Quantitatively Revealing the Distribution of Water within Polymer Colloids via Differential Scanning Calorimetry and Theoretical Prediction of Hydrated Polymer Thermal Profiles

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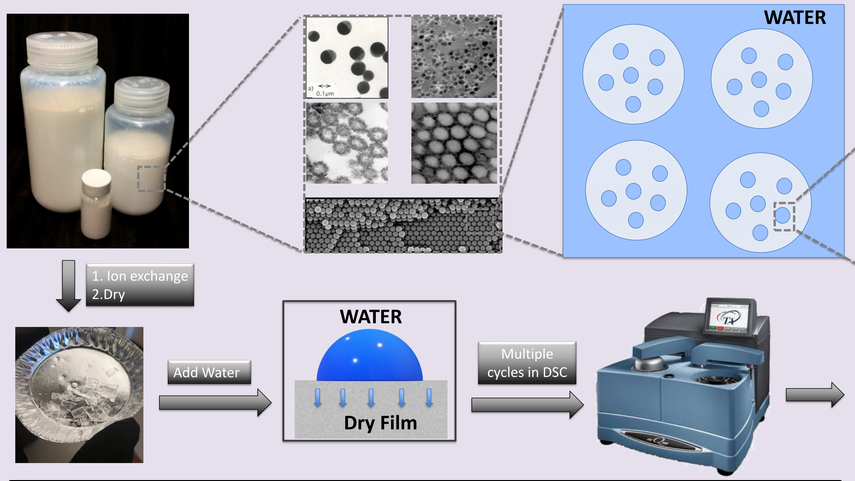
Introduction & Research Approach

Scheme 1: Flow chart illustrating distribution of water within polymer colloids and our experimental approach to analysis.



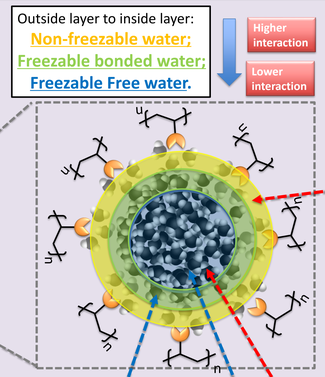
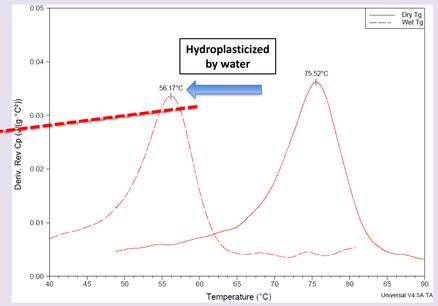


Figure 1.Experimental wet T_g measurement for fully hydrated polymer with our prior method,[4] specific to plasticization by *nfw*



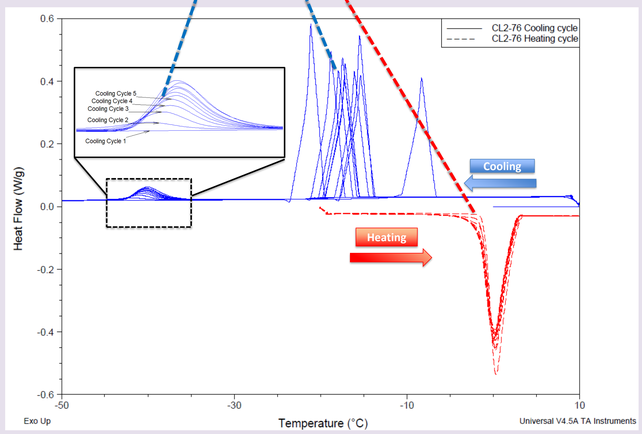
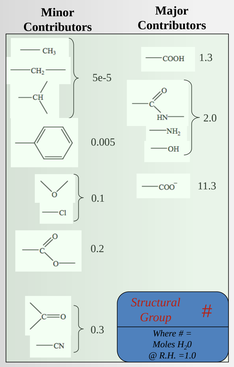


Figure 2: Typical heating (red) and cooling (blue) cycles used for analysis in this revised DSC analysis for assignments of different types of water distributed within a hydrated polymer

- Water can associate with polymers in three states[1] (non-freezable bound, freezable bound and freezable free water) and influence material properties. [2]
- Here we have developed an alternative differential scanning calorimetry (DSC) method to our former approach[1,3] to analyze water distribution in hydrophobic waterborne polymers.
- The corroboration of the result of this to the former methods is evaluated.
- The influence of surfactant (SDS), as a general model for non-polymer polar constituents in the system, on the water analysis and distribution in the polymer materials was explored.

Theoretical T_{g_wet} Prediction

Latex Polymer analyzed



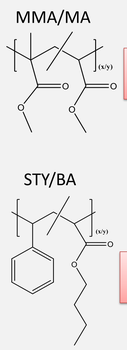


Figure 3: Theoretical non-freezable water (*nfw*) content contribution of chemical structures and polymer chemical structures used in this research.[3]

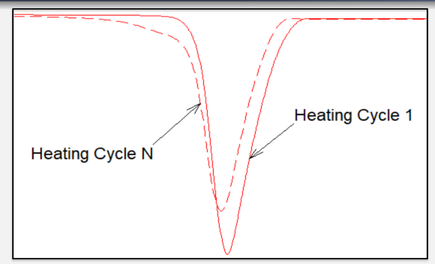
$$T_{g\_wet}=\left(\frac{Wf_{polymer}}{273+T_{g\_dry}}+\frac{Wf_{nfw}}{273-137}\right)^{-1}-273 \qquad \text{(Eq.1)}$$

Table 1: General information for polymers used in this research.

