in each experiment were normalized with the initial volume. The baseline of the droplet was determined by the device and was used in calculation. Potential problems in determining the baseline were not encountered in these experiments.

Experiments with certain substrates which are listed in Table 1 were repeated several times (sometimes 40 times) and their average was used as the representative for that specific substrate. Typical results obtained for a matte-coated paper in repeated experiments are shown in Figure 1.

The raw data obtained for a specific specimen were inspected first for a possible anomaly for any reason, mainly for experimental errors. Once confidence was reached to a satisfactory level, the average of the results obtained for that specific specimen was calculated and taken as the representative

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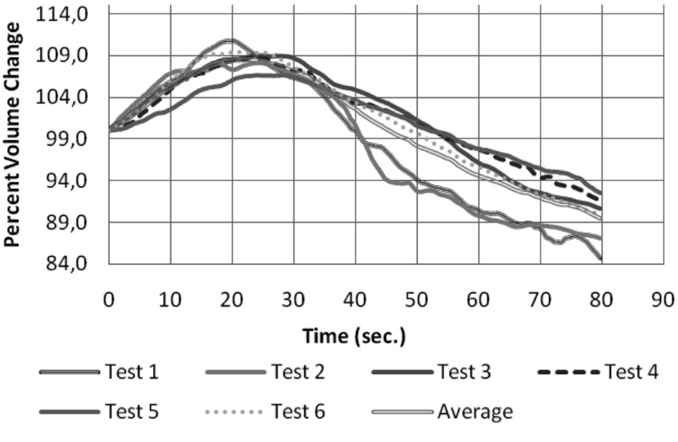

Figure 1: Results obtained for matte-coated paper with repeated experiments.

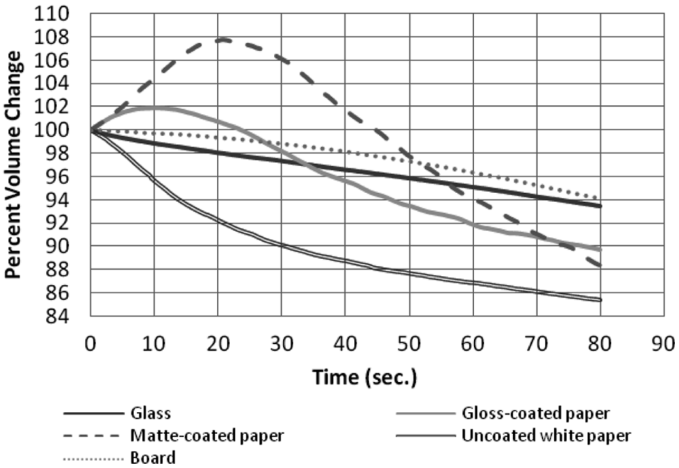

Figure 2: Change in the volume of a sessile water droplet on various substrates.

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for that specimen. In Figure 2 one of these results, namely the percent volume change of a sessile water droplet on a glass, gloss-coated paper, matte-coated paper, uncoated white paper, and board, is shown. The anomaly in the behavior of gloss-coated paper, matte-coated paper, and board is discussed below.

As far as the change of the volume of a sessile droplet on a substrate in time is concerned, three main mechanisms controlling the volume of the sessile droplet at a constant room temperature are observed: evaporation of water, penetration of water into substrate, and deformation (expansion) of the substrate because of increased water content in the substrate. In order to isolate the effect of evaporation, the volume change of a water sessile droplet on a glass surface is observed. These experiments indicate that volume change of the sessile droplet due to evaporation is small compared to the other two effects.

At the early stages of the experiments with the coated papers and boards, an increase in the volume of the sessile droplet was observed. In order to make sure that this observation was not an experimental or reading error, the experiments were repeated several times keeping the parameters of the experiments constant. A typical result for matte-coated paper of this observation is given in Figure 1. For comparison purposes, the results obtained for various substrates are given in Figure 2.

