Molecular Level Challenges in Environmentally Compliant Coatings at the Turn of the Century

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INTRODUCTION

The past decade brought tremendous progress in the development of environmentally friendly polymers for coatings applications, and led to novel waterborne, powder, UV-curable, high-solids coatings and their hybrids. However, it is apparent that small, often considered minor, molecular level changes in macromolecular chemistries or coatings formulations may cause enormous changes in macroscopic properties. It is well documented that the mobility of low molecular weight species may not only affect crosslinking or coalescence kinetics, but also adhesion and other inherently important macroscopic properties. For example, if an initial concentration of surfactant molecules in an aqueous latex suspension is 1% w/w, distribution of the same surfactant in a 100 μm thick latex film deposited on a substrate may vary across the film thickness. If, for thermodynamic or kinetics reasons, surfactant molecules are driven to the film-air (F-A) or film-substrate (F-S) interfaces, their local concentration will be different. For example, if the initial 1% w/w is concentrated in a 10 μm layer near the F-S interface, the effective concentration will be 10% w/w. These levels of surfactant molecules near the F-S interface will not even allow the latex to coalesce. Similar situations may occur in other types of coatings systems, where nonuniform concentrations of low or high molecular weight species can be found across the film thickness. Although in numerous cases where such behavior may not be advantageous, one can design the chemistry on the system to achieve specific properties, for example a crosslink density gradient across the film thickness, such as demonstrated for melamine-polyester. For that reason, understanding molecular level events across the film thickness is essential not only from a scientific point of view, but also from a practical one.

With this in mind, let us consider which molecular entities in latex, urethane waterborne, and powder systems may affect film formation. Taking into account the fact that molecular weight is one of the factors influencing the mobility of molecules and macromolecules during the film formation, low molecular weight species will be more susceptible for migration, provided that there are external or internal forces causing diffusion. For example, during

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T his review paper explores recent concepts and challenges in understanding structure-property relationships in environmentally compliant coatings and the ability of recently developed analytical methods to understand molecular level processes that govern macromolecule behavior. Although the focus is on latexes, polyurethanes, and powder coatings, an ultimate goal is to explore and elucidate the origin of the molecular processes responsible for stratification, phase separation, kinetics, diffusion, and adhesion. In styrene/n-butylacrylate (Sty/nBA) emulsions, the mobility of surfactant molecules in coalesced films depends upon how both monomers were polymerized and formulated. Specifically, a mixture of homopolymers inhibits mobility of low molecular weight surfactants to the film-air (F-A) and film-substrate (F-S) interfaces. For polyurethanes, there is a distinct difference in stratification of isocyanate functionalities for polycarbonate emulsions and polyester dispersions. Finally, for epoxy phenol novolac (EPN) resins powder systems, the relationship between the particle size, adhesion, and crosslinking conditions is established, which has significant effects on throughput efficiency.
latex coalescence, surfactant molecules, being water-
soluble, may migrate to the surface with water flux.\textsuperscript{14} However, if the surface tension difference between a latex
polymer and a substrate is high, they may diffuse towards
the substrate in order to compensate for an excess of the
interfacial energy at the F-S interface.\textsuperscript{5} Thus, there are
competing forces that are ultimately influenced by system
compatibility, covalent and noncovalent bonding, surface
tension, kinetics of solvent evaporation, and others. Similar
situations may occur in thermosetting systems, where
crosslinker or catalyst molecules may preferentially mi-
grate, thus resulting in chemical and physical property
gradients across the film thickness.

In an effort to understand how various components, often
too low concentration levels, may affect film forma-
tion it is necessary to utilize molecular level probes. Ide-
ally, one would like to use nondestructive, molecular level,
and surface selective probes. Among numerous tools, it
appears that vibrational spectroscopy, in particular at-
tenuated total reflectance Fourier transform infrared (ATR
FTIR)\textsuperscript{a} and photoacoustic (PA) FTIR,\textsuperscript{b} are capable of mon-
toring such events. However, the challenge is not to mon-
tor the kinetics of crosslinking or coalescence only, but to
qualitatively and quantitatively identify the molecular
level differences occurring at various depths from the
surface and interface. Although similar principles may
apply to other coatings, this review will focus on illustrative
elements of latexes, such as styrene/n-butyl acrylate
(Sty/n-BA), waterborne polyurethanes, and epoxy pheno-
nol novolac (EPN) powder coatings.

