Free Volume Distribution During Consolidation and Coalescence of Latex Films

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The focus of the work is the effect of molecular architecture on free volume distribution during consolidation and coalescence of aqueous latex emulsions. Two series of model emulsion polymers, iso-butyl methacrylate (i-BMA) and normal-butyl methacrylate (n-BMA) dispersions with varying level of trimethylolpropanetriacrylate (TMPTA) crosslinker, are studied. Coatings are characterized by positron annihilation lifetime spectroscopy (PALS), and atomic force microscopy (AFM). Formation of coherent brittle films without significant interdiffusion is achieved by consolidation below the glass transition temperature (T_g). Consolidation, or ordering/compaction of films following water evaporation at temperatures below the MFFT, results in a decrease in the relative free volume element size, τ_3, as measured by PALS. An increase in the characteristic relaxation time for the consolidation process is evident as TMPTA levels and corresponding gel fraction increase. Consolidation below T_g is accompanied by physical aging. Coalescence and interdiffusion are achieved by annealing films at or above T_g. Annealed coatings show a decrease in T_g and an increase in PALS free volume attributed to erasure of physical aging in combination with the action of the surfactant (sodium dodecyl sulfate) as a plasticizer.

INTRODUCTION

The effect of coating formulation on the interactions between the various components during the stages of film formation, e.g., consolidation/ordering, coalescence/deformation, and interdiffusion, is vitally important to the properties of the liquid and solid film.[1] As discussed by Guthrie,[1] factors such as chain architecture, plasticizers, degree of crosslinking, and molecular weight, affect the intermolecular forces and, hence, the properties of the film via their effect on free volume. Intermolecular forces and free volume control performance variables such as permeability,[2] viscoelasticity,[3] adhesion, and tack.[4] In the present work, butyl methacrylate (BMA) coatings are formulated with a varying chain architecture (isobutylmethacrylate vs. normal-butylmethacrylate) and a varying degree of crosslinker in order to examine the effect on consolidation and coalescence in aqueous latex emulsions. The molecular weight, latex particle size, and level of surfactant are held constant; no coalescent is present. The molecular level free volume as measured by positron annihilation lifetime spectroscopy (PALS) is used to characterize the processes of consolidation and coalescence. Surface morphology is followed via atomic force microscopy (AFM).

Previous work on BMA latex films includes that of Feng and Winnik[5] who studied polymer diffusion in nascent and well-annealed films. They compared the effect of moisture on polymer diffusion in hydrophobic (BMA) and hydrophilic (copolymer of methacrylic acid and BMA) latex polymers finding that water has little effect on diffusion rate in hydrophobic polymer films but increases the diffusion coefficient in hydrophilic polymer films. Physical aging of acrylic latex coatings has been investigated by Perera et al.[6] who suggested that film formation and physical aging may be mutually dependent since both processes involve increased molecular packing and densification. The effect of physical aging on helium permeability of spray cast BMA films has been studied by Hearn and co-workers[7] who found a rapid reduction in permeability for films aged at room tem-

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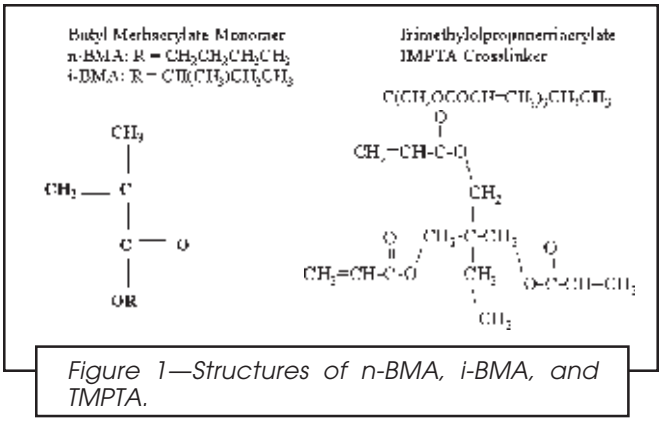

Figure 1—Structures of n-BMA, i-BMA, and TMPTA.

perature. Physical aging of iso-butyl methacrylate (i-BMA) films has been investigated using fluorescence measurements by Royal and Torkelson.[8] Their data suggest that the maximum aging rate in i-BMA (T_g onset = 60°C) is near ambient temperature. The role of crosslinking in BMA latex has been studied by Zosel and Ley[9] who found that crosslinking can prevent coalescence in BMA latex prepared with 2 mol% methylmethacrylate crosslinker. In the study of Zosel and Ley,[9] as in the present work, consolidated films were formed at room temperature, and annealing was used to cause coalescence and interdiffusion. Tamai et al.[10] used AFM to study the effect of crosslinker on film formation in poly(butyl methacrylate-co-butyl acrylate) (BMA/BA) copolymer latex. Tamai et al.[10] varied the level of ethylene glycol dimethacrylate (EGDMA) crosslinker from 0.1 to 4 mol% and found an increased resistance to deformation with higher crosslink density. Annealing was found to promote interdiffusion in low T_g crosslinked BMA latex. By comparison, the present work investigates very low levels of crosslinker from 0.1 to 0.4 wt%. Current trends in latex formulation include the use of multifunctional methacrylate monomers with varying heterogeneity and high gel fraction achieved by addition of as little as 0.1 wt% proprietary crosslinker.[11]

Use of PALS to characterize free volume in coatings has been reviewed by several authors.[12-16] Szeles and co-workers[13,17,18] examined alkyd, vinyl ester, and epoxy coatings using PALS and correlated the effect of water exposure on PALS parameters with the barrier properties of the coatings. Pfau and Mayo[14,19] used PALS to monitor pigment dispersion and effect of solvent addition on viscosity of high-solids coating oligomers. Granata and co-workers[20-23] studied the role of free volume in moisture absorption in protective epoxy and polyimide coatings in order to predict corrosion inhibition. In general, the PALS parameter τ_3 (ortho-positronium pickoff lifetime) is associated with the average free volume element size, and the statistical weight of this component, I_3, is associated with the relative number of free volume elements. The free volume sites probed by PALS are of the order 0.2 to 1 nm in size, hence in latex films, inter- and intra-chain space will be detected while inter-particle voids will not.

