



# The World of Surface Coatings Is Centered Around the Glass Transition Temperature, *But Which One?* Part 2

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As was discussed in Part I of this article [CoatingsTech, Vol. 11 (8) 28-38 (August 2014)], polymeric materials are employed in a wide variety of applications. Whether the desired performance is a mechanical response, specific permeability, chemical reactivity, or general response to any given stimuli, the target properties are strongly affected by the molecular dynamics of all blended materials and reactants. The molecular dynamics of amorphous materials are controlled by the resulting glass transition temperature ( $T_g$ ). This two-part article reviews the importance of  $T_g$  in polymeric coatings and emphasizes the shifting nature of a material's  $T_g$  throughout the service lifetime. In attempting to simplify a complex combination of material dynamics, a polymer's  $T_g$  has often been utilized as a single value parameter throughout history. While correlations exist between the  $T_g$  and many important material properties, a single  $T_g$  value does not communicate the multifaceted material dynamics involved in formulation, application, film formation, cure, or in-service use.

## WHAT ENVIRONMENTAL CONDITIONS AFFECT THE $T_g$ ?

### *Permeability of Applied Coatings*

Although gas and liquid permeability can be dramatically different between polymer types, in general, polymers are relatively permeable and the characteristic is often simplistically attributed to

the relatively low density of polymers regardless of measured  $T_g$ .<sup>57</sup> Coating permeability is described stepwise as: (1) adsorption onto the air/coating interfacial surface, (2) diffusion through the polymer, and (3) desorption and substrate interactions initiated at the polymer/substrate interface.<sup>57,86-88</sup>

Chemical potential is the major thermodynamic driving force for permeant diffusion through a coating, i.e., the nonequilibrium state between the atmosphere/solution, the coating, and the substrate. Diffusion occurs in glassy, leathery, and rubbery polymeric materials at dramatically different rates. Polymer diffusion potential for most permeants is a function of the permeant size ( $\alpha M^{-1/2}$ ) and chemical properties, e.g., affinity, and most often known to follow Fickian diffusion.<sup>57,86,88</sup> Permeation of a gas through a polymer (adsorption, diffusion, desorption) is characterized via the permeability coefficient, and is defined as the product of the sorption equilibrium parameter (a thermodynamic term) and the diffusion coefficient (a kinetic term).<sup>2,57,86-88</sup> Permeability of gases and liquids through polymers is extremely sensitive to environmental conditions (permeation coefficients can be drastically different above and below the  $T_g$ ); thus, several ASTM and ISO standards have been developed to enable a more accurate comparison between various polymer types, materials, and blends of varying polymers and other fillers or additives.<sup>57,88</sup> Dramatic differences exist between a material's permeability/diffusion and transmission rates below, at, or above  $T_g$ , and reveal much about a coating's response to the environment and performance differences between different environmental conditions, e.g., dry and hot versus wet and cold.

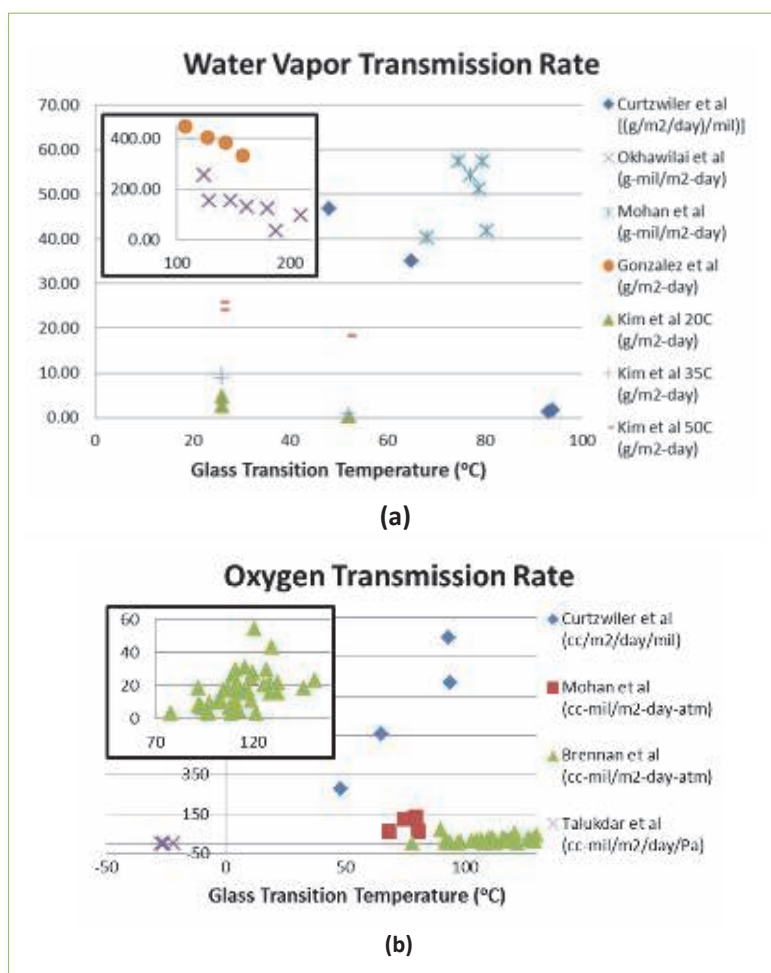
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Any coating at a particular time has glassy, leathery, and rubbery domains. In the rubbery state, polymer chains have higher molecular motion that enables the transport of larger molecules and yet lower void volume to avoid transfer of those same molecules.<sup>87</sup> In the rubbery state, both large and small molecules (relatively speaking) can diffuse through the polymer over time; however, larger molecules require more free volume for diffusion and, therefore, statistically have a reduced number of available locations to reside in the polymer.<sup>88</sup> Critical for coatings are the differences between uptake and transmission. In general, the water vapor transmission rate decreases and oxygen transmission rate increases as a function of  $T_g$  (Figure 14). This is attributed to the larger size of water vapor molecules compared to oxygen; moreover, water has an affinity to certain components within the polymer composition.<sup>2</sup> Given that sorption is a requirement of permeation, sorption of plasticizing molecules, i.e., water, can reduce the  $T_g$  and change permeability coefficients, which can be modeled using the Kelley-Bueche equation.<sup>88</sup> The trends observed in unfilled polymers appear to be relatively independent of backbone chemistry and more dependent on its physical state relative to the  $T_g$ . These trends are not observed in systems containing nano- and meso-scale fillers, where barrier properties can be increased or decreased depending upon the tortuosity versus increase hole volume effects created by the filler and polymer affinity and thermal/solvent induced balance between film formation, cure, and vitrification.<sup>89-94</sup>