**STYRENE/N-BUTYL ACRYLATE LATEXES**

A series of previous studies on latex films indicated that the
mobility of low molecular weight species, in particular
surfactant molecules, may be affected by latex glass tran-
sition temperature ($T_g$), and subsequently, by the free
volume of a polymer matrix,\textsuperscript{9,10} surface tension on the film-air
(F-A) and film-substrate (F-S) interfaces,\textsuperscript{3,31} compatibility,\textsuperscript{12} and coalescence times\textsuperscript{13} to name just a few. Other
factors not only influence the distribution of individual
components, including surfactants, but also may signifi-
cantly affect film formation. For a copolymer latex with $T_g$
below minimum film-formation temperature (MFT), for-
mation of a continuous film will be affected by particle
packing, their deformation, and coalescence, ultimately
leading to interparticle diffusion. For latex blends con-
taining soft and hard particles, film formation is different
because typically hard particles with a $T_g$ higher than
MFT will remain rigid, thus limiting interparticle\textsuperscript{14} dif-
sion during coalescence. The situation becomes even fur-
ther complicated when surfactant molecules begin their
migration to the F-A and F-S interfaces.

In an effort to understand surfactant behavior in latex
blends during film formation, a series of experiments on
latex blends and copolymers containing polystyrene (p-
Sty) and poly-n-butyl acrylate (p-nBA) moieties were pre-
pared.\textsuperscript{15} While latex blends can be prepared by mixing
two independently polymerized p-Sty and p-nBA latex
polymers in a form of polymeric microspheres dispersed
in an aqueous medium, latex copolymers are prepared by
copolymerization. As indicated in the Introduction, our
goal is to elucidate the origin of coalescence and further
advance our understanding of the film formation pro-
cesses in copolymer and polymer blends of p-Sty and p-
nBA. Figure 1, Traces A and B, illustrate ATR FTIR spectra in
the 1340-970 cm$^{-1}$ region of coalesced Sty/n-BA copolymer
latex.

The spectra were recorded from the F-A and F-S inter-
faces, respectively, at approximately 1.9 $\mu$m from each
interface. Although the total amount of SDOSS in the latex for-
mulation is 1.8 w/w\%, it is quite apparent that the F-A and F-S
interfaces exhibit different levels of SDOSS. As previous
studies showed,\textsuperscript{16-12} the majority of the bands in this region
are due to SDOSS surfactant molecules. As shown in Trace
A (F-A), the bands at 1288 and 1232 cm$^{-1}$ are attributed to
asymmetric stretching modes of the C$\equiv$O-Centify-H bonded
with COOH and H$_2$O, respectively. On the other hand, the
bands at 1259 and 1208 cm$^{-1}$ are attributed to the S-O
asymmetric stretching modes of SO$_3$Na$^{\cdots}$COOH and
SO$_3$Na$^{\cdots}$H$_2$O entities. Similarly, the 1056 and 1046 cm$^{-1}$
bands are attributed to the S-O symmetric stretching modes
resulting from the SO$_3$Na$^{\cdots}$COOH and SO$_3$Na$^{\cdots}$H$_2$O
interactions.\textsuperscript{11,13} Trace B of Figure 1 illustrates an ATR spectrum
recorded from the F-S interface. It appears that the bands
due to SDOSS and/or its associations are not detec-
ted. Thus, these results indicate that, for a Sty/n-BA
copolymer latex, SDOSS exudes to the F-A interface.

Let us now compare the above data with the data for
p-Sty/p-nBA latex blends. Figure 2 shows ATR FTIR spectra
recorded from the F-A interfaces of Sty/n-BA copolymer
latex (Trace A) and p-Sty/p-nBA blend (Trace B). As
seen, the copolymer latex (Trace A), for the SDOSS bands
at 1288, 1259, 1232, 1208, 1181, 1056, and 1046 cm$^{-1}$ are
significantly stronger at the F-A interface, indicating that
there is a greater degree of SDOSS surfactant stratification
near the F-A interface. Although these bands are attrib-
ted to SDOSS, our focus will be on the 1056 cm$^{-1}$ and
1046 cm$^{-1}$ bands, as they are responsible for the
SO$_3$Na$^{\cdots}$COOH and SO$_3$Na$^{\cdots}$H$_2$O interactions,
respectively.

