A REVIEW OF WATER RESISTANCE TEST METHODS FOR PRESSURE SENSITIVE ADHESIVES

Laura J Donkus, Technical Service Scientist, The Dow Chemical Company, Collegeville, PA

William B Griffith, PhD, Principal Scientist, The Dow Chemical Company, Collegeville, PA

David Keely, Field Technical Service Manager, The Dow Chemical Company, Louisville, KY

INTRODUCTION

Anyone that has had experience testing pressure sensitive adhesives knows the importance of the test conditions. Past studies have defined a narrow range of standard test conditions that have been widely accepted. For Pressure Sensitive Tape Council methods[1] such as peel and shear, testing must be performed within the window of average temperature of 23°+/-1° C and average relative humidity of 50% +/-2%. Although such care will result in more reproducible results, most real world conditions are outside of this window. Assuming that there are no cure or degradation reactions, changes in temperatures virtually always results in higher modulus materials at lower temperature and lower modulus materials at higher temperature along with the expected corresponding change in PSA performance[2]. When temperature is changed, the heat flow associated with it readily distributes throughout the sample. There is no reason why one part of the adhesive should equilibrate at a different temperature than another.

Changes in moisture content can have much more complex responses. In some materials, water may transport very rapidly through the adhesives whereas others will be slow. In some adhesives and levels of water, moisture may distribute evenly. In others, water may concentrate in pockets within the adhesive or at surfaces. Exactly how the water enters the adhesive will markedly impact performance. Furthermore, the responses can strongly depend on the composition of the adhesive. To illustrate the impact of these effects, a few model systems will be selected and exposed to moisture. In addition, a standard level of surfactant is added to the systems to illustrate how formulation might impact results.

Some of the PSTC test methods explicitly state conditions outside of the standard moisture levels as part of the test method. Perhaps the most obvious ones are PSTC-34 (Water Vapor Transmission Rate) and PSTC-35 (Water Penetration Rate). PSTC-9 (Accelerating Aging of Tapes) has a step where the adhesive is exposed to moisture, but it is re-equilibrated before testing. PSTC test methods that characterize the electrical response of tapes also involve moisture, but will be considered out of scope for the present study since this focuses on a more limited application space. Hence to give a sense of how these various methods relate and a sense of what is happening within the samples, adhesive properties, vapor transmission, water uptake, and visual appearance will studied for a set of model acrylic emulsion systems.

EXPERIMENTAL

Perhaps the first response that would be noted when an adhesive is exposed to water is its appearance. There is no PSTC test method that explicitly states how to measure water whitening resistance (WWR). Major differences can readily be discerned by visual inspections after exposing an adhesive to water. In case where more quantitative *measurements* are sought, whitening is usually measured by opacity or haze. In most WWR experiments, these values tend to track one another. But keep in mind, opacity tracks how much light is transmitted whereas haze relates to what part of the transmitted light is scattered. As opacity increases, an image will look dimmer whereas more haze will make an image appear fuzzier/foggier. Hence, it is possible to have some differences between the measurements. In a previous PSTC presentation[3], the first water whitening resistant water based acrylic adhesive was introduced along with an opacity method to quantify the water whitening. The procedure outlined in that presentation will be used to measure the changes in appearance.

In order for water whitening to occur, there must be two distinct phases within the adhesive. As water enters the adhesive, it can collect in small domains. The contrast between the domains, that is the difference in refractive indices, cause the light to be scattered. Additional confirmation of this mechanism can be confirmed by a standard microscopic analysis. A water based acrylic tape was directly exposed to moisture and then adhered to a PET film to create a PET/Adhesive/PET construction. When cross sectioned and examined by transmission electron microscopy (TEM), the image (Figure 1) clearly shows the PET with the adhesive sandwiched between the film layers. The white domains are a consequence of water absorption.
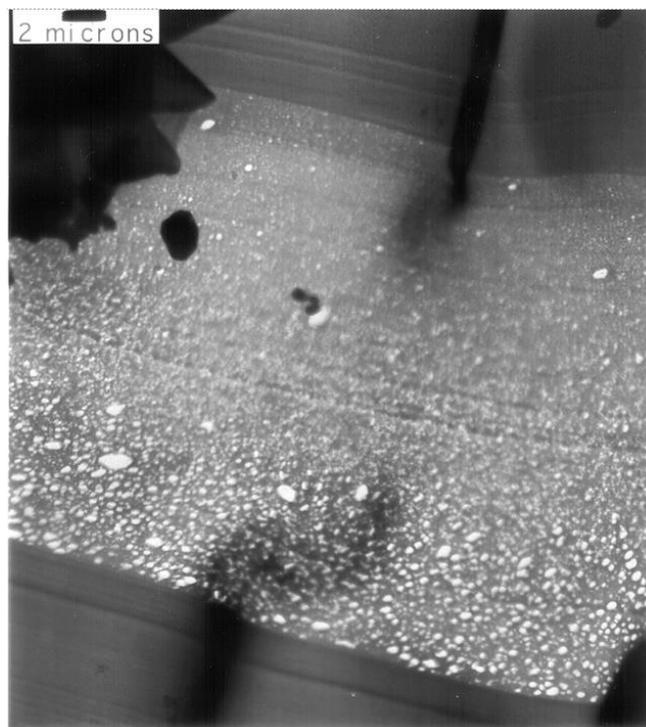
Figure 1. TEM of Adhesive after Water Exposure