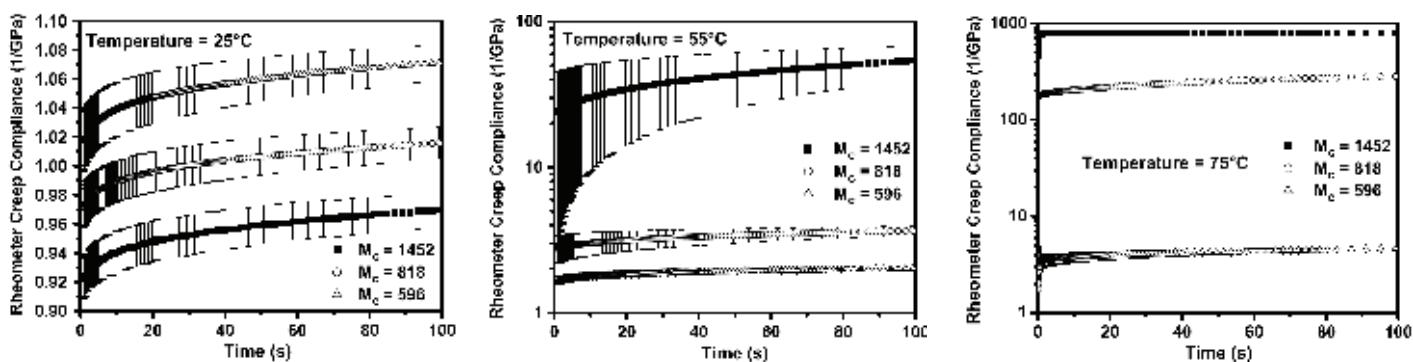
## CREEP AND DUCTILITY WITH RESPECT TO $T_g$

When polymers are subjected to a constant load over a period of time, their viscoelastic character results in deformation known as creep.<sup>2</sup> Resistance, or compliance, associated with creep is dependent on the natural interplay between modulus and  $T_g$ . These characteristics play a vital role in coatings performance over extended periods of time. Van Landingham and co-workers investigated the relationship between crosslink density/ $T_g$  and creep compliance ( $J$ ) in a series of aliphatic epoxy-amine systems by varying the average molecular mass between crosslinks (and, hence,  $T_g$ ).<sup>104</sup> Their research determined through indentation and rheological studies that thermosetting networks of varying crosslink density (and concurrently  $T_g$ ) exhibited similar creep compliance at room temperature.<sup>104</sup> However, as temperature increased, the lower crosslink density correlated with higher creep compliance and also increased creep compliance at a faster rate than those networks of higher crosslink density and  $T_g$  (Figure 15).

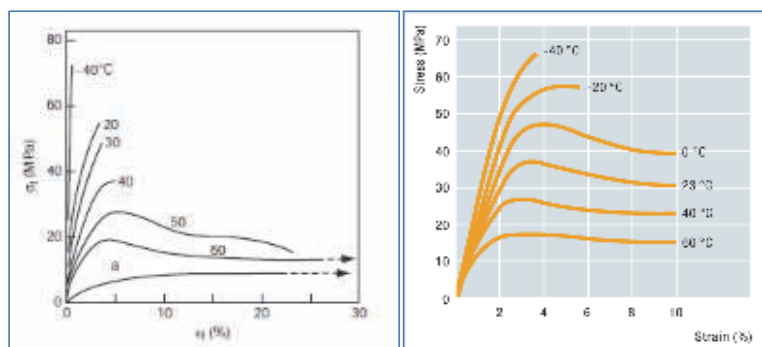


**Figure 14**—Water vapor transmission rate (a) and oxygen transmission rate (b) of various polymeric materials without fillers relative to  $T_g$ .<sup>95-103</sup>

The relationship between mechanical performance and  $T_g$  can also be seen in the brittle/ductile failure of polymers. Polymers will only show brittle or ductile failure well below their  $T_g$ . Aharoni revealed that the length of polymer backbone chain found between effective crosslinks heavily influences the mode of failure.<sup>105</sup> When evaluated at temperatures significantly lower than  $T_g$ , the molecular capacity for only discrete vibrational/rotational/translational movement will result in brittle failure, and upon increasing the temperature, the polymer passes through a brittle-ductile transition temperature ( $T_{bd}$ ) where ductile failure becomes the more dominant mode. Correlations between  $T_{bd}$  and beta relaxation temperatures have been noted in the literature.<sup>106-109</sup> Exceptions to this correlation have led to suggestions that only beta relaxation related to main chain motions, as opposed to substituents, are related to  $T_{bd}$ .<sup>109</sup> Although there is only a weak correlation between  $T_g$  and beta relaxation temperatures, which can be found using a parameter called fragility, these temperatures are always below the  $T_g$  of the material.<sup>110</sup> It can be expected that conditions that alter



**Figure 15**—Creep compliance responses of epoxy-amine systems of varying cross-link density with respect to time at different temperatures.  $M_c$  values 1452, 818, and 596 (g/mol) correspond to  $T_g$  values of 67, 86, and 107 ( $^{\circ}\text{C}$ ), respectively.<sup>104</sup>



**Figure 16**—Stress-strain measurements within a range of testing temperatures for PMMA<sup>2</sup> (left) and transparent ABS<sup>67</sup> (right) reveal that distinctly different polymeric materials respond similarly to mechanical deformation when temperature is adjusted relative to  $T_g$ .

the  $T_g$  of a material will also affect  $T_{bd}$ . Stress-strain curves from tensile tests on polymers at different temperatures can be used to estimate  $T_{bd}$  (Figure 16). There is a strong correlation between the emergence of plastic flow and  $T_g$  of a material.