In this work we use PALS to characterize the free volume relaxation that occurs during the consolidation of latex emulsions. We evaluate the effect of very low levels of crosslinker and variation of chain architecture on the PALS free volume, viscosity, gel fraction, glass transition temperature (T_g), minimum film formation temperature (MFFT), and surface roughness. The effect of annealing is also investigated.

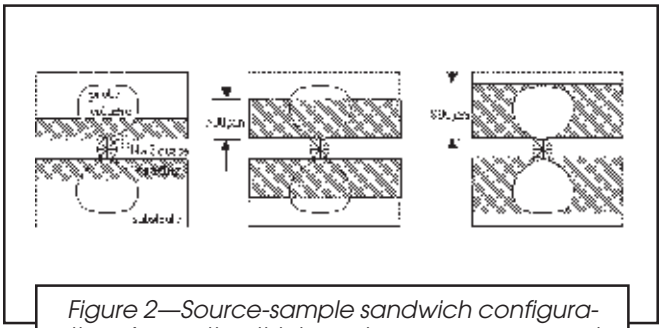

Figure 2—Source-sample sandwich configuration. As coating thickness increases, more and more positrons annihilate in the coating rather than in the substrate, until at a thickness of 800 μm all of the positrons annihilate in the coating.

EXPERIMENTAL

Latex Preparation

A semicontinuous emulsion polymerization method was used.[5] Normal- or iso-butyl methacrylate monomer was

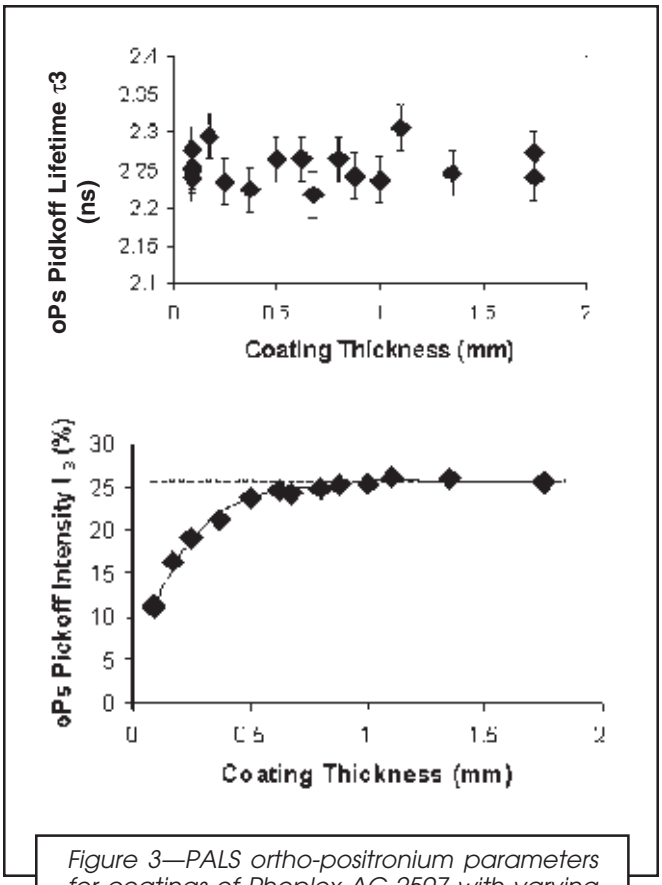

Figure 3—PALS ortho-positronium parameters for coatings of Rhoplex AC 2507 with varying thickness.

distilled and refrigerated prior to use. BMA monomer was added to a heated reactor containing water (deionized and distilled) and surfactant (sodium dodecyl sulfate, SDS) at 80°C. After addition of initiator (potassium persulfate), the reaction was allowed to proceed at 80°C in order to set the seed that subsequently grew to the final predetermined particle size of 104 nm. Dodecyl mercaptan was used as a chain transfer agent, sodium bicarbonate was used as a buffer, and trimethylolpropanetriacrylate (TMPTA) was used as a crosslinker. The chemical structures for normal-butyl methacrylate (n-BMA), i-BMA, and TMPTA are shown in *Figure* 1. Particle size was determined by dynamic light scattering. Molecular weights were determined by gel permeation chromatography. Gel fraction was determined by ultracentrifuge due to the very low level of gel present. Complex viscosity data at 160°C (i-BMA) and 200°C (n-BMA) were fitted to a complex Cross model[24] using non-linear regression to

Table 1—Comparison of Gas Transport, Fractional Free Volume, and PALS Free Volume[27]