Let us now focus on surface/interfacial in-plane distrib-
utions of SDOSS molecules. Figure 3 shows optical im-
geratures obtained from the F-A and F-S interfaces of the
copolymer latex. As seen, aggregates are detected at the F-A
interface, whereas the F-S interface appears to be uniform.
To determine the composition of aggregates, ATR FTIR
microanalysis was performed which was accomplished
by recording spectra using an ATR crystal on the surface
area of 50-100 $\mu$m. While circles marked in Figure 4a
indicate spectral acquisition areas at the F-A interface,
Figure 4b illustrates a series of spectra that correspond to
points A, B, C, D, and E of Figure 4a. While the band at
1159 cm$^{-1}$, due to the C-O-C stretching modes of p-nBA,
does not change its intensity, it appears that the intensi-
ties of the 1056 and 1046 cm$^{-1}$ bands, due to SDOSS,
increase while moving the IR beam from point A to point
E. These results show that the observed aggregates in
Figure 4a are mainly composed of water-soluble SDOSS
islands. In an effort to establish if there is a detectable Sty/
nBA phase separation resulting from SDOSS exudation to
the surface, dynamic mechanical thermal analysis (DMTA)
analysis was performed. The DMTA analysis (not shown)
indicated the existence of one glass transition temperature \( (T_g) \) at 20°C, thus indicating that no detectable phase separation within the copolymer latex components occurs.

In contrast to the SDOSS behavior in Sty/nBA copolymer latex, SDOSS exhibits different behavior in p-Sty/p-nBA latex blends. This is shown in Figure 5 where areas A through E in Figure 5a correspond to the spectra shown in Figure 5b. These results show that only a small fraction of SDOSS is detected at the F-A interface, thus confirming data shown in Figure 2, Trace B.

Experiments conducted on p-Sty/p-nBA latex blends showed that the film formation is significantly affected by suspension blend composition, p-Sty particle size, coalescence temperatures, and their relationship to the \( T_g \) of the polymer blends.\(^{16}\) It was found that temperature also has a significant effect on the exudation of SDOSS molecules when the coalescence temperature exceeds the \( T_g \) of p-Sty. Smaller p-Sty particles in 50/50 p-Sty/p-nBA latex blends tend to expel more SDOSS when the blend coalesces at 120°C. Quantitative ATR FTIR analysis of the F-A interface of 50/50 p-Sty/p-nBA latex blends also shows that at 120°C SDOSS⋅H_2O concentrations are \( 2.65 \times 10^{-2}, 2.04 \times 10^{-2}, \) and \( 1.53 \times 10^{-3} \) mmol/cm\(^3\) for 61 nm, 77 nm, and 102 nm particle size p-Sty, respectively. Concentration levels of SDOSS⋅COOH are \( 2.40 \times 10^{-1}, 2.21 \times 10^{-1}, \) and \( 1.87 \times 10^{-1} \) mmol/cm\(^3\) for 61 nm, 77 nm, and 102 nm p-Sty latexes. Quantitative analysis of surface species can be obtained by using the Q-ATR and Q-Depth algorithms published elsewhere,\(^6\) and require the knowledge of extinction coefficients and experimental ATR depth profiling data. Based on polarization data, SDOSS hydrophilic ends are preferentially parallel to the F-A interface, and hydrophobic ends are preferentially perpendicular to the surface.

**WATERBORNE POLYURETHANES**

As shown in previous studies,\(^7\) crosslinking reactions leading to PUR formation can be quantified by following the decrease of the NCO band intensity at 2271 cm\(^{-1}\) along with the increase of the CO\(_2\) (g) band at 2337 cm\(^{-1}\). The primary interest in following these species results from the fact that when NCO reacts with the active hydrogen of a hydroxy-functional compound, a urethane linkage is formed. This is illustrated in Scheme 1.

Scheme 1.

However, in the presence of water, NCO can also react with H\(_2\)O. This is shown in Scheme 2.

Scheme 2.