## SUBSTRATE EFFECTS ON $T_g$

Many researchers have attempted to quantify and understand polymer-substrate interactions. Polymers at very thin film thicknesses exhibit abnormal behavior compared with bulk measurement methods. Keddie et al. and Wallace et al. studied polystyrene (PS) and PMMA thin films, respectively, and observed that  $T_g$  shifts with film thickness changes below a threshold of bulk thicknesses varied in average chain mobility when comparing air, polymer, and substrate interfaces.<sup>106,107</sup> Favorable attractive interactions between substrate and polymer chains potentially raise the  $T_g$  of thin films with concurrent film thickness reduction (Figure 17). Wallace and co-workers

observed that the apparent  $T_g$  was higher (best measurement method achievable) for thin films of PMMA on a hydrogen-terminated silicon substrate compared with the bulk material  $T_g$ . In the thinnest PMMA films (91 Å), even at temperatures 60  $^{\circ}\text{C}$  above the bulk  $T_g$ , the sample exhibited no measurable transition (top left, Figure 17).<sup>107</sup>

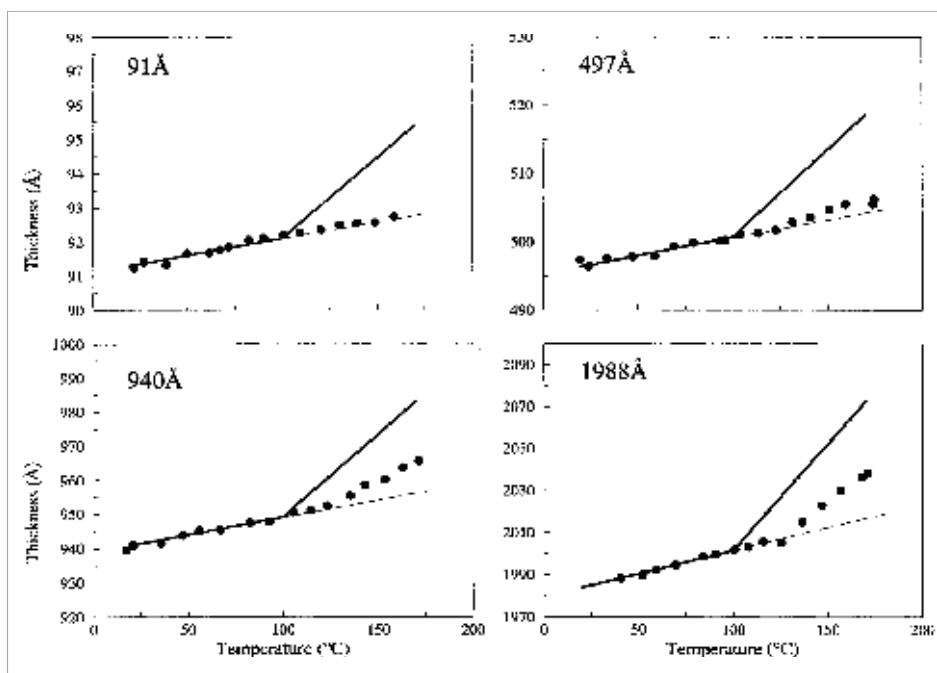
The relationship between film thickness and  $T_g$  increase versus a measured decrease holds for other polymeric materials, as demonstrated by Torres and co-workers with a series of acrylic copolymers (Figure 18), where  $T_g$  is depressed at increasing levels at closer proximity, 0–10 nm, to an elastic substrate and modulus being more heavily influenced at distances up to ~ 100 nm.<sup>108,109</sup>

The thin film behavior also carries over to coating applications where dependence on the polymer/substrate interaction strength influences the  $T_g$  at short-length scales from the substrate.<sup>109</sup> The shift in  $T_g$  with corresponding changes in modulus at interfacial regions where adhesion requirements are developed suggests that the binder-substrate interaction strength is critically influential to coating properties.<sup>109</sup>

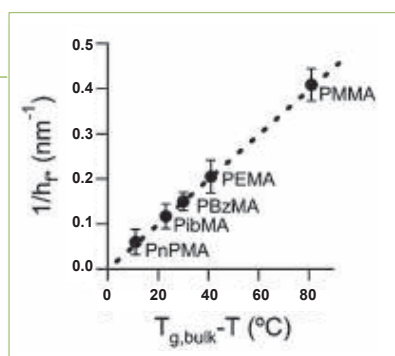
## ADHESION AND $T_g$

Coatings require suitable adhesion for environmental stability and performance over any extended duration. To achieve optimal adhesion, important considerations are the coating-substrate chemical attraction and compatibility as affected by substrate pretreatment chemistry and the resulting surface area.<sup>111</sup> Polar molecular components increase adhesion, e.g., hydrogen bonding versus ionic bonding; however, polarity also has the potential to increase adhesion variability between wet and dry environments.<sup>111</sup> When poor chemical attraction exists between coating and substrate, increased surface roughness is often utilized to promote coating adhesion.<sup>111</sup> Chaudhury quantified that to remove a rubbery adhesive from a solid sub-

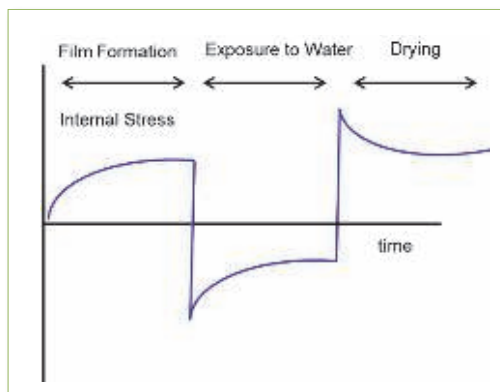




**Figure 17**—Measured thermal expansivity of PMMA on hydrogen-passivated silicon substrates at varying film thicknesses. The solid lines represent the measured  $T_g$  of bulk PMMA, i.e., 100 °C.<sup>107</sup>



**Figure 18**—Correlation between free surface layer thickness ( $h_f$ ) and quench depth into the glass for five polymethacrylates.<sup>110</sup>