Polymer	Oxygen Permeability ($x10^{13}$ cm^3 (STP) $cm/(cm^2 s\ cm\ Pa)$)	FFV (%)[a]	τ_3 (ns) Related to Free Volume Element Size	I_3 (%) Related to Free Volume Concentration
HBA/HNA 73/27 mol% p-hydroxy benzoic acid/ hydroxy-2-napthoic acid Vectra	0.0000585 35°C ref(28)	10.8	1.27	10.0
HIQ-40 nematic 40 mol% HBA/ 30 mol% isophthalic acid/30 mol% hydroquinone	0.00135 35°C ref(29)	10.6	1.54	11.8
PAN Poly(acrylonitrile)	0.0041 25°C ref(30)	12.0	1.75	14.4
HIQ-40 isotropic 40 mol% HBA/ 30 mol% isophthalic acid/30 mol% hydroquinone	0.009 35°C ref(29)	12.8	1.80	15.2
PVOH poly(vinyl alcohol)	0.00665 25°C ref(30)	13.6	1.40	23.1
PEN poly(ethylene naphthalate)	0.0145 30°C ref(31)	14.8	1.58	23.1
PET poly(ethylene terephthalate)	0.0422 30°C ref(31)	14.9	1.65	21.4
PBT poly(butylene terephthalate)	0.054 30°C ref(32)	14.8	1.70	23.6
PCT poly(cyclohexylene dimethylene terephthalate)	0.19 30°C ref(31)	16.3	1.78	27.9
PMMA poly(methyl methacrylate)	0.116 34°C ref(30)	15.7	1.90	28.0
PVAc poly(vinyl acetate)	0.367 30°C ref(30)	17.6	1.94	26.5
PC poly(bisphenol A carbonate)	1.05 25°C ref(30)	16.4	2.00	30.0
PAr Poly(acrylate)	1.36 30°C ref(32)	16.5	2.03	25.2
Rhoplex AC 2507 Poly(methylmethacrylate-co-butyl acrylate)			2.25	26.0
PEU poly(etherurethane)	2.45 30°C ref(33)	17.5	2.25	27.0
PBMA poly(butylmethacrylate)	4.8 25°C ref(34)	16.5	2.32	28.0
PPO poly(dimethyl phenylene oxide)	11.9 25°C ref(30)	19.5	2.47	40.0

(a) Fractional free volume calculated for 25°C according to reference 35.
Permeability measurements made from 25 to 35°C as indicated.
PALS measurements made at 23°C.

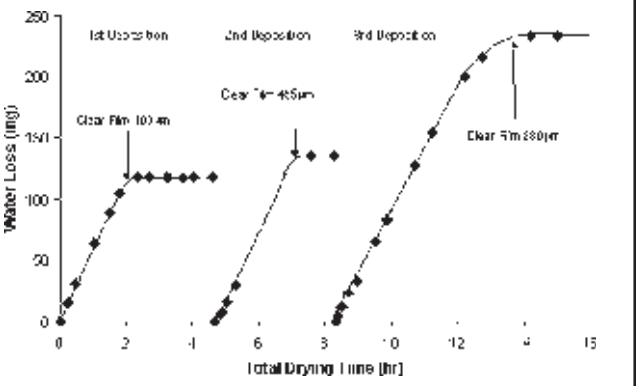

Figure 4—Water loss as a function of time for n-BMA latex dispersion on glass substrate.

obtain the limiting zero shear rate viscosity, η_0, the characteristic shear stress, S_c, power law exponent, n, and relaxation time, $\tau = \eta_0/S_c$.

Coating Formation and Characterization

Coatings were prepared by spreading latex dispersions on glass plates. A total coating thickness of 1 mm was achieved by depositing layers of approximately 100-400 µm thickness that were allowed to air dry for three to four hours (visibly dry) before the subsequent layer was deposited. The coatings were further dried for 24 hr at ambient conditions (23°C, 50% RH) to obtain transparent (n-BMA) to translucent (i-BMA) coatings of thickness approximately 1 mm. Coatings were characterized by PALS as newly dried films (24 hr in air), after 5 and 34 days. Thermogravimetric analysis of dried coatings was performed using a Dupont 2200 TGA under nitrogen purge of 40 cm^3 min^{-1} at a heating rate of 20°C min^{-1}. After drying, selected coatings were annealed in air at or above the T_g. MFFT was determined by the visual method using the bar test and by the resistance method [ASTM D 2354-68]. PALS measurements were performed in ambient conditions using an automated EG&G Ortec fast-fast coincidence unit as described elsewhere.[25] Four to eight spectra were collected sequentially for each sample, and the mean values of ortho-positronium lifetime τ_3 (ns) and intensity I_3 (%) are reported with population standard deviations. Differential scanning calorimetry (DSC) measurements were made using a TA Instruments 2200 in MDSC mode at a heating rate of 5°C min^{-1} and a cycle of 2.45°C min^{-1}. The point at half height of the glassy and rubbery regions of the reversing heat flow curve was assigned as T_g. AFM measurements were made in Tapping Mode™ using a Nanoscope III AFM in a manner similar to that described elsewhere.[26]

RESULTS AND DISCUSSION

Coating Thickness

The energy range of positrons emitted from the ^{22}Na radioisotope means that a coating volume of about 1 mm^3 is probed (for polymer samples of density approximately 1 g cm^{-3}). Szeles et al.[18] have studied the depth distribution of positrons injected from a ^{22}Na source into the coating/substrate system. The positron lifetime spectra for coatings contain contributions from the coating as well as the substrate unless the coating is thick enough to absorb all of the injected positrons. *Figure* 2 shows the PALS experimental configuration with the ^{22}Na source sandwiched between identical coating specimens of varying coating thickness. *Figure* 3 displays the ortho-positronium (oPs) pickoff parameters, τ_3 and I_3, as a function of coating thickness. The volume of coating in the total volume probed by the positrons (*Figure* 2) can be characterized by the statistical weight of the oPs pickoff parameter, I_3, if no oPs formation takes place in the substrate and negligible backscattering occurs. The results show that a coating thickness of at least 800 µm is necessary for all of the positrons to annihilate in the acrylic coating such that the parameter I_3 is characteristic of the number of free volume sites in the coating without having to correct for substrate effects. Note that the τ_3 parameter is characteristic of the coating and independent of coating thickness because oPs formation and annihilation in the substrate do not occur. Thus for the commercial acrylic film (Rohm and Haas Rhoplex AC 2507) shown in *Figure* 3, the characteristic room temperature PALS free volume parameters are τ_3 = 2.25 ns and I_3 = 26.0 %. *Table* 1 compares ambient temperature PALS free volume parameters with gas transport values in various polymers indicating that Rhoplex AC 2507 would have similar oxygen permeability to polyetherurethane (PEU).