When isocyanate reacts with water by condensation, an unstable intermediate, carbamic acid, is formed. The carbamic acid immediately dissociates to evolve into carbon dioxide gas and an amine, which then continues to react with the free isocyanate to form urea. The NCO reaction with water can significantly affect film formation, as the evolution of carbon dioxide gas may result in unexpected property changes. Furthermore, vigorous reactions between isocyanates and amines may cause a rapid increase in molecular weight and viscosity, thus reducing pot life. Since amines are more nucleophilic than OH functional alcohols, urea reactions will occur faster and may predominate the crosslinking process. Under such circumstances, one could conclude that the presence of water is not desirable, especially since its presence may also result in the hydrolysis of polyester linkages. However, the inclusion of hydrophilic polyether tails surrounding NCO groups minimizes the influence of water and polyurethane formation dominates the process.\(^{18,19}\)

The amount of CO\(_2\) generated during polyurethane network formation is influenced by numerous factors, including the amount of water retained in the film at this stage of reaction, relative humidity (RH) of the environment, and the amount of shear stresses imposed on the system. As shown in Scheme 2, CO\(_2\) is produced when NCO reacts with water. Increasing the amount of water or lowering the evaporation rate enables water to be retained within the film, thus increasing the chance of NCO-H\(_2\)O reactions. Since higher relative humidity suppresses water evaporation, reactions shown in Scheme 2 will be favorable. For that matter, higher shear rates imposed on the waterborne PUR system may expose NCO particles to water, thus increasing the likelihood for reactions with water. To account for these features, and in an effort to improve PUR chemical resistance, waterborne polyurethanes are formulated at 2:1 (NCO:OH) stoichiometry.\(^{20,21}\)

To compare these results with the studies conducted on polyacrylate emulsions,\(^{22}\) a polyester-based urethane was formulated at 1:1 NCO:OH and the reaction was followed by observing the decrease of NCO. Figure 6 shows the NCO decrease for polyester and polyacrylate systems formulated at 1:1 stoichiometry and indicates that the rate of NCO consumption in the polyester system is greater, as determined from the slope of \(-9.53 \times 10^{-3} \) M/min. The slope for PUR acrylate is \(-3.05 \times 10^{-7} \) M/min, and this difference stems from the equivalent weight of the two waterborne systems. The acrylic emulsion has an equivalent weight of 3100 g/eq, whereas the polyester dispersion is approximately three times smaller, 1140 g/eq. Thus, when formulating the polyester dispersion as compared to the acrylic emulsion, the polyester requires more isocyanate at a given stoichiometry, which accelerates the crosslinking reactions leading to PUR network formation.

One would also expect that shear rates imposed on both 2K systems may affect the extent of reactions. After all, faster shear rates may expose NCO-containing particles to H\(_2\)O, thus promoting the reactions illustrated in Scheme 2. Therefore, shear requirements for these two waterborne systems should also be considered. Polyacrylate is an emulsion, while polyester is a dispersion, which is reflected in viscosity behavior. The hydroxy-substituted polyacrylic emulsion exhibits a viscosity of 50-500 cps, whereas the polyester dispersion has a viscosity of 6000 cps. From an application point of view, polyacrylates and polyesters exhibit different requirements for obtaining a uniform dispersion. The acrylic emulsion can be mixed with the polyisocyanate by creating a vortex with a magnetic stirring bar, whereas the polyester dispersion requires a three-bladed propeller set at 48 rpm.

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Previous studies have shown that shear rates may also affect the particle sizes of both isocyanate and polyl.18,19 Because shears imposed on waterborne PUR may have an effect on the resulting chemical reactions and the amount of CO2 gas evolved during urethane network formation, we conducted a series of experiments on polyester dispersions. These results showed that as shear forces increase, viscosity decreases, thus indicating shear thinning behavior attributed to structures of NCO-containing particles.21 To disperse NCO in water, it is necessary to have hydrophilic polyester tails attached to the NCO-containing particle which act as a water barrier, thereby minimizing the reactions of NCO with water (Scheme 2). Such a structural feature allows the urethane crosslink to predominate over urea formation. The ongoing studies are focused on polyester-polyurea conversions and the factors governing their three-dimensional distribution.24

It is also apparent that polycrylic emulsions revealed stratification within 0.65 to 1.14 μm at both interfaces.25 However, polyester dispersions do not exhibit this behavior and the equilibrium weight difference between polyester and acrylate, 1140 and 3100 g/eq, respectively, is attributed to this phenomenon. This is schematically shown in Figure 7. The rate of the NCO reaction may determine whether stratification is observed on the monitored time scale. Because NCO is consumed faster for the polyester crosslinked PUR, stratification does not occur within the first few μm from the F-A and F-S interfaces. On the other hand, for a slower reacting acrylate system, stratification occurs within 0.65 to 1.14 μm at both interfaces.