Another approach to measure water whitening is to apply the tape to a substrate before exposing the construction to water. Once water enters the adhesive, whitening will occur by the same mechanism as directly exposing it to water. However, now the water has much more complex pathways it can use to enter the adhesive. Moisture can diffuse through the edges of the adhesive, along the adhesive substrate interface, or even through the substrate or face stock. Typically, how well the adhesive adheres to the substrate is the main factor which can potentially skew results from direct exposure.

Water uptake, that is, the mass that the adhesive absorbs when exposed to moisture, can often yield different results than water whitening resistance. Water whitening will depend on the size of the water rich domains in the adhesive as well as the amount of water that is absorb. Note that if water thoroughly plasticizes the adhesive, no water rich domains will exist and no whitening will occur. Obviously, plasticization will change the rheology of the adhesive by lowering both its modulus and glass transition temperature. Consequently, pressure sensitive adhesive properties will be altered. If all the water enters the adhesive as separate domains, glass transition will not be altered. However, these numerous defects (water rich domains) in the adhesive matrix will alter how the adhesive responds to stresses and can thereby affect adhesion properties

Another aspect to consider is the interfacial chemistry. It is well known that pressure sensitive properties depend on the surface chemistry of the substrate. Once water enters the adhesive, the system in some cases responds as a three component system where a third water rich component is present. The degree to which water enriches at an interface will depend on the hydrophilicity of the substrate. If water does enrich at the interface, it can act as weak boundary layer and reduce adhesion. In such cases, measured adhesive properties will decrease and the failure mode should be adhesive.

Water uptake was easily measured by soaking tape with coated with 2 mils of pressure sensitive adhesives in water for 24 hrs and measuring the mass difference before and after soaking in water. Three different model systems of acrylic water based were tested along with samples spiked with 1% of an anionic surfactant. The results are summarized in Table 1.

Table 1. Water Uptake after 24 hour Soak in DI Water

	A	B	C
As Is	8.9%	28%	14%
+ 1% Surfactant	13.8%	30%	19%

In all three cases, adding more surfactant increased the water uptake, which should not be surprising since surfactants have hydrophilic moieties. Note that there is a significant variation in water uptake. Values reported in Table 1 are calculated based on all of the water going into the adhesive and reflect only the changes on the adhesive mass. This is a fair assumption when compared against uncoated PET controls. So if water is entering the adhesive matrix, how is it partitioning throughout the adhesive? If the water were compatible with the polymer, one would expect it to plasticize the polymer since the

glass transition (not the melting point) is lower than acrylic adhesives on the order of 100°C. If it is assumed that the glass transition temperature (Tg) of water is -150°C and if it is assumed that the mixture obeys the Fox equation, then even 2% water should reduce the Tg of the adhesive by ~4°C. When the Tg was measured on the films before and after exposure to water, the glass transition temperatures of all samples, as measured by differential scanning calorimetry, were found to be reduced by less than 3°C in all cases. This difference is very close to the uncertainty of the calculation and suggests that the vast majority of the water should be in a separate domain rather than with the adhesive. For the samples soaked in water, a crystalline melt transition near 0°C was also detected. In addition, extreme care was taken to ensure that water did not volatilize throughout the DSC analysis. Since samples A, B, and C were predominately synthesized from butyl acrylate and/or 2-ethylhexyl acrylate, monomers which have very limited water solubility, it should not be surprising that the polymers show virtually no compatibility with water. This may not be the case if much more hydrophilic compositions were chosen.

Because the above evidence points to water entering the adhesive as separate domains, it should not be surprising that all three adhesives whiten when exposed to water. To quantify the effect, 1 mil of adhesive was coated onto PET and open films were directly submerged in water. The opacity of each sample was measured immediately after removal from water and the differences between these values and an unexposed sample are presented in Table 2. What may be somewhat surprising is that some of the samples show a slight decrease in water whitening when surfactant is post added. This is repeatable and a consequence of how the surfactant affects the domain size as the water enters the adhesive.