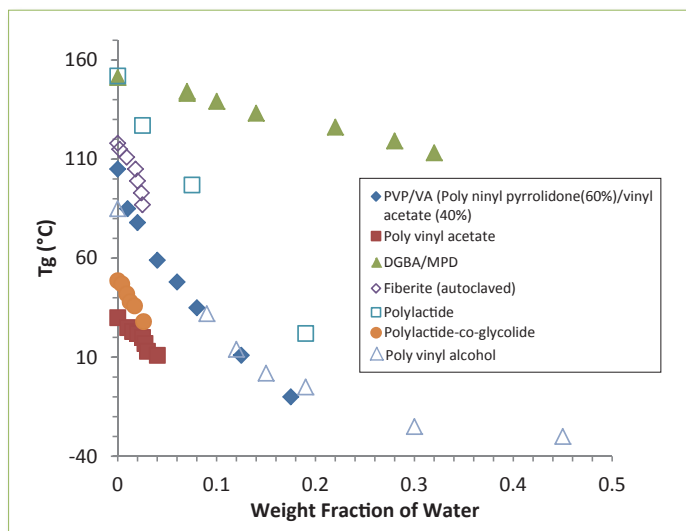
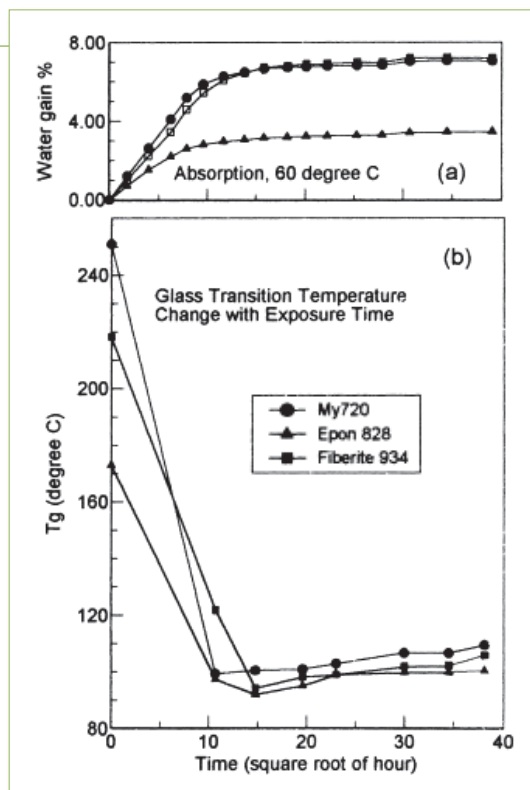
**Figure 19**—Graphical explanation of adhesion mobilization during wet-dry cycles.

strate, the work of adhesion ranged from 10–100 mJ/m<sup>2</sup>.<sup>112</sup> Conversely, the work of adhesion to remove metal films on ceramic is 500–2000 mJ/m<sup>2</sup>. While the majority of energy required to separate adhered faces is expended in inducing elastic and plastic deformation at the interface,<sup>113</sup> the drastic difference in these adhesion results stems from a dependence upon each material's modulus (critically related to  $T_g$  values and the resulting modulus during environmental service) and the chemical attraction between the coating and the substrate.<sup>114</sup>

When a coated substrate goes through wet and dry cycles, the system may experience plasticization, expansion, leaching, and delamination. Locally, this leads to regions of adhesion and delamination where the coating exhibits dynamic adhesive properties during transitions between wet and dry conditions.<sup>115</sup> Figure 19 explains the concept of dynamic adhesion and mobility in terms of internal stress. During film formation,

polymer chains become constrained and accumulate internal stresses as the coating cures and contracts. It is predicted that when water reaches the metal/coating interface, the system experiences its maximum mobility. Interfacial water disrupts adhesive bonds, giving the polymer more flexibility, while water in the polymer induces swelling and moves the moieties involved in the adhesive bonds away from their initial partners. Finally, during the drying cycle, new interfacial bonds are formed but now the distribution of interfacial bonds is farther from ideal, so adhesion increases, but not to that of the pristine sample. If the  $T_g$  is much higher than the service temperature, the  $T_g$  will not drop to the service temperature when exposed to and plasticized by water, and the coating will maintain adhesion to the substrate and the appropriate modulus to avoid easy delamination. When the  $T_g$  is below the service temperature, adhesive bonding becomes mobile, i.e., in the rubbery state, the material modulus is sufficiently diminished to allow more facile removal.<sup>115</sup>

**Figure 20**—(a) Percent water uptake over time, and (b)  $T_g$  change with water uptake over time, of an epoxy-amine composite.<sup>118</sup>



**Figure 21**—Differences in  $T_g$  values versus water content in various polymer systems: PVP/VA,<sup>119</sup> poly vinyl acetate,<sup>119</sup> DGBA/MPD,<sup>120</sup> Fiberite (autoclaved),<sup>121</sup> polylactide,<sup>122</sup> polylactide-co-glycolide,<sup>123</sup> and poly vinyl alcohol.<sup>124</sup>

Legghe and co-workers looked at the differential between wet and dry adhesion and found that 2K epoxy-amine systems gained adhesion when allowed to dry before evaluation.<sup>116</sup> They did not measure the  $T_g$  differences between the wet and dry films; however, other studies on epoxy composites that investigated similar wet to dry recoveries reported that the systems regained their pristine/dry starting point  $T_g$  value.<sup>117,118</sup> These results correlate well with the observations of Funke and Negele supporting that adhesion is diminished when water reaches the interface, resulting in sliding bonds that are adequate once the coating has been dried but inadequate for film retention/adhesion in microscopic regions during high moisture service.<sup>115</sup>

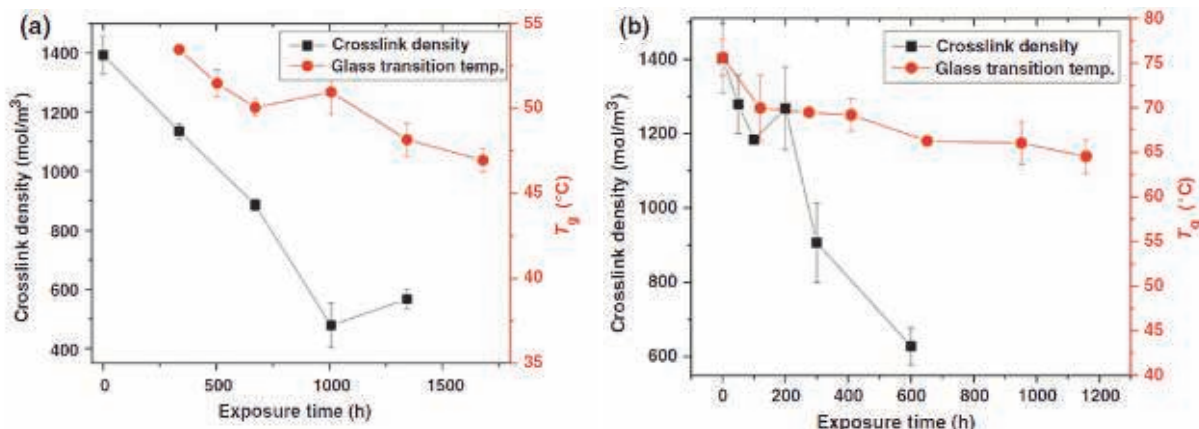
## HYDROPLASTICIZATION OF IN-SERVICE COATINGS

The performance properties of coatings during service should match material goals; nevertheless, the dominant number of lab and testing scenarios cannot account for environmental variety. Under the constantly shifting nature of a given asset in ever-changing service roles, each material-environmental condition will result in a different range and modality of  $T_g$ s. The previous sections validated that many if not all polymer properties scale with  $T_g$ . This section adds another level of complexity by focusing on the environmentally induced material property changes outside of ambient STP conditions.