The polymers in *Table* 1 are listed in order of increasing τ_3 over two classes of amorphous polymers, those that display liquid crystalline-like order and those that do not. The first four polymers show liquid crystalline or laterally ordered domains. These polymers are easily distinguished by their unusually low values of relative free volume concentration as indicated by I_3 (<16%) and their low fractional free volume (<13 %). These polymers have excellent barrier properties. As shown in *Table* 1 the PALS technique is remarkably sensitive to the molecular level free volume that is important to barrier properties of polymer films. In the next section, we consider a subtle change in polymer architecture and determine the sensitivity of PALS to molecular architecture and consolidation/aging during film formation from aqueous latex dispersions.

Consolidation

The water evaporation rate from latex dispersions of low solids content is similar to that of pure water films as discussed by Feng and Winnik[5] with 50 µm films drying completely within three hours. *Figure* 4 shows the water loss as a function of time during preparation of an n-BMA latex dispersion of final coating thickness 880 µm. Film transparency provides a fairly good indication of complete drying. Depending on layer thickness, coatings appeared dry after three to four hours following final deposition of latex emulsion, and each layer was allowed to dry for three to four hours prior to further deposition. Centrally radiating cracks were present in these films, indicating that drying occurred too quickly for the poly-

mer chains to accommodate stress via flow.[26] The PALS measurements were made on 1 mm thick coatings after a further 24 hr of drying in ambient conditions. *Figure* 5 displays the PALS oPs parameters measured over the range of TMPTA crosslinker for the i-BMA and n-BMA series as newly dried films. There is no significant variation in the lifetime and intensity of the oPs pickoff component with level of TMPTA crosslinker for all newly dried films. The results in *Figure* 5 indicate that the room temperature free volume is greater in n-BMA than in i-BMA but that an effect of low levels of TMPTA crosslinker on molecular level free volume is not evident in newly dried films.

Samples of each polymer with 0, 0.2, 0.4 wt% TMPTA were then measured as a function of time. *Figure* 6 shows that consolidation occurs over a long time period following drying with the majority of the consolidation occurring in the first five days. Weight fraction of water remaining in the films after 1, 5, and 34 days of drying was measured by thermogravimetric analysis and found to be 0%. The decrease in the τ_3 parameter during consolidation indicates a decrease in the mean size of the free volume elements. The relative number of free volume elements, I_3, is approximately constant during the consolidation process for samples containing no TMPTA crosslinker and decreases over the first five days for samples containing TMPTA. The PALS results suggest that the slow consolidation process in dried latex films occurs as the free volume element size shrinks. The τ_3 relaxation is approximately exponential and can be modeled using a single relaxation time. Exponential fits are shown in *Figure* 6 for the coatings containing 0.2 wt% TMPTA. *Table* 2 gives the relaxation times and the correlation coefficients for the fits. As shown in *Table* 2, the relaxation time for the consolidation process increases with increasing degree of crosslinking. It appears that the difference in chemistry of these iso- or normal-butyl methacrylate latexes does not appreciably affect the consolidation process.

Table 2—Single Exponential Fits to the τ_3 Relaxation Shown in Figure 6

Coating	Single Exponential Relaxation Time (hr)	Single Exponential Correlation Coefficient
n-BMA 0% TMPTA	31	0.89
n-BMA 0.2% TMPTA	31	0.98
n-BMA 0.4% TMPTA	52	0.86
i-BMA 0% TMPTA	33	0.99
i-BMA 0.2% TMPTA	43	0.98
i-BMA 0.4% TMPTA	43	0.95

As shown in *Figure* 6, consolidation results in a decrease in free volume in all of the coatings. In the uncrosslinked coatings this decrease in free volume is due to shrinkage of the free volume elements, whereas in crosslinked samples, a reduction in both size and concentration of free volume sites occurs during consolidation. Thus comparison of PALS free volume parameters for consolidated specimens (either five days or 34 days after drying) shows a dependence on the level of TMPTA crosslinker; a higher level of TMPTA results in fewer free

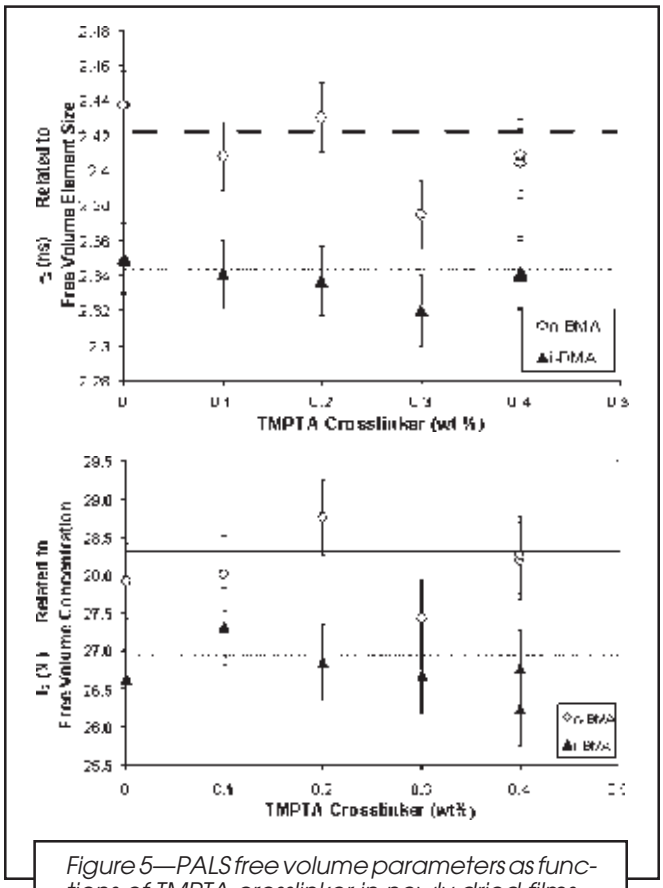

Figure 5—PALS free volume parameters as functions of TMPTA crosslinker in newly dried films.