**EPOXY PHENOL NOVOLAC (EPN) POWDER COATINGS**

Reactions of epichlorohydrin (ECH) with hydroxyl, carboxyl, and amino functional groups will lead to the formation of epoxyd functionalities, which, in comparison to other epoxy derivatives, are capable of withstanding higher shear stresses, but exhibit weaker peel strength. Epoxide modification of phenolic novolac resins will improve the peel strength by reducing shrinkage during cure, as well as by improving chemical resistance, film strength, and adhesion.26 Phenolic novolac resins, which under acidic conditions are the reaction products of formaldehyde and excess phenol, form repeating units such as shown in Scheme 3.26 Due to the high reactivity of hydroxyl functionalities, phenolic novolacs are easily modified with ECH in the presence of an alkali catalyst.26

Scheme 3

In order to cure epoxy resins as thermoset networks, it is necessary to use crosslinkers, such as amines, hydrazines, carboxylic acids, or anhydrides. The choice of a crosslinker will strongly influence the mechanical properties and cure time of the final polymer network. In this study, the use of a phenolic novolac crosslinker will produce a hard, tough thermoset that exhibits excellent adhesion. The mechanism of cure involves two etherification reactions. The first is the reaction of a phenolic hydroxyl and epoxide to form an aromatic ether and 2' hydroxyl via a carbonium ion complex (A). The second involves the reaction of 2° hydroxyl groups and epoxide to form an aliphatic ether (B).25 The second reaction depends on the concentration of oxirane, and the nature and concentration of the catalyst. When 2-MI is used as a catalyst, the extent of reaction for secondary hydroxyl groups has been shown to vary from 50-90%.34

Scheme 4

One of the advantages of using epoxy phenol novolac (EPN) resins is their ability to be formulated into powder coatings. In this study, we will investigate how the particle size of EPN powder coatings affects chemical reactivity and adhesion at the film-substrate (F-S) interface. In an effort to understand the crosslinking reactions of EPN with phenol novolac resins, isothermal differential scanning calorimetry (DSC) measurements will be utilized to monitor the thermal kinetic behavior of EPN powder coatings and to obtain activation energies of the crosslinking reactions. In an effort to understand molecular level processes as a function of particle size, time, and temperature leading to crosslinking reactions, attenuated total reflectance (ATR) FTIR spectroscopy will be used. In view of these considerations, we will attempt to correlate these findings with adhesion measurements.

In order to elucidate the origin of the crosslinking reactions of the polyfunctional epoxy and phenolic that form a crosslinked macromolecular structure, it is important to determine how particle size will affect the kinetics of crosslinking reactions. For that reason, we compared reaction kinetics of 21 and 83 μm diameter powders to determine the activation energies of the crosslinking reactions shown in Scheme 4. Ultimately, our goal is to determine the relationship between the particle size and adhesion of powder coatings. In a typical coalescence scenario for powders, the EPN powder is heated and the powder particles reach a molten state in a finite time period in which the reactions involved in the crosslinking process occur. Since the ring-opening of the oxirane functionality is an exothermic reaction, it can be followed by DSC. Although both powder coatings have the same chemical makeup, the effect of particle size on the reaction kinetics may be affected by diffusion processes occurring at a given time and temperature.

Previous studies have examined the kinetic behavior of epoxies using thermo-analytical measurements.35,36 In an effort to determine temperature ranges for isothermal measurements, DSC was performed, which showed that the onset of the reaction exotherm is at 80°C, which is the point at which the lowest isothermal measurement can be made. Subsequent isothermal measurements were made at equal intervals throughout the exotherm range. The reaction heat (Qr) measured from DSC traces is shown in Table 1, from which the average Qr is calculated.