Water and sunlight are the most dramatic environmental parameters that affect polymers in any application. Water within polymeric materials effectively reduces its  $T_g$ . Such water is classified as bound or free water. Bound water associates closely with polymer substituents, while free water disrupts interchain van der Waals forces and acts as a plasticizer.<sup>117</sup>

Zhou and Lucas studied the effects of water on a polymer's  $T_g$  and determined the types of water in the polymer network.<sup>117,118</sup> Water content was studied through its interactions with the epoxy network via nuclear magnetic resonance (NMR) spec-

**Figure 22**—(a) Polyurethane and (b) epoxy system accelerated weathering results from Croll and co-workers.<sup>128</sup>



trospecty and physical property differences within the epoxy matrix were measured in terms of  $T_g$  by DSC. Zhou and Lucas evaluated an epoxy-amine composite that exhibited a 112°C reduction in  $T_g$  upon saturation with water (Figure 20). When the same samples were carefully dehydrated, the  $T_g$  recovered to values in the same range as pristine dry starting point samples. It is noteworthy that a low-level, quantifiable amount of Type II water was retained even after careful drying.<sup>118</sup> Between different polymeric materials with varying  $T_g$ , important differences exist in the rate of  $T_g$  decrease as a function of water content (Figure 21).

Tsavalas and Sundberg developed a hydroplasticization  $T_g$  prediction method based on the Fox equation [equation (1)].<sup>4</sup>

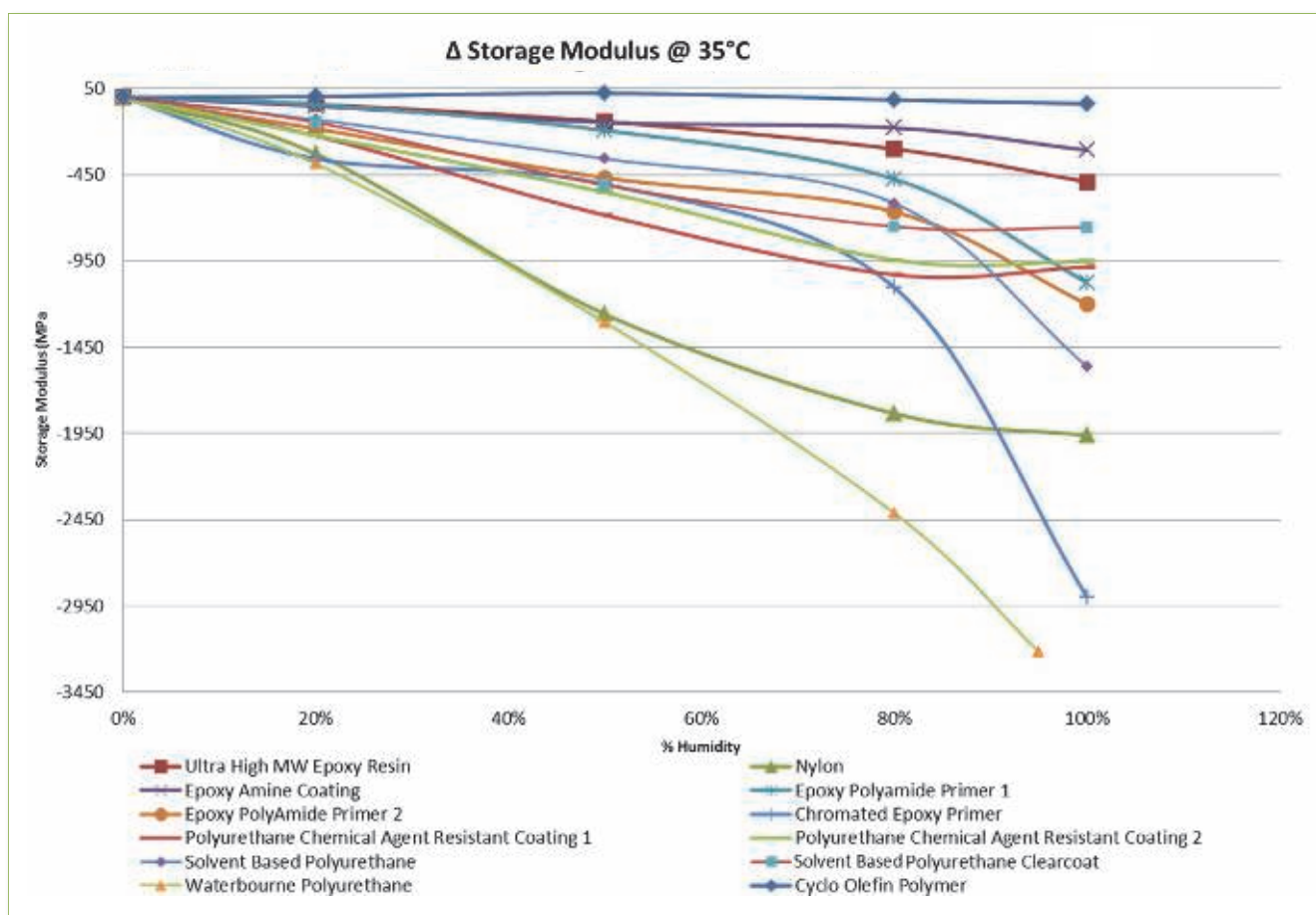
$$\frac{1}{T_{g,wet}} = \frac{x_{water}}{T_{g,water}} + \frac{x_{polymer}}{T_{g,polymer}} \quad (1)$$