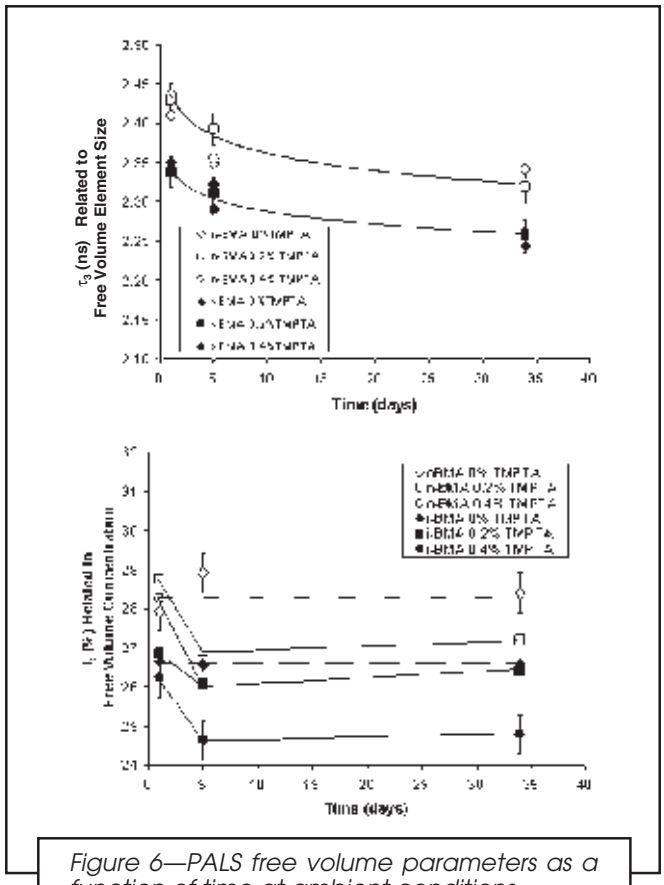

Figure 6—PALS free volume parameters as a function of time at ambient conditions.

volume sites (reduced I_3) as shown by open symbols in *Figure* 7.

The effect of chain architecture and the level of crosslinker on PALS free volume in consolidated coatings is shown in *Figure* 7 (open symbols). Consolidated films of n-BMA have larger free volume elements and more of them than i-BMA. Increasing the level of TMPTA crosslinker does not change the free volume element size but does decrease the concentration of elements. *Table* 3 contains the important characteristics of these n-BMA and i-BMA latex samples. An increase in TMPTA crosslinker results in increased gel fraction and viscosity but no change in the soluble molecular weight, T_g, or MFFT.

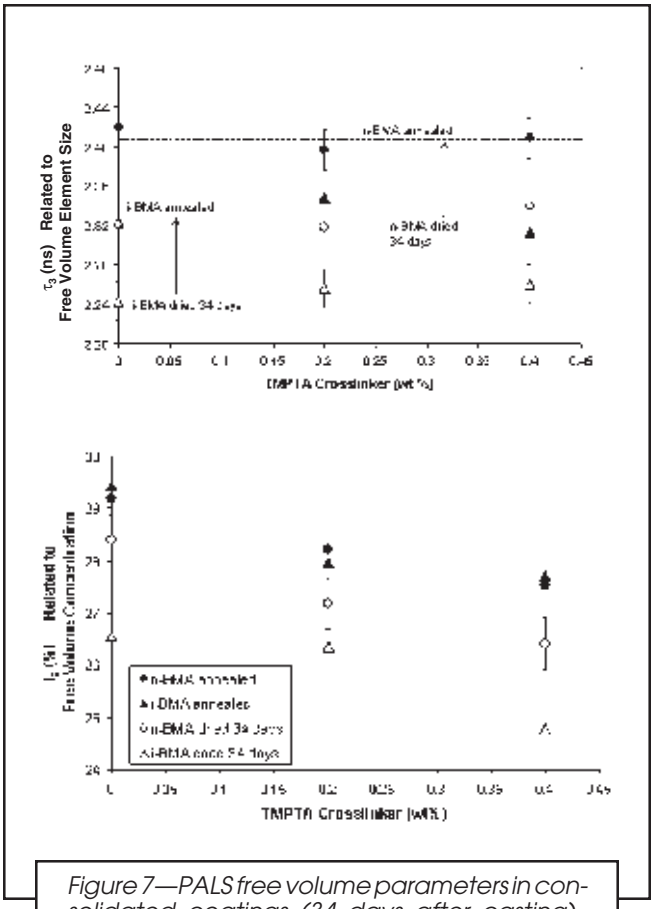

Figure 7—PALS free volume parameters in consolidated coatings (34 days after casting)–open symbols and annealed coatings–dark symbols.

Also shown in *Figure* 7 (dark symbols) are the results of an annealing experiment. Films of n-BMA were heated to 40°C in air, held for 40 min and air-cooled while films of i-BMA were similarly heat treated at 70°C. The trend of fewer free volume elements with increasing TMPTA levels is still present but annealing has caused both τ_3 and I_3 to increase.

