



NEW ADVANCES IN HIGH PERFORMANCE WATERBORNE RADIATION-CURABLE EMULSIONS AND DISPERSIONS

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New advances in waterborne UV technology are considered from the perspective of the molar mass of the polyacrylate molecule and the different stabilization mechanisms of the resulting waterborne colloids, ranging from emulsions to dispersions. The main characteristics of emulsions are presented, with an emphasis on the parameters that govern the emulsification process and the colloidal stability of the final product. High-solid (65%), VOC-free emulsions with low viscosity are delivering outstanding performances as hardcoats for spray application on plastics. These emulsions can be blended to model radiation-curable polymer dispersions, either as such or after a proprietary hardening. It is thus possible to design complex dispersions with differentiated polymer particles, resulting in coatings with specific tensile properties that can be analyzed by various elastic models. The best reinforcing effect is obtained when a composition gradient is formed between hard submicron-sized inclusions and the surrounding continuous matrix, as evidenced by advanced atomic force microscopy (PFQNM). The coatings prepared using a multiple-phase pattern of hard and soft unsaturated polymeric components offer distinct chemical- and mechanical-resistance benefits in pigmented systems. All the products meet the environmental expectations of today's coating industry.

This paper received the Siltech Innovation Award at the 40th Annual International Waterborne, High-Solids and Powder Coatings Symposium, February 4–8, 2013, in New Orleans, LA.

EMULSIONS AND DISPERSIONS

Stabilization of Radiation-Curable Dispersions and Emulsions

The stabilization of radiation-curable molecules in water is primarily dependent on their physico-chemical nature and their molar mass, whether they are present as liquid-in-liquid (emulsion) or solid-in-liquid (dispersion).¹ Most of these heterogeneous systems are stabilized either by electrostatic or steric repulsion at the interphase of the droplets (in the case of an emulsion) or particles (in the case of a dispersion), preventing their coalescence or flocculation.² The electrostatic nature of the stabilization can be either anionic or cationic, while the steric contribution to the stabilization usually results from nonionic polyalkoxylated species. To complete the big picture of stabilization in aqueous systems, the above chemical functionality ensuring stabilization can either be covalently incorporated into the component of the dispersed phase (internal stabilization) or be provided by a surfactant adsorbed on the interphases (external stabilization). It must be noted, however, that these two cases can coexist.

Merits of Emulsions

For more than 30 years, radiation-curable compositions have been used as hardcoats because of their excellent mechanical- and chemical-resistance properties. Their chemical nature consists of acrylated oligomers present-

ing a high acrylate functionality (expressed as the number of acrylic unsaturation present on the molecule) associated with a high acrylate density (expressed in meq/g)—as is typically achieved with urethane acrylates. Due to their high viscosity, it is necessary to dilute the hardcoat composition with a solvent (which constitutes a severe concern for the environment and for occupational safety) or with low-viscosity monomers (which deteriorates the cured coating performance). As a consequence, the introduction of water-based compositions is the most valuable alternative for meeting the market demand for hardcoats with a low viscosity and a minimal environmental impact (low VOC). Due to the nature of the target urethane acrylates to bring in water, we essentially considered making and stabilizing emulsions as a complement to existing radiation-curable polyurethane dispersions (UV-PUDs).³ These new-generation waterborne hardcoats focus on industrial plastics and consumer electronics as a significant growth segment targeting surface finishes with advanced aesthetic, protective, and functional features.⁴

Emulsion Stabilization

Emulsions are formed when two immiscible liquids, usually water and a hydrophobic molecule, are mechanically agitated so that one liquid forms distinct droplets in the other one. The mean droplet diameter of the dispersed phase is usually between 0.1 and 10 μm . Such emulsions are thermodynamically unstable and become kinetically stable in the presence of tensio-active molecules adsorbed to the interface. The presence of the emulsifier causes a reduction of the interfacial tension and enhances the stabilization of the emulsion. The type of emulsion—oil-in-water (o/w) or water-in-oil (w/o)—is determined by the volume ratio of the two liquids as well as the solubility of the emulsifier in the two phases and the temperature. The concept of “hydrophilic-lipophilic balance” (HLB) is commonly used for nonionic emulsifiers as a way to match optimal emulsion stability due to the most efficient coverage of the interfaces.⁵

