Water whitening of polymer films: Mechanistic studies and comparisons between water and solvent borne films

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ABSTRACT

Water whitening of polymer films derived from solution, bulk and emulsion polymerization processes was studied by the use of UV–vis-NIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), as well as visual observations. In addition to quantifying the wavelength dependent light scattering of the films over time, the different physical forms of water present in blushed films were quantified by DSC. SEM was used to observe sections of the films and characterize the scattering domains responsible for the whitening phenomenon. We studied the same polymers with and without the surfactants and salts used in emulsion polymerization, and compared the blushing of water borne and solvent borne films. We have found that all of the wide variety of (co)polymers we used water whiten under the right conditions of time and temperature. Residual surfactants and salts in latex derived films make the blushing process more rapid and more extensive than for the same polymer without them, but they are not the principal cause for water whitening. Neither is the particulate nature of the starting point for latex films, as the same whitening process occurs in solvent borne films of the same polymer. Both absorbance measurements and SEM images show that there is water domain size growth within the polymeric matrix over time. The size and number of the water domains are responsible for the water whitening effect and both can be restricted by the stiffness of the polymeric matrix. Mechanistic modeling of the time dependence of whitening has led to the prediction that the extent of whitening of non-latex based polymer films is directly proportional to the inherent water solubility in the polymer as well as the diffusivity of water within the polymer at the temperature of testing.

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1. Introduction and background

It has long been known that polymers are plasticized by water. Indeed many reports exist for the distribution of water in polymers used in the textile, food, and coatings industries [1 and references therein]. Cellulosic materials have been the most widely studied, typically by calorimetry, with respect to the physical behavior of absorbed water [2–6]. Hatakeyama et al. [7,8], have coined nomenclature distinguishing each category of water associated with the material as "freezing free water", "freezing bound water", and "non-freezing bound water". The last of these is closely associated with hydrophilic functionalities in the polymer and contributes to plasticization. We have previously reported on both the prediction [9]

and the experimental measurement [10], by differential scanning calorimetry (DSC), of this plasticization due to the non-freezing bound water content.

Beyond plasticization by water, for some systems and under some circumstances, polymer films also whiten, or blush. The opacity comes from water scattering centers of appropriate size within the film. Indeed, these occluded domains of water are comprised of the freezing free and freezing bound water content in the film [11]. While there have been many reports of blushing of water borne films, especially those containing residual surfactants and salts, some reports on similar events in bulk polymers and solvent borne films are also found. The papers by Brown [12] and Johnson et al. [13,14] are typical of water sorption studies in which polymer films were suspended in water vapor at various partial pressures. The weight gain versus partial pressure curves have two distinctly different sections with the second being described as "anomalous water uptake" [12]. This section was analyzed by assuming that a dual site adsorption mechanism was at play where the water sorption in the second part of the data set was associated with clusters of

"associated" water molecules in the near vicinity of "unassociated" water molecules that are "bound" to the more polar constituents along the polymer chain. The Cluster Integral analysis of Zimm and Lundberg [15] was often used to determine the average number of water molecules clustered together in the specific neighborhood of a bound water molecule. Often the number of molecules in the cluster was calculated to be of the order of a few molecules, depending on the polarity of the polymer. Prausnitz and co-workers [16] wrote a wonderful paper along these lines by comparing the water sorption characteristics of four polymers with varying polarity and applied the Zimm-Lundberg cluster integral analysis as a function of the thermodynamic activity of the water (partial pressure/pure water vapor pressure) up to 0.9. The results from these collected authors (not meant here to be an exhaustive list) suggest that before any water whitening occurs, the water in the polymer already exists in two, distinctly different forms, one in very close proximity to a constituent on the polymer chain and the other clustered around the first. Although there are some comments in these papers about the effect of both forms of water on polymer properties, neither form has been associated with film whitening.

Some time ago Johnson and co-workers [13,14] reported that when molten polyethylene (PE) was saturated with water and then temperature quenched, it turned white. Subsequent evaluation via SEM showed that there were "domains" of 1–3 μm in diameter in the PE. In experiments with polycarbonates (PC) they found that water whitening only occurred at temperatures above its glass transition temperature (T_g). These results suggest that the apparent "domains" created during water whitening were restrained in size by the stiffness of the polymer matrix at the experimental temperature. The other important result came from the use of DSC to measure the water content of the polymer as a function of water immersion time. Their data for poly(vinyl acetate) (PVAc) show the differentiation between the water absorbed as "bound" and "clustered", the latter responsible for water whitening. Further, their data clearly demonstrate that whitening is only seen *after* the plasticizing water is at saturation. Thus the water whitening process appears to require two, sequential steps.