A potential explanation of this observation can be as follows: The expansion of the substrate due to the increased water content in the substrate is so faster than the decrease in the volume of the sessile droplet due to evaporation and penetration of the water in the sessile droplet into the substrate, that the volume of the sessile droplet appears increased at the beginning of the experiments.

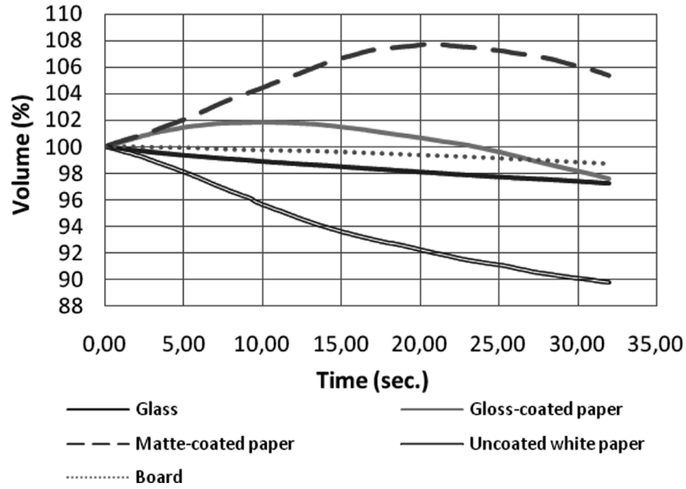

Figure 3: Abnormal change in the volume of the droplet.

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Even the change of the water droplet on the board exhibits strange behavior; the volume of the water droplet on the board decreases at a slower rate than the one on the glass (Figure 3) at the early stage of the experiments. The explanation presented given above for the behavior of the coated paper can be applied to the behavior of the water droplet on the board.

The observed contact angle measurements exhibited a trend which was common in all experiments; the contact angle data in all experiments started with high values and they steadily decreased with time. A typical example for the results obtained from the experiments for one specimen is shown in Figure 4, and in Figure 5 the average contact angle change of water for

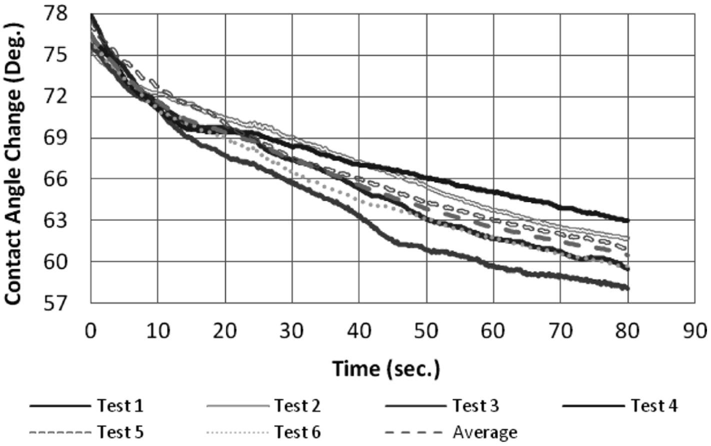

Figure 4: Change of contact angle of water for matte-coated paper obtained with repeated experiments.

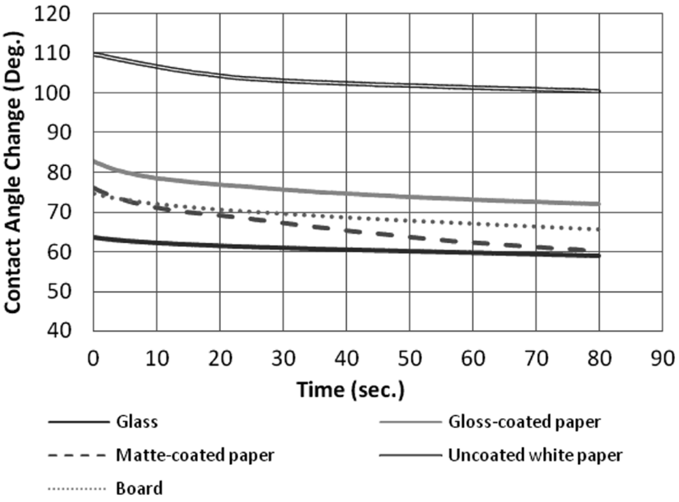

Figure 5: Change of the contact angle of water for various substrates.