Emulsion Processes

The purpose of the emulsification equipment is to break up one liquid phase in the other, thereby creating new interfaces that will be populated by the tensio-active material to provide colloidal stability.⁶ It has been shown that droplet deformation and subsequent breakup under flow are governed by the mechanical energy and by two dimensionless groups, namely (a) the viscosity ratio η_d / η_c , where η_d and η_c are the viscosity of the droplet and the continuous phase, respectively, and (b) the capillary number $Ca = \tau_c a / \sigma$, which expresses the ratio between the viscous stress of the matrix fluid and the capillary (or Laplace) pressure σ / a , where σ denotes the interfacial tension and a refers to the undeformed drop radius.¹⁶ In concentrated emulsions, droplet breakup and recombination occur simultaneously and will always tend to reach a dynamic equilibrium, considering

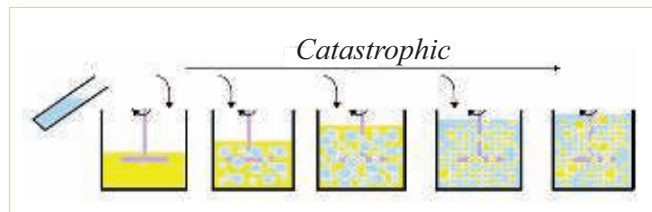


Figure 1—Schematic representation of catastrophic phase inversion observed when adding water into oil under high shear agitation.

that the capillary pressure increases for small droplets, which become less easy to break than the larger ones. A stable droplet size window is usually defined as a function of mixing power per volume. Outside the equilibrium, the droplets disruption is accompanied by coalescence when they cannot be stabilized quickly and efficiently enough after leaving the dispersing zone.

The energy required to produce the emulsion is provided by mixing impellers or high-pressure homogenizers either in batch operations or in a continuous process.⁷ Oil-in-water emulsions can be manufactured by direct emulsification or via phase inversion. In direct emulsification, the oil phase is simply added to the aqueous phase. In “catastrophic” phase inversion (*Figure 1*), the water is added to the oil phase until a critical water-in-oil fraction is reached and the dispersion inverts to produce the required oil-in-water emulsion.⁸ Phase inversion is a phenomenon that takes place because of a change in volume fraction, such that the dispersed phase spontaneously inverts to become the continuous phase. A “transitional” phase inversion similarly occurs when there is a change in the surfactant’s affinity toward the two phases induced by changing the HLB of the surfactants, the ionic strength of the water phase, or the temperature. The mixing energy is used the most efficiently at the phase inversion to break down the emulsion to small droplets with high interphase areas. The phase inversion can thus be regarded as the highest instability of the emulsion, and this metastable window is known as the range of ambivalence. The range’s limits may vary considerably and can be studied, for instance, by using conductivity experiments.⁹

EXPERIMENTAL

The solid content was measured gravimetrically after drying for 2 hr at 105 °C. The viscosity was measured at 25 °C using a Brookfield viscometer at 50 rpm. The hydrodynamic particle diameter (d_h) was determined by dynamic light scattering, using a Malvern™ Autosizer LoC instrument connected to a Malvern Series 7032 Multi-8 correlator. The colloidal stability was assessed by multiple light scattering at 60 °C, using a Turbiscan™ instrument. The phase separation was expressed as percent of clarification relative to the total height and/or as the number of days before critical destabilization. The minimum film formation temperature (MFFT) was measured on a Rhopoint™ 90 automatic gradient-heated metal plate. The molar mass distribution

was determined by gel permeation chromatography on the soluble polymer fraction in tetrahydrofuran.

