# New Methodologies for Separating Glass Transitions from Energy of Film Formation in Polystyrene Latexes

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ABSTRACT: Polystyrene latexes were synthesized to study water evaporation details, and to separate the energy of film formation from the glass transition temperature. Three experimental techniques were employed in the present work to study the formation of polystyrene latex films: standard differential scanning calorimetry (DSC), modulated DSC, and the Mahr method applied to modulated DSC. High-resolution thermogravimetric analysis (TGA) was used to study the water evaporation. The TGA experiments revealed evaporation curves consistent with the notion of surface tension and tortuosity effects being the controlling factors. The method of Mahr was combined with the new software package for DSC to provide an improved method of separating the glass transition of polystyrene from its surface tension-based free energy of film formation. The result was that the films formed under the extremely mild conditions employed had 30-70% of their surfaces obliterated by interfacial adhesion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1763–1768, 1999

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#### **INTRODUCTION**

It is often difficult to separate reactions, transitions, and physical changes that occur in similar temperature ranges. Consider the case of the

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glass transition and the surface energy of film formation in polystyrene latexes. Three experimental techniques were employed in the present work to study the formation of polystyrene latex films: Standard differential scanning calorimetry (DSC), modulated DSC, and the Mahr method applied to modulated DSC.

Several different methods have been used in the past to try to separate these phenomena. In 1970, Mahr<sup>1</sup> described the compensated calorimetric method (CCM). Using CCM, simultaneously occurring reversible and nonreversible

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phenomenon can be separated. The key to this procedure involves the special use of the reference cell. In standard DSC experiments, the reference cell is empty. For a CCM experiment, the reference cell contains a sample of the material that has already under gone the irreversible phenomenon. This reference sample must be of a nearly identical mass and pan weight to the actual sample.

Instead of a single run, each CCM experiment involves three runs. The first run has the reference sample in the sample cell, so that it undergoes the nonreversible change. The second run has the reference sample in the reference cell and the actual sample in the sample cell. In this step, the reference undergoes the same reversible phenomenon as the sample so they are filtered out. Since the reference has undergone the nonreversible phenomenon, it is clearly identifiable. The third step just reruns the program, without touching or changing either the sample pan or the reference pan. The third step develops the base line and shows how fully the reference filtered out the signals from the sample.

A recent development in the DSC field has been modulated DSC (m-DSC).<sup>2,3</sup> In this, as in standard DSC, a constant heating rate is applied to the sample. Another signal, usually a sinusoidal heating rate, overlays the constant rate in m-DSC. Assuming the appropriate analyzing software, the sinusoidal heating rate imposed on the temperature ramp allows reversible and nonreversible phenomenon to be separated.

Of course, DSC or modulated DSC measures the change in energy and/or heat capacity during a temperature ramp. A thermogravimetric analyzer (TGA) is often used in conjunction with a DSC to monitor weight changes as functions of time and/or temperature brought about by these reactions, physical phenomenon, or other transformation. In a regular thermogravimetric analyzer (TGA), a sample is heated at different rates and the weight change and rate of weight change are monitored. In a high-resolution (Hi-Res) mode,<sup>4</sup> the instrument heats rapidly when little or no weight change is occurring, but automatically adjusts during periods of weight change. Either the TGA slows down the heating rate to obtain more information, or it varies the heating rate to keep the rate of reaction constant.

An important route in preparing films involves latex synthesis, followed by water evaporation and film formation.<sup>5</sup> The rate of water evaporation and the drying of films has received significant attention in the past. Sheetz<sup>6</sup> saturated blot-

ting paper with a latex dispersion, and measured the rate of water evaporation. Pramojaney<sup>7</sup> used a wind tunnel to determine the drying rates of latex films. Poehlein et al.8 evaporated water from thin films under laminar airflow. A 60/40 styrene/butadiene statistical copolymer latex was used, as film former. The films were prepared with a 10-20 mill bar gap, and the standard conditions of 72°F, 50 % relative humidity, and an air velocity of 0-4 mph were used to evaporate the water. The rate of water loss was determined gravimetrically. The wet latex area was determined photographically. In each case, the rate of water evaporation was substantially constant until the particles were forced into contact. Then, the rate of evaporation declined.