The PALS results presented thus far are consistent with current views of latex particle consolidation and the role of surfactants. By definition, film formation can only occur above T_g. If drying is complete before coalescence and film formation, then excess voids are present in the coating that slowly diffuse over a period of days.[36] The diffusion of voids and relaxation of the polymer causes a gradual contraction of the coating long after it is considered dry.[37] The surfactant between the latex particles gives the voids a diffusion pathway.[38] Subsequent annealing can cause the surfactant to act as a plasticizer such that the free volume increases and the T_g of the film decreases.[39] In addition to the effects of surfactant, one must consider the glassy nature of these coatings. At room temperature, both n-BMA (T_g = 36°C) and i-BMA (T_g = 70°C) are in the glassy state. Physical aging of glassy polymers is a gradual densification that occurs below T_g resulting in a reduction in free volume, reduction in molecular mobility, and an increase in T_g.[40] Annealing at or above T_g can reverse physical aging—a process termed de-aging. Physical aging of acrylic latex coatings has been investigated by Perera et al.[6] who suggested that film formation and physical aging may be mutually dependent since both processes involve increased molecular

Table 3—Latex Characteristics

	Poly(n-BMA) TMPTA Crosslinker					Poly(i-BMA) TMPTA Crosslinker				
	0%	0.1%	0.2%	0.3%	0.4%	0%	0.1%	0.2%	0.3%	0.4%
% Solids	18.6	18.9	19.1	19.9	18.9, 19.1	19.6	18.6	20.5	18.1	17.2, 17.8
Diameter (nm)	108	107	104	108	105, 107	100	108	108	96	100, 104
M_n (x1000)		88	92	57	58, 88	88		51	107	74, 90
M_w (x1000)		491	327	399	335, 348	348		390	690	437, 537
M_z (x1000)		2160	8760	2110	1230,1150	1150		2190	3620	1950, 2350
M_w/M_n		5.6	3.6	7.0	4.7	3.9		7.6	6.4	5.9
Gel fraction (%)		0.9	0.7, 1.5	8.2	18.1, 18.8	0.6		0.2	0.6	1.8
IV		0.88	0.92	0.90	0.94, 0.94	0.82		0.95	1.01	0.84, 0.95
η_o (Poise) (x1000)		11.9	21.6	32.7	64.2	45.7				50.5
CSS (dyn/cm^2) (x1000)		16.6	26.7	37.3	50.4	46.8				29.0
τ (sec)		0.72	0.81	0.88	1.27	0.97				1.74
PLE		0.51	0.48	0.44	0.39	0.41				0.42
MFFT (°C) res		37	37	46	43, 50					
MFFT (°C) vis		28	30	30	30, 34	79		80	76	79, 80

CSS, characteristic shear stress, S_c, is an estimate of the rubbery plateau modulus when n = 0.
$\tau = \eta_0/S_c$ is the longest stress relaxation time estimate.
PLE, power law exponent, n, is equal to zero for a single relaxation time distribution (Maxwell model).
Complex viscosity measurements made at 160°C for i-BMA and 200°C for n-BMA.
res = resist
vis = visible

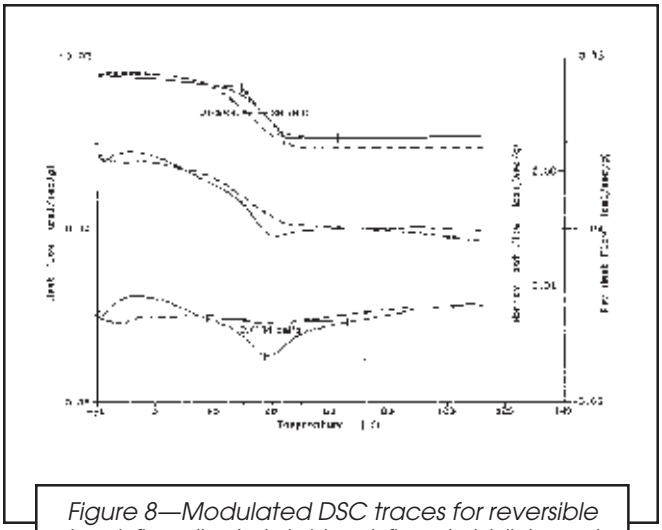

Figure 8—Modulated DSC traces for reversible heat flow (top), total heat flow (middle), and non-reversible heat flow (bottom) for n-BMA 0.3 wt% TMPTA. Consolidated 60 days–solid line; annealed (second scan)–dashed line. T_g values are calculated from top trace; excess enthalpy values are calculated from bottom trace.

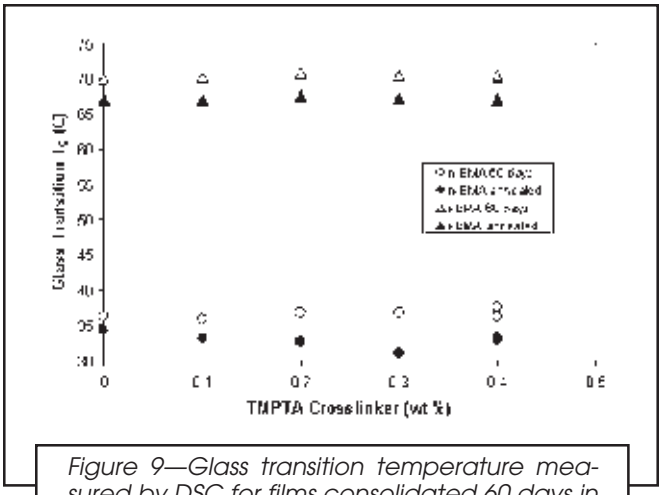

Figure 9—Glass transition temperature measured by DSC for films consolidated 60 days in ambient conditions (open symbols) or annealed (closed symbols).

packing and densification. The effect of physical aging on helium permeability of spray cast BMA films has been studied by Hearn and co-workers[7] who found a rapid reduction in permeability for films aged at room temperature. Room temperature aging in n-BMA coatings over a period of 28 days showed a rapid decrease in permeability occurring over the first two days following casting. Physical aging of i-BMA films has been investigated using fluorescence measurements by Royal and Torkelson.[8] Their data suggest that the maximum aging rate in i-BMA (T_g onset = 60°C) is near ambient temperature.