The glass transition temperature (T_g) of the dispersed particles was determined by differential scanning calorimetry using a Mettler™ DSC823e instrument. The dispersion was dried in a standard aluminum crucible. The measurements were conducted at a heating rate of 10 °C/min under a flow of nitrogen gas.

The tensile properties were measured at room temperature with a Zwick™ Z010 elongation testing machine at a cross-head speed of 1 mm min⁻¹. Rectangular-shaped specimens (3 cm × 0.5 cm) were cut from the coatings. At least five independent measurements were performed for each sample. The free-standing films were prepared from the aqueous resins applied on an untreated polypropylene plastic film (30 μ), using a bar coater. To obtain films of suitable thickness, five layers of ≈ 35 μm wet were applied on top of one another, and every layer was dried for 1 hr in an air-convection oven. The effect of the drying temperature was studied at 40 and 80 °C. The coatings could easily be removed from the substrates after drying for the determination of the thermo-mechanical properties.

Atomic force microscopy in the peak force mode (PFQNM) used a Bruker™ AXS ICON AFM (Santa Barbara, CA) driven by a Nanoscope™ V control unit operating in air and in ambient conditions (temperature and pressure). The thin films were prepared on cleaned glass substrates, using a bar coater and drying temperatures of 40 and 80 °C. The probe used has a resonance frequency of about 300 kHz. The experiments were conducted in the Laboratory for Chemistry of Novel Materials, University of Mons, by Prof. R. Lazzaroni and Dr. Ph. Leclère.

RESULTS AND DISCUSSION, PART I: EMULSIONS FOR HARDCOATS

Emulsification

A thorough structure–property analysis was based on criteria such as the structural categorization of the

emulsifier and the subsequent use of the HLB concept. The experiments involved a catastrophic phase inversion obtained by adding water into the mix of the organic components at variable temperature and stirring conditions, followed by dilution. All the results hereafter refer to a model composition having a 65w% solid content, constituted of 92w% of a proprietary hexafunctional aliphatic urethane:acrylate composition and 8w% of a proprietary emulsifier composition.

The phase inversion was detected qualitatively as the maximum of the emulsion viscosity, immediately followed by a strong drop in viscosity. The conductivity of the system was measured, and it provided a more accurate image of the phase inversion and the ambivalent region corresponding to the plateau around 78 wt% solids (*Figure 2*). The total dissipated energy during the phase inversion, represented by the stirring time with a Cowles impeller, significantly reduced the droplet size during phase inversion. This is the result of the moving equilibrium between droplet breakup and coalescence as well as the surfactant distribution between the continuous phase and the droplet's surface (*Figure 3*).

The emulsifier plays an essential role on the droplet size, viscosity, and colloidal stability of the final emulsion. The colloidal stability decreases (with a droplet size increase) by reducing the level of emulsifier in the composition. The effect of the temperatures of water and organic phase plays a more limited role within a temperature range covering 20–80 °C for water and 40–80 °C for the organic phase.

It was shown that the stirring efficiency at the phase inversion is strongly linked to the type and geometry of mixer. It was also found that the emulsion concentration at which shear stress is applied strongly affects the colloidal stability of the emulsions after 10 days at 60 °C, since the stability decreases gradually (with a droplet size increase) when the emulsion concentration in the high-stress regime is reduced from 80 wt% (at the phase inversion) to, respectively, 75, 70, and 65 wt%.