## **EXPERIMENTAL**

## **Polymer Synthesis**

All of the experiments were carried on a polystyrene latex, made using the following recipe: 180 mL distilled water, 60 g analytical-grade styrene monomer, 0.25 g NaHCO<sub>3</sub>, 0.25 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and 0.90 g sodium lauryl sulfate. The polymerization was carried out at 70°C under a nitrogen atmosphere. After 3 h, approximately 99% of the monomer was polymerized, as determined by weight. As measured by gel permeation chromatography, the number-average molecular weight of the latex was  $1.1 \times 10^6$  g/mole. Via transmission electron microscopy, the particle sizes were determined to be  $D_n = 56.8$  nm, and  $D_w = 61.33$  nm, yielding a polydispersity index of 1.080.

The experiments were conducted on the latex in one of three states: in dispersion, air dried, or freeze dried. The solvent was deionized water. Some of the air-dried latex was cleaned by water extraction for approximately 12 h. Finally, some of the dispersion was quickly frozen. The water was then sublimed off at -80°C and under vacuum, yielding a powder. This prevented deformation of the latex particles due to the drying process.

#### Instrumental

A TA Instruments DSC 2920 Modulated DSC and a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer were used in the following experiments. These instruments were used in both their standard form, utilizing only features available on earlier models, as well as in their newer form, utilizing their modulated and Hi-Res software packages, respectively. All the samples used in the Hi-Res and standard TGA experiments were in air dried latex form and had a mass between 60 and 80 mg. For each different temperature, at least two samples of similar mass and under similar conditions were tested.

The PS latex was studied to determine information about the evaporation rates of water in the suspension, using both standard TGA and the Hi-Res mode. For the standard TGA, the sample was heated to the desired temperature and held isothermally until the rate of weight loss was zero and had been for several minutes. The temperatures at which the latex was tested were 60, 70, and 80°C. Then the heating rate was 15°C/min for the lower temperature and 20°C/min for the remainder, reducing overshoot of the desired temperature.

Two modes of operation (standard and modulated) were used for the DSC experiments. All of the different methods of preparation of the latex were used with the DSC and m-DSC. The sample pan was an aluminum pan, without a lid. The only exception was the freeze-dried powder. Since it was so fluffy, very little would fit it in the aluminum pan so a larger, uncrimped hermetic pan was used.

The standard DSC experiments had three steps. First the sample was heated to approximately 80°C and held there for 15 min to dry the sample. Next, it was heated at 1°C a min to 110°C, above the minimum film formation temperature. Finally, it was held isothermally at 110°C for 5 min. The CCM experiments followed the above steps, for the reference, the actual sample, and the baseline check.

The m-DSC experiments followed the above steps as well, with a few modifications. First, the drying temperature was raised to 85°C, while the drying time was lowered to 10 min. Second, the heating rate from the drying step was slightly higher, 5 vs. 1°C/min.

## RESULTS

Two series of experiments were carried out: First, a series of drying experiments were carried out using the Hi-Res TGA. The intent was to evaluate the rate of water loss, especially the last portions of water in the latex. Then, a series of experiments were carried out with the modulated DSC,



**Figure 1** A TGA plot of water evaporation at 80°C, solid line. The derivative curve, dashed line, shows a plateau of 4.1%/min water loss, followed by a curve illustrating the last traces of water evaporation at 25.8% of dry polymer residue.

in an effort to separate the glass transition from the heat of film formation, and eventually determine the fraction of latex surface obliterated by the heating experiments.