In isothermal analysis, the DSC curve shape is indicative of the kinetics. In the isothermal trace shown in Figure 8, an immediate exothermic peak is followed by exponential decay, which is characteristic of an nth order kinetics model. Using these data, an extent of cure (α) as a function of isothermal reaction temperature was determined.

As shown in Figure 9, a 21 μm particle diameter powder...
system exhibits a higher extent of reaction at temperatures up to 155°C, as compared to that of the 83 μm diameter. As the temperature increases above 155°C, the extent of crosslinking difference between the two particle sizes narrows, and at 185°C, the extent of crosslinking between the two powder coatings is similar. Based on these data, it is apparent that the delayed increase in the coarser particle reaction is due to the difference in particle size.

If one assumes that crosslinking kinetics at various temperatures obey Arrhenius behavior \( \ln(\kappa) = \ln(A) - \frac{E_{\text{act}}}{RT} \), where \( A \) is the frequency factor (s\(^{-1}\)), \( R \) is the gas constant (8.31 J mol\(^{-1}\)K\(^{-1}\)), \( T \) is the temperature (K), and \( E_{\text{act}} \) (kJ/mol) is the activation energy. The thermal response data can be determined\(^{30}\) to derive the crosslinking reaction rate constant, \( \kappa \). When \( \ln(\kappa) \) is plotted as a function of \( 1/T \), the slopes allow us to obtain activation energies \( E_{\text{act}} \) for 21 and 83 μm particle size powder systems, which are 41 kJ/mol and 58 kJ/mol, respectively. The results for \( E_{\text{act}} \) as well as the frequency factor, \( \ln(A) \), and reaction order, \( n \), are summarized in Table 2.

Based on this data, if the crosslinking reactions are solely controlled by the kinetics of chemical reactions, the \( E_{\text{act}} \) values for the 21 and 83 μm diameter powder coatings should be the same. In view of the differences between the activation energies, two questions need to be addressed: (1) why activation energies are different and (2) which processes other than kinetics control crosslinking behavior. Before we address these issues, let us consider the differences between the particle kinetics data which suggest that activation energies are intrinsically related to the film formation process. In order for crosslinking reactions to occur, reacting functional groups must be in close proximity to each other. Because diffusion of polymer chains depends on viscosity, particles converted to a molten, lower viscosity state react faster. Thus, it is appropriate to consider thermal conductivity and its effect on the melting behavior of both diameter powder particles.

Several studies have shown the dependence of reaction rates in thermally crosslinked systems with the increase of molecular weight, which directly involves a change in melt viscosity.\(^{38,39}\) In the reactions shown in Scheme 4, the rate of crosslinking is kinetically controlled up to the point of vitrification.\(^{30}\) At the onset of melting, the extent of crosslinking and the melt viscosity are low. As the reactions continue, the coating will form a stable interface with the substrate as the adhesive interphase forms.

In order to understand the crosslinking behavior of EPN powders, let us consider the effect of particle size on the melting point. Observing the melt behavior of powders as a function of temperature shows that powder packing plays a key role in which the melting point of a specimen will depend on the thermal conductivity of the heated surface. Since the thermal conductivity coefficient of air is much lower than that of organic polymers, the presence of voids will extend the time required for a specimen to melt due to the lower contact area between neighboring particles. In the case of EPN powders, thermal conductivity of a 21 μm particle size will be approximately four times greater than an 83 μm particle.\(^{41}\) Therefore, smaller particle size powders will be expected to reach a molten state 25% sooner than larger sizes. Therefore, the extent of crosslinking reactions at a given temperature will be greater for smaller particles. As the temperature increases, the magnitude of thermal transfer will also increase. Thus, the extent of reactions for larger particle sizes will be similar to those with a smaller particle size. In essence, a combination of time-temperature-particle size transition will determine the extent of crosslinking.

Although thermal techniques are useful in determining the thermal behavior of polymers, they are insufficient when the quantitative analysis of crosslinking groups is desired. The degree of crosslinking in EPN powder coatings can be determined spectroscopically by monitoring oxirane and hydroxyl functionalities. However, our particular interest lies in the reactions occurring near the film-substrate (F-S) interface because this interface is ultimately responsible for adhesion. For that reason, we will utilize ATR FTIR spectroscopy.