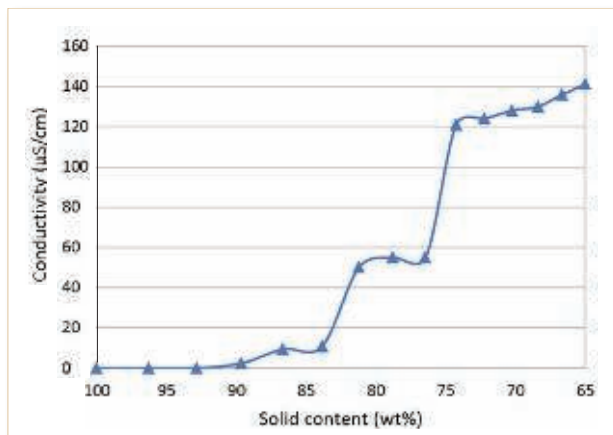


Figure 2—Variation of the conductivity as a function of solid content. The ambivalent range (plateau) shows the phase inversion.

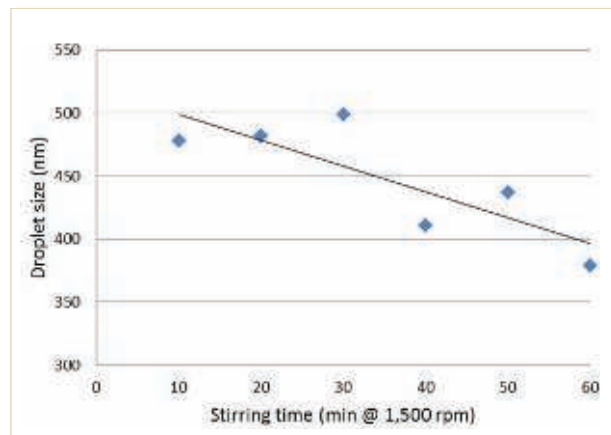


Figure 3—Variation of the droplet size as a function of stirring time (Cowles disperser with saw-tooth blade mixer, 1,500 rpm) during phase inversion.

The colloidal stability further decreases upon subsequent dilution of the emulsion to 60, 55, and 50 wt% corresponding to the expected depletion of the emulsifier from the droplet interphases and the sedimentation of the droplets down to close packing. In this mode of destabilization (kinetically unstable), the droplet size remains almost the same, in contradiction with a system whose droplet size is increased up to complete phase separation (thermodynamically unstable).

Product Characteristics

The characteristics of our model emulsion (referred to as product A) are reported in *Table 1*. The product is characterized by an unusual ratio between high solids and low viscosity, appreciated for further formulation and application by spray; it can be further diluted with water to meet every specific formulation requirement prior to application. The reduced amount of water is beneficial for transportation and application costs. The minimum film formation temperature is below 0 °C, which is expected for an oligomer that is not physically drying, meaning that the film obtained after water evaporation and prior to cure is tacky. The emulsion stays colloidally stable for a period exceeding 10 days at 60 °C. It does not contain any volatile organic content (VOC).

Benchmarking

To better appreciate the benefits of the new emulsion (product A) in terms of hardcoat performance, an investigation of the basic coating properties was carried

out. It involved the benchmarking with a reference UV-PUD (called product B, a proprietary highly unsaturated aliphatic polyurethane dispersion in water) and a reference radiation-curable hardcoat (called product C, a proprietary hexafunctional aliphatic urethane acrylate oligomer further diluted in a solvent). *Table 2* details the formulations that were considered in this study.

All three formulations were applied by bar coater on glass (coat weight approx. 50 g/m² dry), on Leneta® opacity charts, or on plastic substrates (coat weight approximately 10 g/m² dry). The coat weight of the formulations was adapted in order to obtain a comparative dry coating weight for evaluation. Water and solvent flash-off was carried out for 5 min at 50 °C, and radiation curing was carried out with two passes at 10 m/min under a 120 W/cm Hg lamp. All the compositions provided a clear coating with a gloss (60°) measured ≈ 95% on the opacity charts. All the coatings were conditioned for 24 hr at room temperature (RT) before being further tested.