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various substrates are shown. The reasons for this persisting trend can be explained as follows: at the beginning of the experiments, the contact angle is between the water and the substrate. As the water penetrates into the substrate the sessile droplet is in contact not only with the substrate material but also with water, which, in turn, causes a decrease in the surface energy and therefore the contact angle exhibits a steadily decreasing trend. It is clear from this observation that the dynamic contact angle should be taken into account in order to understand the behavior of a sessile droplet in full detail. Another possible factor for this trend would be the effect of gravity. At the beginning of the experiments, the size of the droplet is the largest and the hydrostatic pressure at the bottom of the droplet due to gravity is high which, in turn, causes an increase in the contact angle at the early stages of the experiments.

All three mechanisms that affect the volume change of a sessile droplet were investigated by researchers. Several mathematical models have been developed at various complexities for them. For example, the penetration of liquid droplets into porous materials such as papers and boards has attracted the attention of scientists in various fields, and mathematical models to predict how the liquid penetrates into porous media have been developed. In the model developed in Denesuk et al. [7], porous media was modeled as a continuum that consisted of perfectly aligned capillary tubes and the droplets were modeled as a spherical cap. In our study, the area between the droplet and the porous media is considered to be a function of the permeability of the porous materials.

The results obtained in this experimental study exhibit a significant deviation from each other. The main reason for this behavior is speculated to be

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the variation in the micro structural and surface parameters of the papers and the boards used in the experiments. Although the papers are supposedly from a same batch (but this point was not checked) there was no indication that the micro structural parameters, such as fiber length, fiber contact area, coarseness, etc. are the same in each sheet, even at a different location in the same sheet. Despite the significant scattering of data, the typical trends in those behaviors are the focus points in the present paper.

The volume of the droplet and the contact angle were calculated by the algorithms available in the experimental device. These calculations were based on the measurements of the profile of the sessile droplet and on the assumption that the profile of the droplet is a circle (or ellipse in some cases). Possible deviations (for example, oscillations of the droplet due to the initial velocity during landing on the substrate surface or due to the ground vibrations) in the profile of the droplet from this assumption may add some randomness to the results. It is assumed that this situation is more sensible at the beginning of the experiments and therefore the data for the early stage of the experiments have been treated with caution.

Because of the surface roughness and depending on the magnification, the edge of the sessile droplet, especially the contact angle may exhibit random behavior. In our study, the magnification used in the experiments was chosen appropriately to reduce this possible random behavior in the contact angle measurements.

It is well-known [8] that gravity has a significant effect on the shape of a sessile droplet, and therefore on the contact angle measurements. It is also known that the smaller the size of the droplet the smaller the effect of gravity. Therefore, the size of the droplet was chosen as small as possible to reduce the effect of gravity. As is indicated above, the persisting trend in the contact angle measurements can be interpreted as the effect of gravity on the behavior of the sessile droplet on a substrate, and therefore on the contact angle measurements.

An experimental study in which the microstructural parameters of paper, such as fiber length, porosity, hygroexpansion characteristics, and characteristics of fiber-fiber bonding are controlled is highly recommended. Despite the care given for the usual parameters used to determine the papers, such as density, surface roughness, and air permeability, the results exhibit a significantly large variation in the present experimental study. Therefore, experimental studies where the “fine characteristics” of paper are taken into account would be highly useful to understand the behavior of ink on a printing substrate.