Figure 8 shows our representative DSC traces for consolidated (1st scan) and annealed (2nd scan) coatings. The presence of an enthalpic peak at T_g in the first scan DSC data suggests physical aging. It appears that consolidation at room temperature is accompanied by physical aging. First scan DSC data were collected 60 days after casting. Second scan DSC measurements are used to approximate annealing at or above T_g. DSC measurements confirm that annealing reduces T_g. *Figure* 9 shows the T_g as a function of TMPTA crosslinker for consolidated and annealed coatings. Annealing causes the T_g to decrease by approximately 4°C for n-BMA and approximately 3°C for i-BMA with no apparent dependence on amount of crosslinker. Excess enthalpy for coatings aged 60 days is tabulated in *Table* 4. It appears that i-BMA coatings age faster at ambient temperature than n-BMA coatings, but that aging rate is independent of degree of crosslinking at the low levels of crosslinker studied here. As discussed by Royal and Torkelson,[8] maximum aging rate is approximately room temperature for i-BMA and, presumably, well below ambient temperature for n-BMA. Perera et al.[6] suggested that aging rate decreases with increasing crosslink density in organic coatings. Excess enthalpy results for our samples show no trend with level of crosslinker. Relaxation times for the consolidation process over 34 days (*Table* 2) do show a decrease in consolidation rate with increasing level of TMPTA crosslinker. Also included in *Table* 4 are excess enthalpy values for i-BMA coatings annealed for 40 min at 70°C and then aged for 60 days in ambient conditions. Annealing causes an increase in the aging rate of i-BMA films at room temperature, which is consistent with increased mobility and free volume due to plasticization via the surfactant.

Table 4—Excess Enthalpy Values for Consolidated (60 days) Films

Wt% TMPTA Crosslinker	ΔH (cal/g) n-BMA As-Cast, Then Aged	ΔH (cal/g) i-BMA As-Cast,Then Aged	ΔH (cal/g) i-BMA Annealed,Then Aged
0	0.63	1.27	1.47
0.1	0.59	1.05	
0.2	0.83	1.08	1.50
0.3	0.71	0.99	
0.4	0.73, 0.72	0.96, 1.04	1.38

Table 5—PALS Parameters for Newly Dried and Freshly Annealed Films

Sample Condition	Poly(n-BMA) τ_3 (ns) ± 0.03			Poly(n-BMA) I_3 (%) ± 0.3			Poly(i-BMA) τ_3 (ns) ± 0.03			Poly(i-BMA) I_3 (%) ± 0.3		
wt% TMPTA→	0%	0.2%	0.4%	0%	0.2%	0.4%	0%	0.2%	0.4%	0%	0.2%	0.4%
Newly Dried	2.44	2.43	2.41	28.0	28.7	28.3	2.35	2.34	2.34	26.6	26.8	26.2
Freshly annealed	2.42	2.40	2.41	29.2	28.2	27.5	2.32	2.32	2.34	29.4	28.0	28.3
34-days consolidation	2.32	2.32	2.34	28.4	27.2	26.4	2.24	2.26	2.26	26.6	26.4	24.8

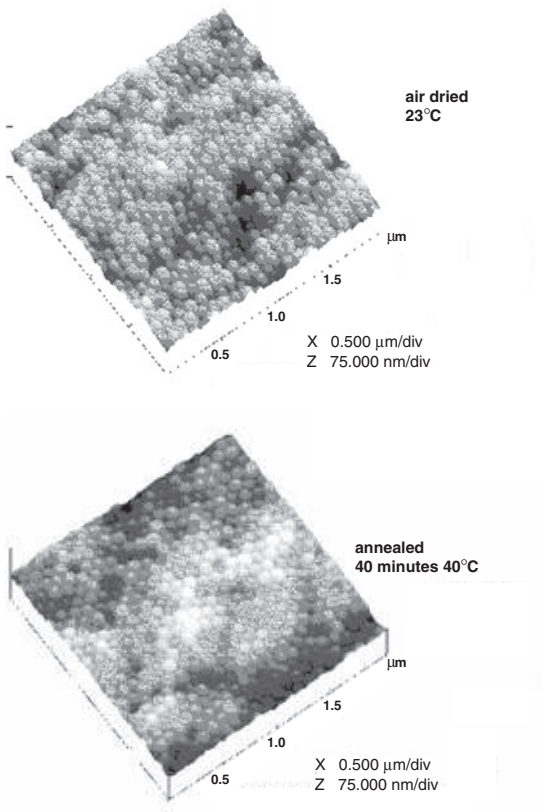

Figure 10—AFM images of n-BMA 0.2 wt% TMPTA as dried and annealed for 40 min at 40°C.