Adhesion Performance

The initial adhesion was assessed at RT using the crosshatch tape adhesion test and reported using a 0–100% scale. The cured coatings from formulations A, B, and C had good adhesion (100%) on poly(methylmethacrylate) (PMMA) (except for formulation B), acrylonitrile butadiene styrene (ABS), poly(vinylchloride) (PVC), poly(ethyleneterephthalate) (PET), poly(cyclohexyl dimethylene terephthalate) (PCTg) and isopropanol-cleaned polycarbonate (PC). There was, however, no adhesion (0%) recorded on polystyrene (PS), corona-treated polyethylene (PE), or corona-treated polypropylene (PP), so that a specific primer coat could be required in these particular cases. It is, however, usual that adhesion would vary depending on the grade and supplier of the plastic substrate.

Mechanical and Chemical Resistance Performance

Table 3 details the hardness and scratch resistance of all three formulations. The emulsion displays similar or higher performance when compared to the reference products. The steel wool scratch resistance is measured

Table 1—Characteristics of the Model System (Product A)

Aspect	White liquid
Solid content (wt%)	65 ± 1.5
Viscosity (mPa.s)	500 ± 200
pH	4 ± 1
Droplet size, d _n (nm)	500 ± 200
MFFT (°C)	<0
Colloidal stability at 60 °C (days)	>10

Table 2—Coating Formulations

Ingredients	Formulation A Emulsion	Formulation B Reference Water-based UV-PUD	Formulation C Reference Solvent-based RC Oligomer
Product A (65 wt%)	100	—	—
Product B (35 wt%)	—	100	—
Product C (60 wt%)	—	—	60
Dowanol® PM (co-solvent)	—	—	40
Esacure® HB (photo-initiator)	2.8	1.5	2.8
Tego® Twin 4100 (flow/wetting)	0.5	—	—
ADDITOL® VXW 6396 (flow/wetting)	—	0.4	—
UCECOAT® 8460 (1:1) (thickening)	—	1.5	—
MODAFLOW® 9200 (flow/wetting)	—	—	0.25

on coated PC after the surface was rubbed with steel wool in a back-and-forth motion, using a 1 kg load. The surface damage was assessed on a scale from 1 to 5 (5 = no damage).

Table 4 discloses the stain resistance of coatings evaluated on coated Leneta opacity charts. The stains were applied under a glass slide for 16 hr, then removed with water and detergent. (For tar and black marker, the exposure is 1 hr or 5 min, respectively, after which the stain is removed with isopropanol). Here again, the new prototype ranks as highly as the benchmarks. All of the cured coatings show more than 100 acetone double rubs.

Table 5 presents the water resistance of the cured coatings on polycarbonate and acrylonitrile butadiene styrene (ABS) using three test protocols, namely (24 hr; RT), (2 hr; 80 °C) and (72 hr; 90 °C; 95% RH). The products perform optimally on ABS, but on PC, some weakness appears with the most severe test protocols. The slight difference with Formulation A could be attributed to the presence of the emulsifier.

RESULTS AND DISCUSSION, PART II: TOWARD COMPLEX SUB-MICRON MORPHOLOGIES^{10, 11}

Blending a Radiation-curable Emulsion into a Radiation-curable Dispersion

Our development was an opportunity to investigate innovative blends of our polyacrylate emulsion with conventional energy-curable polyurethane dispersions, in order to

boost their performance. It requires the pH of the emulsion to be adjusted above 7 by the addition of an amine (for instance, triethylamine or Advantex[®]) or sodium hydroxide.