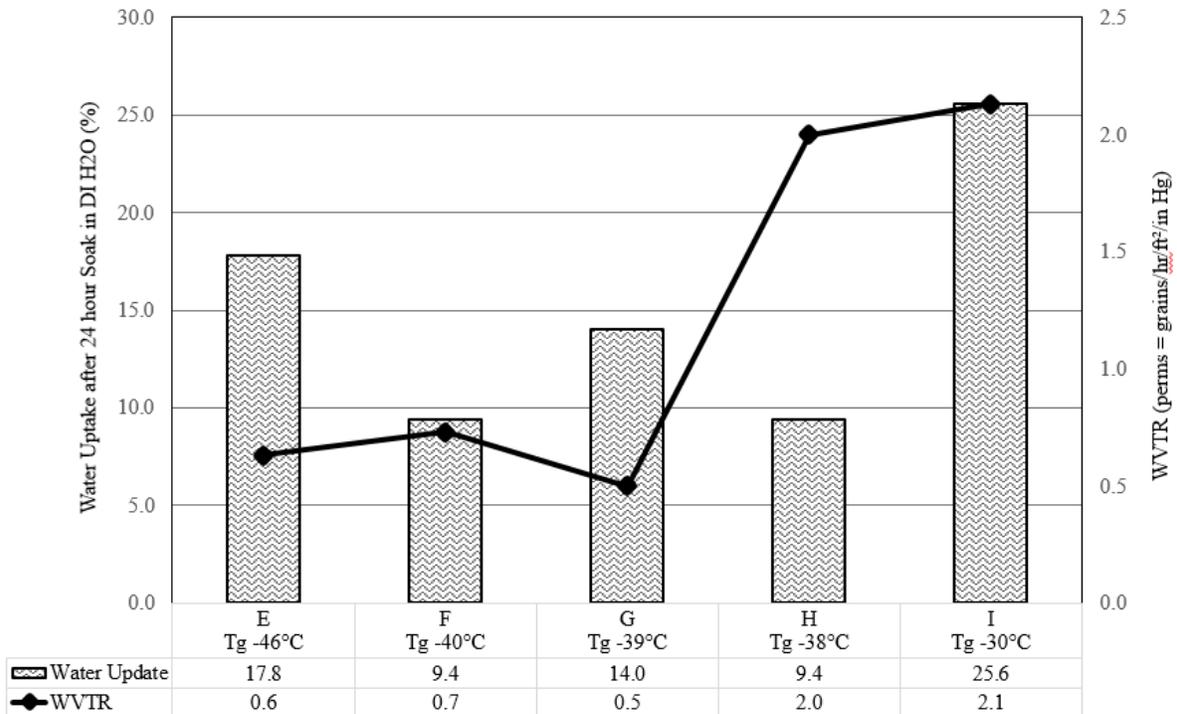**Table 2.** Difference in % Reflectance after Water Exposure

	A			B			C		
	1 hr	4 hr	24 hr	1 hr	4 hr	24 hr	1 hr	4 hr	24 hr
As Is	14%	21%	28%	23%	30%	29%	0.0%	1.2%	6.9%
+ 1% Surfactant	12%	21%	28%	20%	28%	30%	0.0%	1.9%	13%

Plotting the water retention data and the water whitening data for all six samples is another indication that the relationship between the two is very poor. In fact, when the data in Figure 2 is fitted to a line, the correlation coefficient is very low ($r^2 = 0.10$). Simple visual inspection of Figure 1 shows that there is a large distribution of sizes in the water rich domains. Adequately quantifying the distribution, working through all the computations to relate the contribution of the individual scattering centers and the multi-reflection paths that will occur within the film is well beyond the scope of the present study.
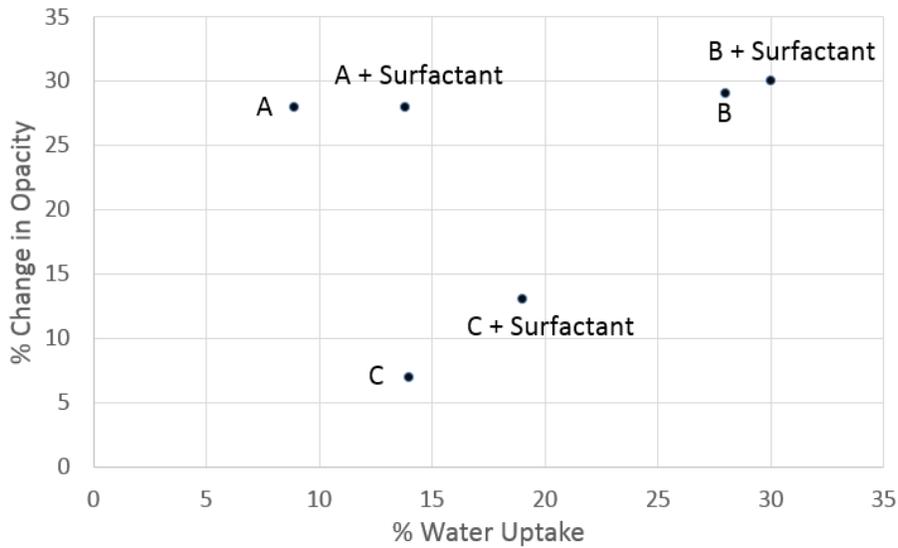
Figure 2. Water Uptake versus Water Whitening