Sample	Chemical Composition (wt%)	Theoretical Non-freezable water content (wt%)	DSC Measured Dry T_g (℃)	Theoretical wet T_g (℃), Eq.1
MMA/MA	71:29	3.76	75.5	56.16
STY/BA	75:25	0.8	65.9	61.9

Results & Discussion

How to calculate non-freezable water content from the melting peak shown in DSC curve?



$$Wf_{nfw\_total}=\frac{A_{M\_1}-A_{M\_n}}{A_{M\_1}}*Wf_{water} \qquad \text{(Eq.2)}$$

$$M_{water}=Wf_{nfw\_total}*M_{total} \qquad \text{(Eq.3)}$$

$$Wf_{nfw}=\frac{M_{water}}{M_{water}+M_{polymer}} \qquad \text{(Eq.4)}$$

- We make the assumption of no water adsorption in the first heating cycle.
- Any decrease of the area under the water melting peak during cycles is attributed to the increase of the weight fraction of non-freezing bound water content (Wf_{nfw}).
- Here, A_{M_1} and A_{M_n} are the areas under the water melting peak in the first heating cycle and the N^{th} heating cycle, respectively. Wf_{water} represents the total water content added into the sample. M_{total} is the mass of the whole sample, and $M_{polymer}$ is the mass of the polymer alone in the experiment.

Results & Discussion (cont.)

Figure 4: Experimental Wf_{nfw} values versus number of cycles for polymer samples of different polarity

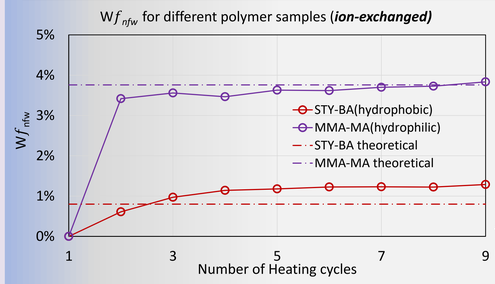


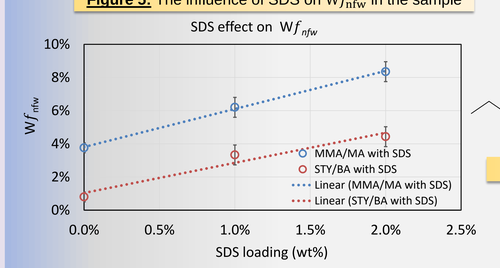
Table 2: Comparison between experimentally measured wet T_g and calculated wet T_g (from the new measurement technique) for polymers with strongly different polarity

Sample	Experimental wet T_g (℃) [a]	Calculated wet T_g (℃) [b]
STY-BA	59.50	59.55
MMA-MA	56.17	55.81

a. Experimental wet Tg was directly read from DSC signal after the hydration of the dried polymer (*see Fig. 1*)
b. Equations (2-4) were used to obtain Wf_{nfw} (*see Fig. 2*) , and the Wf_{nfw} was applied in Equation (1) to get "Calculated wet Tg"

- Non-freezable water content given by DSC results can match the theoretical number very well for both hydrophobic and hydrophilic samples.
- The accuracy of this characterization method is high.

Figure 5: The influence of SDS on Wf_{nfw} in the sample



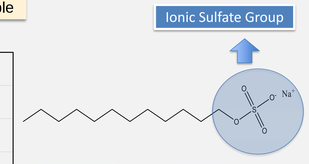


Figure 6: Structure of SDS

- Polymer with SDS can have much higher Wf_{nfw}, because of the sulfate group
- The increase in Wf_{nfw} is approximately correlated to *2x* the SDS *Wf*

Sample	SDS loading (BOP)[a]	Experimental wet T_g (℃) [b]	Calculated wet T_g (℃) [c]
MMA-MA	1wt%	54.03	44.03
	2wt%	53.32	35.52
STY-BA	1wt%	58.99	49.1
	2wt%	56.85	45.11

Table 3: Comparisons between experimental wet T_g and calculated wet T_g for samples with SDS.

a. SDS loading was based on the mass of dried polymer
b. Experimental wet Tg was directly read from the DSC signal after the hydration of the dried polymer (*see Fig. 1*)
c. Equations (2-4) were used to obtain Wf_{nfw} (*see Fig. 2*) , and the Wf_{nfw} was applied in Equation (1) to get "Calculated wet Tg"

- Experimental wet T_g cannot match calculated wet T_g for samples with SDS
- The extra non-freezable water content adsorbed by the SDS added into the sample will not impact the wet Tg of the polymer, because SDS is not part of the polymer chain (i.e. not miscible with the polymer).

Conclusions

- The three types of water distributed within the polymer matrix can be qualitatively and quantitatively characterized via DSC
- The non-freezable water can change the polymer properties.
- SDS will dramatically increase the measured non-freezable bound water content, but the extra non-freezable water content adsorbed by SDS will not contribute to the T_g depression specific to the polymer.

References

(1) Lei, Y.; Child, J. R.; Tsavalas, J. G. *Colloid Polym. Sci.* **2013**, *291* (1), 143–156.
(2) Jiang, B.; Tsavalas, J. G.; Sundberg, D. C. *Prog. Org. Coatings* **2017**, *105*, 56–66.
(3) Tsavalas, J. G.; Sundberg, D. C. *Langmuir* **2010**, *26* (10), 6960–6966.
(4) Jiang, B.; Tsavalas, J.; Sundberg, D. *Langmuir* **2010**, *26* (12), 9408–9415.

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