Product A (65 wt%) was added to another commercial radiation-curable polyurethane dispersion (35 wt%) (called product D, which was similar to but softer than product B) while increasing consequently the solid content of the blend. A stable mixture (10 days at 60 °C) was recorded up to a blend ratio of 70:30 (product D:product A), corresponding to a final solid content of ≈ 44 wt%. The products were formulated, applied, and cured on glass and polycarbonate according to the protocol described previously. They show a perfect crosshatch tape adhesion at RT. Table 6 shows a significant boost in hardness (Persoz), scratch resistance (steel wool rubs), and abrasion resistance (Taber haze) when product D was formulated with product A. The steel wool scratch resistance was measured on coated PC after rubbing the surface with steel wool in a back-and-forth motion, using a 1 Kg load. The number of double rubs creating visible surface damage is recorded. The Taber haze (CF10F) was conducted on coated PC using 100 cycles and a 500g load.

The complex morphology of these stable water-based compositions, based on the presence of distinct particles (dispersion) and droplets (emulsion), supposes that the final film composition would homogenize after drying to a much more homogenous composition obtained after mixing of the low and high molecular weight nanophases.

Table 3—Mechanical Performance of Cured Coatings

Property	Formulation A Emulsion	Formulation B Reference Water-based UV-PUD	Formulation C Reference Solvent-based RC Oligomer
Persoz hardness (glass) (sec)	342	356	361
Pencil hardness (glass)	8H	5H	8-9H
Steel wool scratch 10 double rubs (1kg; PC) (0-5)	5	3	5
Steel wool scratch 100 double rubs (1kg; PC) (0-5)	5	2	5

Table 4—Stain Resistance of Cured Coatings^a

Stain Resistance Test	Formulation A Emulsion	Formulation B Reference Water-based UV-PUD	Formulation C Reference Solvent-based RC Oligomer
#1 Black shoe polish	5	5	5
#2 Tar	5	5	5
#3 Black marker (Artline [®] 70 N)	5	5	5
#4 Blue colorant (BB750 H2O)	5	5	5
#5 Sudan red colorant (SR380-WS)	5	5	5
#6 Yellow colorant (SG146-WS)	5	5	5
#7 Eosine	5	5	5
#8 Iso-betadine	4.5	4	5
Average stain resistance	4.9	4.9	5

(a) Ranking from 1 = severe trace visible to 5 = no trace

Table 5—Water Resistance of Cured Coatings Expressed by Tape Adhesion after Exposure^a

Water Resistance Test	Formulation A Emulsion	Formulation B Reference Water-based UV-PUD	Formulation C Reference Solvent-based RC Oligomer
24 hr; RT (ABS) (%)	100	—	100
2 hr; 80 °C (ABS) (%)	100	—	100
72 hr; 90 °C, 95% RH (ABS) (%)	100	—	100
24 hr; RT (PC) (%)	100	—	100
2 hr; 80 °C (PC) (%)	0	—	100
72 hr; 90 °C, 95% RH (PC) (%)	0	—	0

(a) Ranking from 0% = no adhesion to 100% = excellent adhesion.

Blending a Pre-cured Dispersion to a Radiation-curable Dispersion

Heterogeneous particle reinforcement can be achieved when one of the two components is precrosslinked in the water phase prior to film formation. We have found that it is possible to crosslink dispersed droplets or particles of unsaturated oligomers and polymer by exposure to ultraviolet light and in the presence of a photoinitiator. Crosslinking of the particles takes place in situ in the aqueous system and, hence, hard insoluble particles can be obtained that are no longer film-forming at RT. The crosslinking of the polyurethane particles upon UV exposure was followed by monitoring the increase of the T_g of the dried dispersion. *Figure 4* shows the heat flow thermograms of the dispersed particles (product B) after 0, 15, 30, 45, and 60 min of exposure to the UV light of a medium-pressure Hg lamp (≈ 30 W/cm). The T_g values obtained at the inflection point of the transition are, respectively, -18 , 16 , 26 , 35 , and 37 °C and show a shift of the glass transition temperature as a result of the acrylate double bonds consumption (plateau). Typically, the crosslinking broadens the glass transition, reflecting the buildup of an inhomogeneous network upon photopolymerization.