As is briefly outlined in the Introduction, there are several mathematical models at various complexities for hygroexpansion of moisture-sensitive materials, such as cellulose-based paper products, evaporation of a sessile droplet, and penetration of water into a porous media. All these mathematical models have been developed independently from each other. It would be a significant contribution for many professionals from various disciplines, such as flexography and gravure printing industries, to unify all these theories for modeling the relationship between the ink and the cellulose-based paper and board products.

Recent theoretical and experimental progress in various fields of nanomechanics has not been satisfactorily applied to modeling the behavior of paper. Especially, homogenization techniques based on mixture theory developed for materials heterogeneous at nano scale can be employed to model the behavior of paper taking into account the microstructural parameters and the moisture content. Indeed, in a group of models [7], that have been developed to study the absorbency in papers, the medium is envisioned consisting of capillary tubes. These models can be improved by adopting the modern techniques mentioned above in this field.

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CONCLUSIONS

In this study it was observed that the size of a sessile droplet on a cellulose-based substrate is controlled mainly by three mechanisms: evaporation of the water to the environment in the ambient conditions, absorption of the water by the substrate, and the hygroexpansion (swelling) of the substrate because of the moisture content. In this experimental study the evaporation component was monitored by observing the sessile droplet on a glass substrate. Although these observations indicate that the effect of evaporation on the overall change of the volume of the droplet is not significant, it could be significant with a different fluid and at different ambient conditions. The other two, absorption and hygroexpansion are inter-related, and are competing with each other; due to absorption the volume of the droplet decreases, but because of swelling it will appear to be increasing. Because of these competing factors the behavior of the sessile droplet on cellulose-based substrates can be complicated.

It is becoming clearer with time that the conventional parameters to describe a cellulose-based paper and board product are becoming less sufficient. This situation is also realized in this experimental study. Even though the same paper was used for the same type of experiments under special care, significant scattering has been observed in the experimental measurement which are beyond human and/or experimental error. It is reasonable to claim that the microstructural parameters are responsible for such variations in the experimental result. Therefore it is concluded that in the next generation of testing cellulose-based paper products the microstructural parameters, such as the physical, mechanical, and geometrical properties of fibers, the geometrical and mechanical properties of fiber-fiber bonding, and the physical and geometrical properties of the porosity network in the paper, should be taken into account.

The experimental study presented in this paper can serve for the purpose of determining the hygroelastic coefficients of moisture sensitive materials, such as cellulose-based paper products. If the hydroelastic behavior of the material is assumed to be isotropic, then the protocol presented in this paper can be employed without any modification. This subject will be presented in full detail in a forthcoming paper.

REFERENCES

[1] Thompson, B. (1999). *Printing Materials: Science and Technology*, Pira International, UK, pp. 325–355.

[2] Brielles, N., Chantraine, F., Viana, M., Chulia, D., Barnlard, P., Rubinstein, G., Lequeux, F., and Mondain-Monval, O. *J. Colloid Interface Sci.* **328**, 344 (2008).

[3] Wang, J., Thom, V., Hollas, M., and Johannsmann, D. *Journal of Membrane Sci.* **318**, 280 (2008).

[4] Navaz, H. K., Markicevic, B., Zand, A. R., Sikorski, Y., Chan, E., Sanders, M., and D'Onofrio, T. G. *J. Colloid Interface Sci.* **325**, 440 (2008).

[5] Ramon, G., and Oron, A. *J. Colloid Interface Sci.* **327**, 145 (2008).

[6] Laudone, G. M., Mathhews, G. P., and Gane, P. A. C. *Ind. Eng. Chem. Res.* **43**, 712 (2004).

[7] Denesuk, M., Smith, G. L., Zelinski, B. J. J., and Uhlman, D. R. *J. Colloid Interface Sci.* **158**, 114 (1993).

[8] Kabeya-Mukeba, L., Vandewalle, N., and Dorbolo, S. **1** (2007). (http://bictel.ulg.ac.be/ETD-db/collection/available/ULgetd-05162007-073939/)

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