There are a large number of literature reports on the water sensitivity of latex derived polymer films but only a few of them specifically report on water whitening, even though it was likely to have happened in many of the cases reported. We cite a few of these reports here [17–28] without the intent to provide an exhaustive list. Among the earliest papers that specifically describe water whitening of latex films are those by Wheeler [29], Wilkes [30], Cote [31] and Bindschaedler [32]. These authors primarily used PVAc latices containing some poly(vinyl alcohol) (PVOH) and found that the films quickly became white and opaque upon immersion in water. Much or all of the blame went to the PVOH surfactant creating continuous phases and/or pockets within the films. In a patent by Wood [33] it was claimed that by deionizing the latex, the blushing of acrylic films could be significantly reduced, and that increasing the pH of these vinyl acid containing latices to 6–7 made further, important improvements. Feng and Winnik [34] found a similar effect of neutralization, this time for poly(n-butyl methacrylate) (PBMA) latices made with methacrylic acid (MAA). In addition they found that when whitened films were thoroughly dried at $T > T_g$, the film regained clarity, only to blush again when re-immersed in water. Bassett [35] reported on the rate and extent of blushing of latex films made from VAc and VeoVa™ monomers (branched vinyl esters), relating the extent of whitening to the oxygen content of the copolymer – he called this correlation the "hydrophilic budget".

SEM observations of freeze fractured surfaces of water whitened, latex based, films were studied by Agarwal and Farris [36]. They used films created from blends of two, acrylic copolymer latices (without deionization) having different T_g's; one above

and one below the water immersion test temperature. SEM photos of the freeze fractured surfaces showed domains of several microns in diameter in the films. Okubo et al. [37] worked with polystyrene (PSt) latices made with 8 mol% MAA (dry state polymer T_g of 112 °C) and did similar SEM investigations. However they separated the P(St-co-MAA) from the serum phase, dissolved the polymer in THF and then cast solvent borne films, and then immersing them in water at pH = 13 for one hour. At room temperature (RT) there was no blushing but at 150 °C the film was white and opaque. Fractured surfaces of these treated films were observed in the SEM and domains of several microns appeared in the sample treated at 150 °C. No domains were found in the sample treated at RT.

Within the past few years Leiza and colleagues [38] have shown reductions in water whitening of latex films when replacing common, anionic surfactants with certain polymerizable surfactants. In addition, they reported that water whitening was quite sensitive to the final pH of latices stabilized by carboxylic acid groups, much in line with the earlier observations of Wood's patent claims [32]. Recently, Liu et al. [39] offered a very detailed set of analytical characterizations (particularly NMR relaxometry) of the whitening features of films cast from a single copolymer, P(St-co-2EHA-co-BMA-co-AA) with 8 wt% carboxylic acid content, produced via three different methods (emulsion polymerization, solution polymerization, and as a secondary dispersion). They concluded that the total amount of sorbed water is not necessarily a good indicator of water whitening, but that together, the amount and location of water regions within the film determined the extent of water whitening.

As a result of reviewing the above literature it is clear that most, if not all, polymers will water whiten under certain conditions. Further, for non-latex based systems, there appears to be a sequential process of water absorption into polymers that, in the first step, has water hydrogen bound to specific constituents on the polymer chain, then additional water becomes clustered in close proximity to the bound water [11], and finally much larger domains (> 1 μm) of water are formed in a final act. The purpose of our study has been to examine the mechanism by which the water domains grow with time, as well as the rate at which whitening increases in films composed of a wide variety of (co)polymers. In addition, we sought to contrast the differences in the rates and extents of whitening between latex and solvent borne films of the same polymer composition.

2. Experimental aspects

2.1. Materials

Most materials considered in this work were prepared by us via simple emulsion or solution polymerization techniques. We produced latices at 20% polymer solid contents and used sodium dodecyl sulfate, SDS, (99%, Acros) as the surfactant (ca. 1% of polymer weight), potassium persulfate (99.99%, KPS, Alfa Aesar) as the initiator (ca. 0.1–0.2% of water weight), and bicarbonate of soda as the buffer (ca. 0.1% of water weight) when desired. All of the polymerization reactions were conducted at 70 °C in 250 mL jacketed, glass reactors. The monomers styrene (St), n-butyl acrylate (BA), n-butyl methacrylate (BMA), methyl methacrylate (MMA), methyl acrylate (MA), 2-ethylhexyl acrylate (2EHA), and methacrylic acid (MAA) were all obtained from Acros and were cleaned of inhibitor by passing them through activated alumina columns prior to reaction. Some latices were cleaned of salts, ionic surfactants and water soluble oligomers by first diluting to 10% solids, then mixing them with a mixed-bed ion-exchange resin (Dowex MR-3, Aldrich) and stirring them overnight on a shaker table. Solution polymerizations were also conducted. Monomers and benzoyl peroxide (97%, BPO, Aldrich) as initiator (ca. 0.1% of total weight) were dissolved in