Both Water Uptake and Water Vapor Transmission Rate (WVTR) were evaluated for a number of different acrylic polymers with glass transition temperatures ranging from -46°C to -30°C. While Water Uptake measures the amount of water taken in by the sample, WVTR quantifies the amount of water that passes through when the sample is acting as a barrier. As shown in Figure 3, with this set of acrylic polymers, there is no correlation between Water Update and WVTR or with Tg and either test.

	E Tg -46°C	F Tg -40°C	G Tg -39°C	H Tg -38°C	I Tg -30°C
Water Update	17.8	9.4	14.0	9.4	25.6
WVTR	0.6	0.7	0.5	2.0	2.1

Figure 3: Water Uptake vs Water Vapor Transmission Rate

To illustrate the impact of water on pressure sensitive adhesive properties, each sample was coated at a 0.8 mil dry film thickness onto 2 mil PET film and lamented to panels for standard peel tests. Peel measurements were made after a 24 hour dwell. One set of panels was equilibrated in a constant temperature/humidity room maintained at standard PSTC test conditions. Another set was submerged in a 23°C water bath for 24 hours. Peels were measured for this latter set immediately after removal from water. Results are listed in Table 3.

Table 3. Effect of Water Soak on 180° Peel from SS and HDPE

		A (As Is)	A + Surf.	B (As Is)	B + Surf.	C (As Is)	C + Surf.
Stainless Steel (g/in.)	Dry	860 A	1111 A	581 A	585 A	738 A	785 A
	H_2O Soak	544 A	373 A	24 A	63 A	293 A	142 A
	Retention	63%	34%	4%	11%	40%	18%
HDPE (g/in.)	Dry	543 A	429 A	400 A	416 A	453 A	283 A
	H_2O Soak	507 A	0 A	113 A	0 A	366 A	0 A
	Retention	93%	0%	28%	0%	81%	0%

The "Dry" samples all display higher adhesion on Stainless Steel than HDPE. The additional 1% surfactant has a varying effect on the "Dry" samples, probably because of the complexity of how it impacts plastic deformation. In all cases, exposing a sample to water reduces adhesion. What may be somewhat surprising is that in every case, the adhesives "As Is" (no extra surfactant) have much higher retention on HDPE than Stainless Steel. In fact, two of three "As Is" adhesive have higher peel for the water soak samples on HDPE than stainless steel. The extra surfactant grossly changes this result. It does reduce the values on stainless steel, but for the water soaked samples on HDPE panels, the peel is reduced to zero.

One hypothesis is that the results are related to the surface chemistry. Stainless steel is clearly more hydrophilic than HDPE. Thus, if there are no other effects, one might speculate that water collects more at the stainless steel/adhesive interface than the HDPE adhesive interface. Moreover, exactly this same effect has been observed in cases where a hydrocarbon hot melt tape was examined, that is, much more reduction on stainless steel than HDPE. Even for the hydrocarbon adhesive case, the peel will eventual be lower on stainless steel than HDPE for samples submerged in water. Note that a hydrocarbon hot melt tape should very little, if any, surfactants or water solubles. The effects of the additional post added surfactant may introduces a fourth component into the behavior. Adhesives low in surfactant may not have an adequate concentration to thoroughly cover the interface. Owing to the low surface energy of the HDPE surface, there may be a driving force for the surfactant to migrate to this interface to reduce the interfacial tension between the adhesive and HDPE surface. The hydrophilic portion of the

surfactant may then provide the channel for water to enter thereby creating a weak boundary layer. There is no corresponding mechanism for very polar surfaces.

CONCLUSIONS

As this paper demonstrates, there are many valid ways to quantify the water resistance of a pressure sensitive adhesive. However, each measures water resistance under very specific conditions, which unfortunately often do not correlate with one another. This means when one is asked about the water-resistance of a specific tape or adhesive, it is critical to first determine the application and conditions. Best results are achieved by correlating the proper test methods with the application in question.

LITERATURE CITATIONS

1. PSTC Test Methods for Pressure Sensitive Adhesive Tapes, 16th Edition, 2014

2. D. Satas (editor), Handbook of Pressure Sensitive Adhesive Technology, 3rd Edition (Satas and Assoc., 1999)

3. Donkus, L. J. (1997), "Solvent-Like Performance from Emulsion PSAs: Advances in Water-Whitening Resistance" in *Adhesives Age*, July, pp. 32, 35-37

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