Figure 10 illustrates the ATR FTIR spectra of 83 μm particle size epoxy-modified phenol novolac powder coating films at various stages of crosslinking. Traces A-D illustrate the spectra recorded at the F-S interface of 83 μm particle powder crosslinked at 110°C for 0-60 min. As a first step in spectroscopic analysis, it is necessary to establish the origin of infrared bands. As seen, the bands at 1012 and 900 cm\(^{-1}\) decrease with increasing crosslinked time due to the asymmetric and symmetric C–O–C stretching modes of oxirane. The bands at 1029 and 826 cm\(^{-1}\), also exhibit lower intensity at extended crosslinking times due to the O–H and O–C groups of the phenolic crosslinker. The 1461 cm\(^{-1}\) normal vibrations of phenolic hydroxyl groups and detected 1440 cm\(^{-1}\) band due to hydrogen bonding, also decrease. The band at 1507 cm\(^{-1}\) is due to the benzene ring, and therefore, is independent of the degree of cure, but proportional to the amount of the coating. Since this band remains constant at all stages of cure, it will be used as an internal reference standard in these studies.

In an effort to relate oxirane consumption to adhesion, let us quantify oxirane concentration. Using quantitative procedures outlined in previous studies,\(^{8}\) analysis is made of the decrease in oxirane concentration as a function of crosslinking time. ATR FTIR spectroscopy is used to monitor the intensity of the oxirane bands at 900 cm\(^{-1}\) due to oxirane breathing vibrations.\(^{7}\) Because the quantitative use of ATR FTIR spectroscopy requires a calibration curve, one was constructed (not shown) which relates known concentrations of oxirane as a function of the 900 cm\(^{-1}\) band intensity.\(^{22}\) Using Beer-Lambert’s law, one can determine a molar absorption coefficient of oxirane from the slope of the calibration curve equal to 528.7 L/mmol-cm, followed by a quantitative assessment using Q-ATR\(^{6}\) of the oxirane concentration at various crosslinking times.

When oxirane concentration is plotted as a function of the reaction time for a given temperature oxirane concentration decreases. Figure 11 shows decreasing oxirane concentrations for the 21 and 83 μm powder systems at increased reaction times and temperatures. Quantitative analysis of the film-substrate (F-S) interface shows a change in the oxirane concentration changes from 5.87 × 10\(^{-3}\) M to 2.11 × 10\(^{-2}\) M for the 21 μm particle size upon crosslinking at 185°C for 20 min. Likewise, for the 83 μm particle under the same conditions, the oxirane concentration decreases.
from an un-crosslinked concentration of $5.02 \times 10^{-5}$ M to $2.63 \times 10^{-3}$ M. Thus, the oxirane functionality decreases at a faster rate for smaller particle sizes, with the differences more apparent at intermediate temperatures and reaction times.

As a means to determine differences in reactivity as a result of the surrounding environment, the films were analyzed using ATR spectroscopy at the F-A and F-S interfaces. A spectral comparison between the interfaces showed virtually no variation in the 900 cm$^{-1}$ band for the 21 µm particle size. For the 83 µm particle, a slightly higher oxirane concentration (10^{-5} M difference) is observed at the F-A, suggesting that the thermal and chemical conditions encountered at the F-A and F-S are similar for the 21 µm particle size powder system, but other factors may influence the crosslinking reactions of the 83 µm coating. In addition, profiling studies of the powder coatings revealed that no crosslinking stratification is observed from 0 to 2 µm below the surface.

Adhesion measurements of powder coatings to Al substrates for both particle sizes crosslinked at 110, 140, and 170°C for 10 min are illustrated in Figure 12. These results indicate that consistently higher adhesion occurs at all crosslinking temperatures for the 21 µm particle size. Correlation of the data obtained from DSC and ATR measurements indicates that a significantly higher extent of crosslinking would be expected for the 21 µm particle coating under these conditions. Since the reactions involved in the crosslinking process will also contribute to chemical and mechanical interactions, enhanced adhesion would be expected. The thermal lag associated with larger particle size may also reflect the lower adhesive values for the 83 µm film, as the film fails to properly wet the substrate. These observations are reflected in the difference in the activation energies, in which 21 µm is lower than 83 µm diameter particles. It should be noted that these results also indicate obvious connections between the effect of particle size on the production throughput and the economics of the process.