The wet  $T_g$  is the  $T_g$  of the polymer containing a known amount of water. The experimentally determined  $T_g$  of water (137 K) was used to calculate the wet  $T_g$ .<sup>4</sup> Kim et al. developed a model to estimate the  $T_g$  as a function of film thickness. Although the phenomenon of thin film

$T_g$  depression has been extensively reported, the mechanism is still not well understood. Equation (2) operates off the normalized  $T_g$  relationship with normalized thickness ( $t^*$ ). This equation is polymer-independent and has exhibited a good correlation with experimental work.<sup>125</sup> Other predictive models have compared the  $T_g$  prediction equations for fully miscible (Gordan–Taylor equation), partially miscible, and immiscible blends, as well as copolymers.<sup>126</sup>

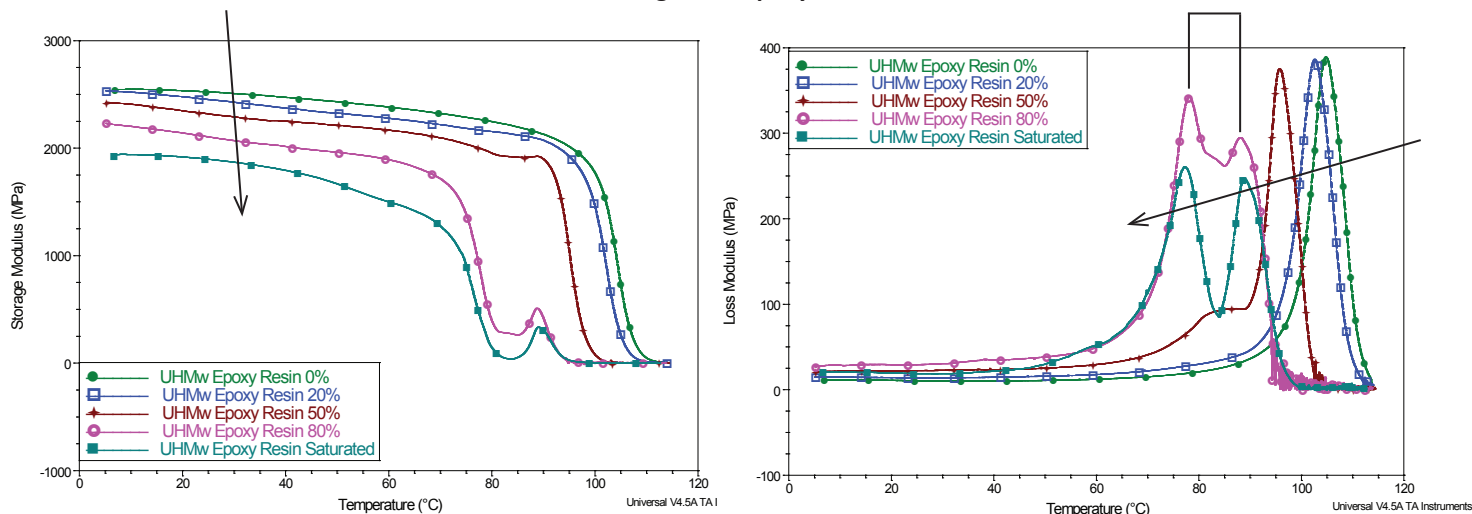
$$T_g^* = \frac{t^*}{1 + t^*} \quad (2)$$

In epoxy networks, the combined effects of plasticization and physical aging on the viscoelastic behavior have been studied with DMA through immersion followed by analysis above and below the network  $T_g$ .<sup>127</sup> The duration of immersion required for these epoxy networks to equilibrate was as long as three months at ambient conditions in deionized water. The authors noted a decrease in  $T_g$  due to hydroplasticization, but when samples were conditioned above their  $T_g$  and re-measured, the same samples exhibited a closely matching  $T_g$  to the pristine/original sample(s).<sup>127</sup> With accelerated weathering techniques, there are not many studies that report the effect on  $T_g$ .



**Figure 23**—Summary of the differential in DMA-measured storage modulus for a variety of materials after conditioning at 0, 20, 40, 60, 80, and 100% RH for 4 hr.

## Ultra High MW Epoxy Resin



**Figure 24**—DMA storage modulus and loss modulus (mechanical  $T_g$ ) plotted vs temperature and RH conditions from 0 to 100%.

| % Humidity | Primary Mechanical $T_g$ °C | Storage Modulus (Mpa) |
|------------|-----------------------------|-----------------------|
| Saturated  | 78.15                       | 1835                  |
| 80%        | 79.79                       | 2041                  |
| 50%        | 98.41                       | 2265                  |
| 20%        | 103.35                      | 2400                  |
| 0%         | 105.95                      | 2492                  |

\* $T_g$  at 20% relative humidity estimated due to water release overlap.

\*Cured at 200°C for 1 hour.

Croll and co-workers reported that with samples exposed in a Q-Sun chamber without water spray, there was a decrease of 10°C in  $T_g$  and about 1000 mol/m<sup>3</sup> in crosslink density as the exposure time increased (Figure 22).<sup>128</sup>

The data in Figure 23 reveal the dramatic differences from one polymer type and coating class to another as to how modulus is affected by the presence of different levels of water. The extreme examples shown include the cyclo olefin polymer that exhibits almost a constant modulus value, regardless of the relative humidity (RH). The other extreme includes two thermoplastic polymers and a waterborne polyurethane coating, each dropping more than 1900 MPa in modulus between 0% and 100% RH.

DMA characterization curves for a thermoplastic polyepoxide (Figure 24) show diminishing storage modulus values with increasing RH. The top right image in Figure 24 shows a consistently reduced mechanical  $T_g$  and an emerging multi-modal loss modulus peak as RH values increase from 40% to 100%.