Figure 1 illustrates a TGA water evaporation curve at 80°C. Note that the water is evaporated after 45 min at 50°C, data not shown. The large plateau on the derivative of weight loss reflects the constant evaporation rate. The contact point is at the end of the plateau.

The water evaporation weight vs time and the rate of weight loss vs. time curves all had very similar shapes, regardless of the temperature of the test. The first few minutes shows the increasing temperature as the rate of water evaporation increases. After the temperature stabilized, the rate of evaporation is constant. This represents the larger portion of the evaporation. Finally, after the particles come into contact with each other, capillary forces come into play. The point at which this occurs is shown by a change in evaporation rate. The point where the particles come into contact with each other (the contact point) is where the constant evaporation rate begins to decrease. The evaporation rate slows down as more and more particles come into contact and eventually reaches zero. Table I shows the data at various temperatures. The constant rate region is the largest portion of the evaporation process. As previously noted, the particle contact point is presumably when capillary forces begin to have an effect. The initial and final weights are self-explanatory.

The data for the Hi-Res TGA is illustrated in Figure 2 showing the weight loss vs time and the

	Temperature (°C)		
Quantity	60	70	80
Ave. rate of weight loss, %/min	3.34	4.69	6.26
Ave. % weight loss to dryness	65.9	69.2	68.9
Ave. % weight loss to particle contact	51.8	49.7	51.3

Table IWeight Loss Studies at VariousTemperatures

temperature vs. time. The Hi-Res TGA slows the heating rate as the evaporation occurs. This is shown by the flattening present in the temperature vs. time curve. These data confirm the standard curves of the literature. Their value lies in that through Hi-Res TGA, a more detailed picture can be obtained, especially the last portions of the drying.

Then, a series of DSC runs were undertaken. The air-dried and cleaned latexes both changed from an opaque solid to a translucent solid, suggesting partial but incomplete film formation. The freeze-dried powder remained in powder form, with no change in transparency. There was some joining of the individual particles but they broke apart easily.

The standard DSC experiments were unable to separate the  $T_g$  and film formation energies (see Figure 3). This figure illustrates an enthalpic re-



**Figure 2** A Hi-Res TGA plot of water evaporation with the temperature being increased at 2°C/min. Note that the actual temperature of the water/latex mix remained nearly constant during most of the evaporation. The temperature ramp was stopped at 90°C.



**Figure 3** A nonmodulated DSC plot, with the temperature increase of  $5^{\circ}$ C/min. The nominal glass transition temperature is 106°C, but the experiment was unable to resolve the glass transition from the energy of film formation. This is experiment one of the compensated calorimetric method of Mahr.

laxation, followed by a glass transition, typical of many such studies. Figure 3 is also the first step in the Mahr trio of experiments.

Figure 4 shows the second step of the CCM. The large peak is the energy of film formation thought due to the obliteration of the latex surface and its surface tension energy.

Modulated DSC also worked well at separating the phenomena (see Figure 5). Illustrated are the total heat flow, reversible heat flow, and nonre-



**Figure 4** The compensated calorimetric method of Mahr, experiment two, as explained in the text, where the reference sample previously run, is compared with the new sample. The area under the curve, determined by computer, yields the energy of film formation. Experiment three of Mahr, which determines the baseline, is not shown.



Figure 5 A modulated DSC plot, the temperature increased at 5°C/min. Three curves are illustrated. The solid line represents the total heat flow, as would be obtained in a non-modulated experiment. The short-dashed line is the reversible heat flow, with the glass transition at the tangent, about 104°C. The nonreversible heat flow, long-dashed line, yields the energy of film formation as the peak area, computer generated.

versible heat flow. The large peak in the nonreversible heat flow plot is the film formation energy.

Then, the Mahr method was combined with the modulated method. Figure 6 shows step two of the m-CCM. Total heat flow, reversible heat flow, and nonreversible heat flow are all shown. The large peak in total heat flow and nonreversible heat flow is the energy of film formation. The values associated with the reversible heat curve are seen to be small and erratic. Ideally, this value should be zero. Deviations from zero may be caused by small differences in sample or pan weights, or the appearance of other phenomena.