In summary, particle size may significantly influence the crosslinking kinetics as well as the adhesion of powder coatings to metal substrates. Enhancement of the adhesion of the 21 µm particle size crosslinked is attributed to time-temperature-particle size (TTPS) transition, and it appears that smaller particle sizes exhibit higher adhesion. The effect of particle size is attributed to the higher thermal conductivity of the finer powders, resulting in improved wetting of the substrate in a molten state, thus promoting chemical and mechanical adhesion. Smaller particles provide shorter crosslinking times, thus powder conalocence plays a significant role in achieving crosslinking and proficient adhesion. As far as the relationship between the particle size, throughput, and economics of the production process is concerned, one would anticipate that at a certain optimum particle diameter the total cost will be optimum. However, as the particle size increases, the production cost will increase due to longer cure times and requirements for thicker films to obtain desirable properties. At the same time, below a certain particle diameter, the production costs will increase again due to the equipment requirements and hazards associated with the possibility of powder dust explosion. When considering throughputs, it is anticipated that higher throughput efficiency will be achieved for a smaller particle size, but for certain particle diameters, this benefit will level off.

CONCLUSIONS

Although developments of novel polymers and chemicals utilized in coatings and thin films will continue to be an important part of coatings science, recent advances in modern surface/interfacial methods, combined with thermal and mechanical measurements, present numerous opportunities for enhancing our knowledge in this important field. Taking advantage of the existing knowledge of physico-chemical processes and analytical tools allows us to design and control macromolecules, crosslinkers, along with other coatings components to obtain specific properties. It is quite apparent that as we enter the 21st Century, what was considered ‘coatings art’ in the past is becoming coatings science with a spectrum of new challenges.

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References


Table 1

<table>
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<tr>
<th>Reaction System</th>
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Table 2

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Figure 1—ATR FTIR spectra in the 1340-970 cm\(^{-1}\) region of 50/50% Sty/n-BA copolymer latex: (A) F-A Interface; (B) F-S Interface (Coalescence time: three days, RH = 80%).

Figure 2—ATR FTIR spectra in the 1340-970 cm\(^{-1}\) region of 50/50% Sty/n-BA latex: (A) copolymer F-A Interface; (B) Polymer blend F-A Interface (Coalescence time: three days, RH = 80%).
Figure 3—Optical images of 50/50% Sty/n-BA copolymer latex: (a) F-A interface; (b) F-S interface (Coalescence time: three days, RH = 80%).

Figure 4—(a) Optical image of 50/50% Sty/n-BA copolymer latex F-A interface; (b) ATR FTIR spectra in the 1340-970 cm⁻¹ region of Sty/n-BA copolymer latex F-A interface (Coalescence time: three days, RH = 80%).

Figure 5—(a) Optical image of 50/50% p-Sty/p-nBA latex blend F-A interface; (b) ATR FTIR spectra in the 1400-940 cm⁻¹ region of p-Sty/p-nBA polymer blend F-A interface (Coalescence time: three days, RH = 80%).
Figure 6—Isocyanate concentration changes resulting from crosslinking reactions in polyester (■) and polyacrylate (○) systems formulated at 1:1 (NCO:OH) ratio.

Figure 7—Schematic representation of isocyanate distribution in the polyester dispersion and the polyacrylate emulsion.

Figure 8—Isothermal DSC measurements of EPN powders.

Figure 9—Extent of reaction plotted as a function of reaction temperature.
Figure 10—ATR FTIR spectra of 83 μm powder specimen: (A) Uncrosslinked EPN powder coating, (B) EPN powder coating crosslinked at 110°C for 10 min, (C) EPN powder coating crosslinked at 110°C for 30 min, and (D) EPN powder coating crosslinked at 110°C for 60 min.

Figure 11—ATR FTIR measured oxirane concentration (mM) plotted as a function of crosslinking time under isothermal conditions.

Figure 12—Pull-off adhesion (psi) measured for powder coatings on an Al substrate for 21 μm and 83 μm particle powder films crosslinked at 110, 140, and 170°C for 10 min.