## SOLVENT-RELATED EFFECTS ON $T_g$

Some level of residual solvent is common in solvent-based systems, especially when dried without an oven-drying step. Feng and Farris investigated the influence of curing conditions on the material  $T_g$ . As baking temperature increased, the  $T_g$  also increased, reaching a plateau at approximately 238°C. The residual stress formed during bake time was found to be sensitive to humidity but also reversible; sensitivity decreased through elongation of baking time.<sup>129</sup>

Other groups investigated the sorption and desorption behavior of polymeric systems in full water immersion or at varied RH. A polyvinyl alcohol (PVOH)/polyvinyl acetate system (Figure 24) exhibited a change in  $T_g$  of approximately 60% with ~6–9% water content while epoxy-based systems exhibited a  $T_g$  depression of roughly 5% when absorbing similar amounts of water. In most studies, an initial sharp increase in water uptake was observed which followed Fickian diffusion of water.<sup>130</sup> After this initial fast uptake, there was an equilibration period that transitioned to polymeric material saturation. This behavior was similar to the

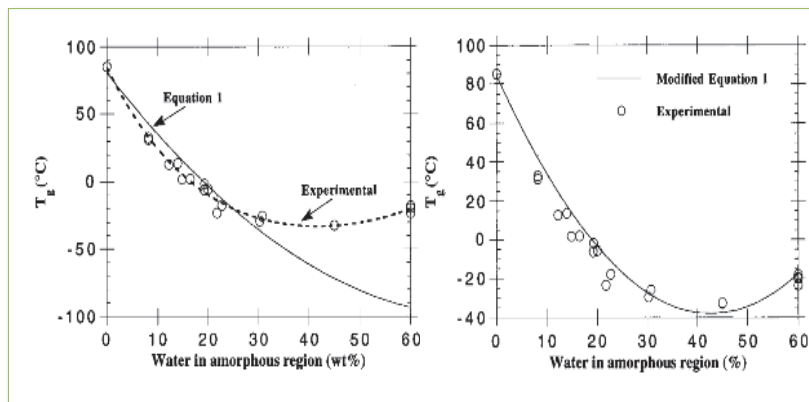


observations reported by Feng and Farris. The initial  $T_g$  depression was significant to the coating system, and varied from as little as 10°C to almost 100°C. Within these decreases in  $T_g$ , many systems go through a phase change from the glassy to rubbery state. Factors that affect this diffusion behavior include the stoichiometry of crosslinkers that can skew the behavior to be non-Fickian diffusion. For epoxy-amine systems, depending on the amine content, the plasticization effect of  $T_g$  can vary from 5–20°C.<sup>130</sup> Metal-bound polymeric materials experience the same diffusion behavior described earlier and are commonly tracked with electrochemical impedance spectroscopy (EIS). Zhang and co-workers studied water transport in epoxy coatings with EIS and reported that over a period of four months, an epoxy coating on mild steel and LY12 Al alloy exposed to 3.5% NaCl solution experienced a 12°C drop in  $T_g$ .<sup>131</sup>

The plasticization effect of water on PVOH was studied via positron annihilation lifetime spectroscopy (PALS), NMR, and DMA. Water immersion samples analyzed by PALS exhibited an increase in the polymer free volume cavity size, suggesting an increase in chain mobility, while NMR analysis indicated the disruption of hydrogen bonding. As with the polymer systems discussed already, PVOH was also found to experience a significant decrease in  $T_g$  as the measured in-service  $T_g$  value dropped 110°C and contained almost 50% water in the amorphous regions.<sup>124</sup> To produce a better fit, Hodge and co-workers modified the Fox equation to account for only the water that was acting as a plasticizer, and found that including the fraction of water that freezes in the sample yielded a poor fit for  $T_g$  prediction (left and right portions of Figure 25).

In drug-delivery microspheres containing polylactic acid (PLA) and poly (lactic-co-glycolic) acid (PLGA), Passerini and Craig reported that the microspheres retained a significant amount of water after preparation, which plasticized the microspheres and reduced the  $T_g$  by as much as 20°C. This has implications for understanding the release behavior of drug-loaded microspheres. It has been shown that drug-delivery rate is related to  $T_g$ .<sup>122</sup>

The data in Figure 26 was compiled from DSC and thermogravimetric analysis of solvent cast films of a thermoplastic polyepoxide blended with ethyl 3-ethoxypropionate (EEP). The results were interesting, as the dry/solvent-free high molecular weight polymer  $T_g$  was 93°C. Dissolving in EEP and casting for film formation at ambient resulted in an 11 wt% retention of solvent as that ratio of materials resulted in a  $T_g$  around 30°C, which therefore vitrified (stopped allowing solvent evaporation at the same rate, as the blend was glassy in nature).



**Figure 25**— $T_g$  of PVOH fit with Gordon-Taylor equation (left) and with a modified Gordon-Taylor to account for only amorphous water content (wt%).<sup>124</sup>

The same solvent cast blend, when thermally annealed at 60°C for one hour, resulted in a measured  $T_g$  of 67°C (again representative of glassification and a solvent retention of 5.5 wt%). After 30 days of ambient storage, the same materials were seen to retain > 10 wt% solvent. Altogether the data reveal that glassy polymers (this example and many others) can retain slow-evaporating solvents at sufficiently high quantities to alter physical properties and the overall material characteristics in every measureable manner.

As discussed previously, the internal strain of a coating is related not only to adhesion, but also to residual solvent and water content. Croll developed a method to calculate internal strain from the volume of solvent lost after the coating has solidified. The solidification point was identified as the moment at which the solvent concentration depressed the polymer  $T_g$  to the experimental temperature.<sup>132</sup>