#### DISCUSSION

In the Hi-Res TGA experiments involving the latex, the evaporation rate was controlled by the temperature (Table I). Another important aspect of latex drying is the particle contact point, which showed some variation. The percentage of latex, by weight, in a sample was found to be constant.

Differing from previous experiments, the present latexes were not film formers under the conditions of water evaporation. Thus, the kinetics of the last water to evaporate yield information about effects of water-polymer surface tension and the tortuosity of the in-contact spheres.

The energy of film formation is the surface energy, sometimes called the surface tension. The value used was the average determined by Wu,<sup>9</sup> 44  $erg/cm^2$ . Since the energy, as found in these experiments, was consistently less than this literature value, it was assumed that the latex did not complete the transformation. The fraction of surface area obliterated is shown in Table II. The fraction of surface area obliterated was calculated by first estimating the total surface area from the diameter of the latex particles, then multiplying by the surface tension (44 ergs/cm<sup>2</sup>) to obtain the maximum (100%) energy liberated on perfect film formation. Dividing this number into the actual energy liberated produced the fraction of surface obliterated. Alternate explanations of why the experimental value was smaller than that expected by full film formation include particle-particle bonding during air drying, energy of rearrangement of the surfactant, etc. However, the values in Table II are supported by the translucent nature of films formed, which is usually caused by excess light-scattering, indicative of a two-phased system.

The reason so little surface area was obliterated for the freeze-dried latex was because the conditions were very mild; fairly low temperature and little additional pressure. This means the



**Figure 6** A modulated DSC plot using the Mahr method. The reversible heat flow, actually very slight negative, should ideally be zero. The area under the nonreversible heat flow curve yields the heat of film formation, again as calculated by computer.

Sample No.	Status	Modulated	Surface Energy Liberated (J/g)	Fraction of Surface Obliterated
1	Dried	No	1.696	72.92
2	Dried	Yes	1.491	64.11
3	Dried	Yes	1.546	66.47
4	Dried	Yes	1.753	75.38
5	Freeze-dried	No	0.693	28.94
6	Freeze-dried	No	1.090	46.87
7	Freeze-dried	No	1.049	45.10
8	Cleaned	No	1.224	52.63
9	Cleaned	No	1.612	69.31
10	Cleaned	Yes	1.378	50.25
11	Cleaned	Yes	1.591	68.41
12	Cleaned	Yes	1.606	69.05

Table II Film Formation and Surface Area Results

particles were not ideally packed and had little contact with each other. The reason tests six and seven have slightly higher more surface destroyed than test five is because they were packed better.

Figures 5 and 6 illustrate a very important relationship between the reversible and nonreversible phenomena. The nonreversible heat flow is smaller than the reversible heat flow by almost a factor of ten. This means the reversible reaction (the glass transition) dominates the nonseparated curve in Figure 3.

#### **CONCLUSIONS**

Hi-Res TGA provides more options in conducting rate analysis of reactions and other physical phenomenon. The increased sensitivity allows more information to be gathered from the experiment. The constant rate functions yield a more accurate illustration of the temperature range for a weight change.

For these specific experiments, TGA helped determine some of the characteristics of the evaporation of water for a polymer latex. In all cases, approximately 74% of the sample's weight was from the water. The evaporation rate was found to depend on the temperature nonlinearly, probably controlled by such factors as the water-polymer surface tension and the tortuosity of the system with the spheres in contact.

The present analysis, using the m-CCM technique, provided the best separation of the glass transition temperature and the heat of film formation. This allowed the relatively small heat of film formation to be quantitatively analyzed, with the conclusion that due to the mild heating conditions, film formation was incomplete. Beyond the present experiments, however, the new methods permit a more accurate analysis of the complex phenomena that relate to latex film formation.

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