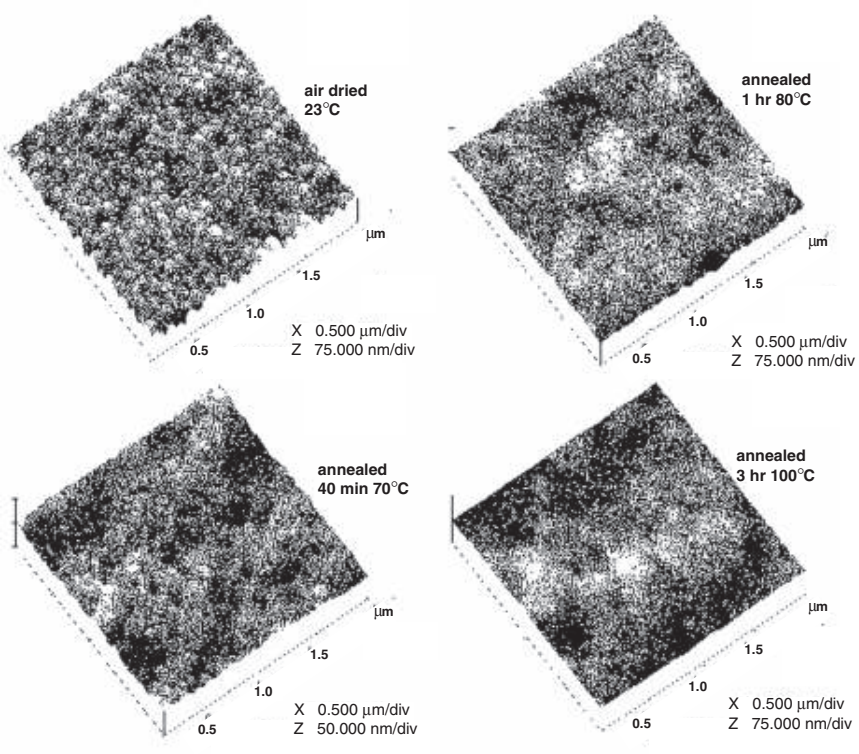

Figure 11—AFM images of i-BMA with 0.2 wt% TMPTA as dried and after annealing.

Coalescence

In an effort to separate the annealing effects (on PALS free volume) of de-aging from those of surfactant plasticization, we compare in *Table* 5 the PALS free volume parameters τ_3 and I_3 for newly dried films (no aging effects) with freshly annealed films (no aging effects). The values for aged un-annealed films are also included. Annealing de-ages the films and restores the τ_3 values to those of newly dried films. However, the action of the surfactant as plasticizer in annealed films is suggested by the increase in I_3 values above that of the newly dried films.

Annealing also changes the film morphology. AFM images of consolidated and annealed coatings (shown in *Figures* 10 and 11) confirm that the film surface becomes flatter on annealing. The reduction in surface roughness suggests particle deformation and may indicate that plasticization aids coalescence over the range of crosslink density examined here. For consolidated films the AFM images show spherical particles and the approximate particle size agrees with that measured for the latex dispersions, within the limitations of the technique.[26] Surface images of the consolidated films show face-centred-cubic (fcc) packing similar to that found for monodisperse n-BMA films prepared from surfactant free dispersions.[41-43] When films are annealed at or above T_g for 40 min, the surface roughness decreases. The AFM images indicate that annealing causes particle deformation but there is not enough surface interdiffusion to obscure the inter-particle boundaries. The surface roughness (peak-to-valley distance) is approximately 11 nm across the range of crosslinker, which is much smaller than half of a latex particle diameter. The mean surface roughness decreases to 1-2 nm after annealing. Annealing for longer times and higher temperatures results in further film flattening as illustrated for i-BMA (0.2 wt% TMPTA) in *Figure* 11.

Tamai et al.[10] found that surface roughness in as-cast films was a function of amount of crosslinker (mol% EGDMA of 0.1, 0.5, 1, 2, 4%). No dependence of surface roughness on amount of crosslinker was observed in the present work; however, only very low crosslinker levels were studied herein. As noted by Tamai et al.,[10] small extents of latex particle crosslinking (0.1 to 2 mol%) have only a small effect on particle deformation measured on the surface by AFM. Deformation of latex particles during annealing was shown by Tamai et al.[10] to be a function of level of crosslinker with less deformation evident in the 4 mol% EGDMA film, although peak-to-valley distances were decreased similarly across the range of crosslinker. Effects of low levels of TMPTA crosslinker on particle deformation during annealing were not observed in our AFM study.

One question arising from the PALS study of annealed films was the role of surfactant in the free volume increase observed on annealing at or above T_g. This increase in free volume above that measured for newly dried films was attributed to plasticization of the latexes by the surfactant, and there is some supporting evidence for this in the DSC data. Perez and Lang[43] used AFM to compare the effect of annealing above T_g on surface roughness in PBMA latex films with and without SDS surfactant. They attributed some observed disorder in the hexagonal packing of the spheres, which occurs on annealing, to surfactant exuded from the interior of the film. We do not observe this disordering effect in any of our annealed films, perhaps because the surfactant can act as a penetrant/plasticizer.

SUMMARY

This research has suggested the following:

(1) There is a strong correlation between the PALS free volume parameters and permeability in polymer films.

(2) Ambient temperature consolidation in latex dispersions (n-BMA, 104 nm diameter, T_g=36°C; i-BMA, 104 nm diameter, T_g = 70°C) occurs via shrinkage in free volume element size.

(3) Crosslink density affects the consolidation process with higher crosslink density relaxing more slowly during ambient consolidation and crosslinking leading to a reduction in free volume concentration during consolidation.

(4) The consolidation rate does not depend significantly on the difference in chemical architecture between iso- and normal-butyl methacrylate.

(5) The room temperature PALS free volume distribution of n-BMA latex (T_g = 36°C) differs to that of i-BMA (T_g = 70°C) with n-BMA having larger free volume elements, presumably due to the proximity of T_g and measurement temperature.

(6) Consolidation below T_g is accompanied by physical aging in these latex systems.

(7) If drying is complete before coalescence and interdiffusion, then subsequent annealing at or above T_g can cause the surfactant to act as a plasticizer such that the free volume increases and the T_g of the film decreases. Annealing also results in de-aging, particle coalescence and some interdiffusion.

(8) Action of the surfactant as plasticizer may aid coalescence and interdiffusion as measured by surface roughness using AFM.

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