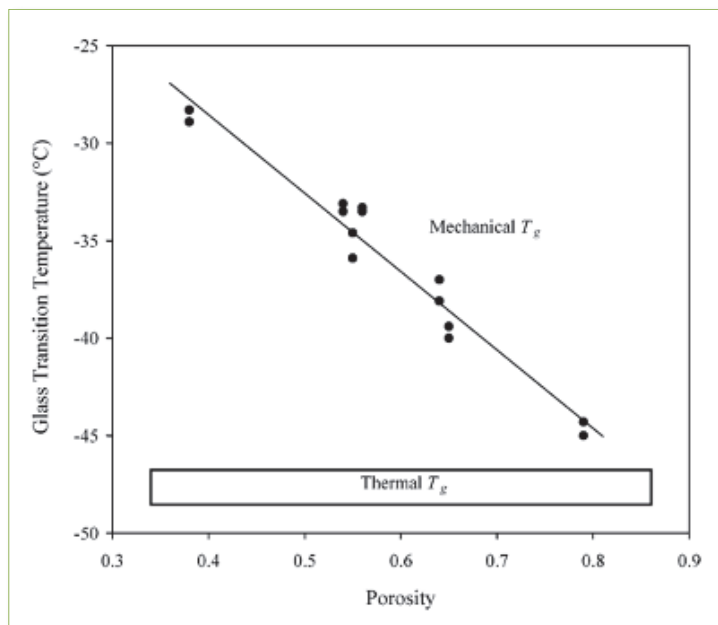
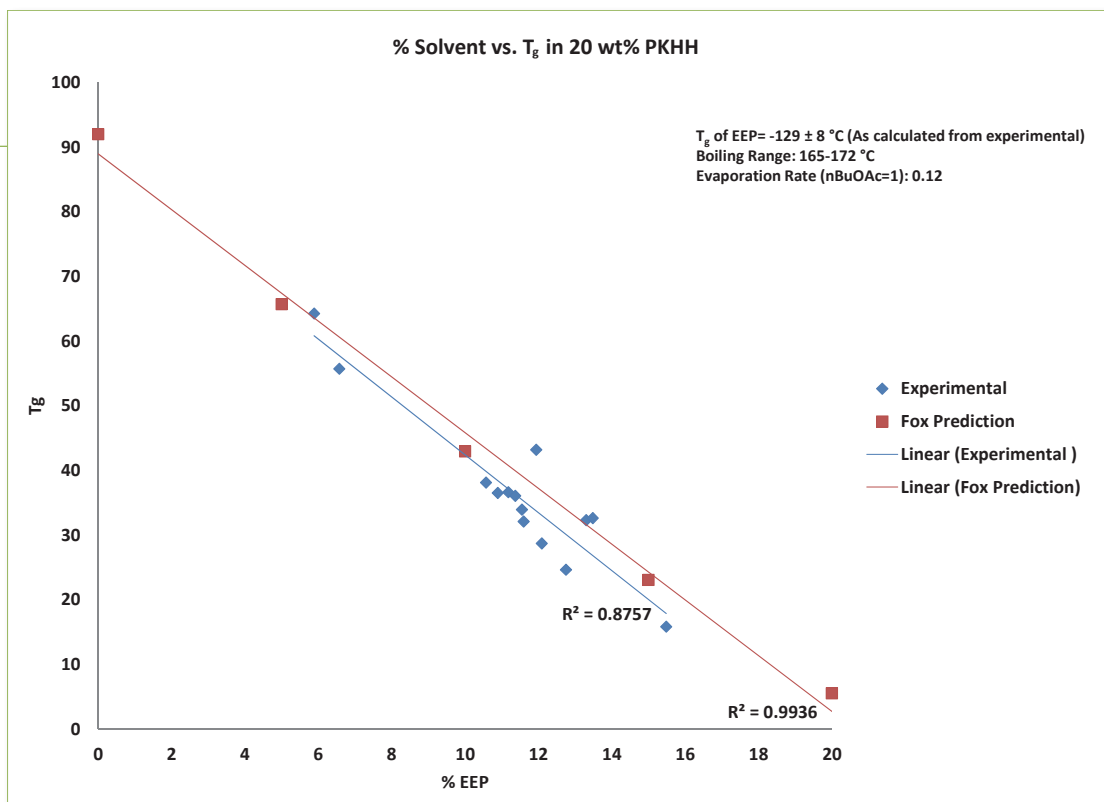
Water is not the only plasticizer in coating materials that depresses the  $T_g$ . In a study with polyaniline, 15% *N*-methyl pyrrolidone (NMP) decreased the  $T_g$  by 80°C.<sup>133</sup> Another study looked at the effect of water-soluble and water-insoluble plasticizers in poly(vinylpyrrolidone).<sup>134</sup> A loading level of 30% water-soluble plasticizers decreased the  $T_g$  and elastic modulus. Up to 10% loading, water-insoluble plasticizers decreased the  $T_g$  and elastic modulus, but no further decrease in properties was noted with increase in plasticizer content.<sup>133</sup>

## FROZEN AND MOBILE POROSITY AND HOLE VOLUME FROM LIQUID EXCHANGE IN VITRIFIED MATERIALS

Although all polymeric substances are thought to exhibit some inherent porosity (free volume), it is not entirely clear how or to what extent this property affects the  $T_g$ . Kasapis and co-workers examined



**Figure 26**—High molecular weight thermoplastic polyepoxide  $T_g$  values as measured by DSC after varying cure times and temperatures as cast from EEP, along with the predicted (squares) values for  $T_g$  using the Fox equation and a calculated EEP  $T_g$  of  $-129^\circ\text{C}$ .



**Figure 27**—Relationship between  $T_g$  and porosity volume fraction in dehydrated apple tissue, as measured via DMA and DSC.<sup>135</sup>

dehydrated apple samples with a varying volume fraction of pores while maintaining constant moisture content. A linear correlation between mechanical  $T_g$  and porosity was found, lowering by nearly  $20^\circ\text{C}$  from 38–79% unoccupied volume, although no change in measured thermal  $T_g$  was observed throughout the same range (Figure 27).<sup>135</sup> Ross and coworkers investigated how porosity affected the  $T_g$  measurement using an array of polymers and starch extrudates via DMA, controlled-strain rheometry, and DSC. This group also determined that mechanical methods were much more sensitive than thermal methods to porosity. However, an opposing trend was observed in that the samples with the highest porosity exhibited a  $T_g$  approximately  $20^\circ\text{C}$  higher than the least porous materials.<sup>136</sup>

It is reasonable to expect that polymers used in coatings would contain or develop some degree of porosity, as they rely upon the evaporation of small molecules such as water or solvents during film formation. Askadskii and Tager have theorized that temperature-dependent polymer characteristics such as coefficient of molecular packing, density, molar volume, and specific volume can be utilized to accurately predict the nature of porous polymers based on the polymer chemical structure and to analyze fractional free volume, although this has not yet been utilized in determining a direct correlation between porosity and  $T_g$ .<sup>137,138</sup>

## SUMMARY

Many materials exhibit a measurable  $T_g$ . The measured single value has become the standard for amorphous coatings thermal analysis. However, the use of a single value is a macroscopic concept that does not adequately represent the molecular and dynamic situation for a surface coating that must, by definition, be a blend of materials, applied and adhered to a substrate, and subjected to a wide range of environmental conditions. In combination, all these situations result in different measured in-service  $T_g$  values at different points in time and location. Therefore, in an attempt to understand the world of surface coatings in a realistic context, we propose that all the various  $T_g$  values affect performance along with our ability to quantify and predict the structure-property relationships that deliver protection, decoration, and function in coatings. <sup>CT</sup>

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