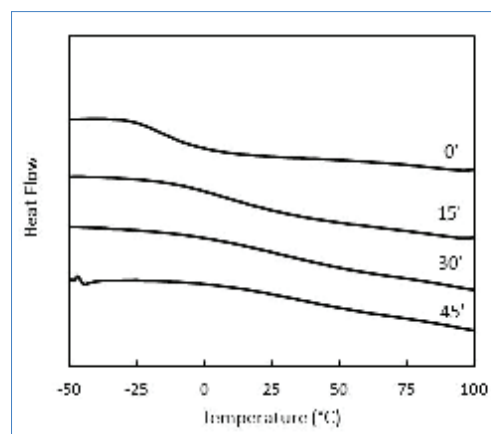
Table 6—Performance of Cured Coatings Obtained from Mixing Product A and Product D (Ratio in wt%)

	Product D: Product A (100:0)	Product D: Product A (70:30)
Persoz hardness (s) (glass)	250	340
Steel wool scratch (double rubs) (1kg) (PC)	5	50
Taber haze (%) (CF10F; 100 cycles; 500g) (PC)	28	12

To study the mechanical behavior of dry films prior to UV curing, dispersions were prepared by blending the film-forming product B along with a second hard constituent. In the first case, the hard constituent was formed by transforming product B into product B2, using in situ photopolymerization of the particles. Second, we prepared another hard variant of product B, referred to as product B3, obtained by the chain elongation (instead of chain capping) of the same unsaturated polyurethane backbone and clearly differentiated by its very high molecular weight distributions. The properties of these products are reported in *Table 7*.

Tensile Properties

Preliminary blending experiments indicated a slow increase of the MFFT up to a critical volume concentration (≈ 50 %), where a strong increase of the value is observed as a consequence of the discontinuity between the soft film-forming component and the hard particles.

**Figure 4**—DSC thermograms of particles B upon increasing UV-exposure times.**Table 7**—Characteristics of Product B and Variants

	Product B	Product B2	Product B3
Solid content (wt%)	35	35	35
Viscosity (mPa.s)	50	75	60
pH	7.5	7.5	8.0
d_h (nm)	70	75	60
Colloidal stability 60 °C (days)	>10	>10	>10
T_g (°C)	-14	37	118
M_w (Da)	15,000	N/A	>100,000
Solubility in THF (%)	100	0	~ 15

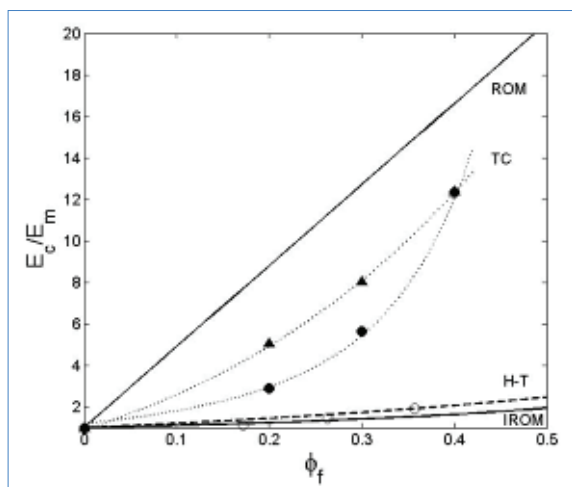


Figure 5—Plot of the reduced Young's modulus of the composite as a function of the volume fraction of hard dispersion (uncured). The open symbols (○) = films where hard precrosslinked polyurethane particles B2 were used as filling compound; solid symbols = films where chain-elongated polyurethane particles B3 were used as filling compound; (●) = films prepared at 40°C; and (▲) = films prepared at 80°C.

The reinforcing effect resulting from the incorporation of the hard particles into the coating prior to UV curing is well established from the tensile properties. The reduced Young's modulus (scaled with respect to the matrix modulus) was thus investigated up to a volume fraction of hard particles equal to 0.4, as shown in Figure 5.

Various micromechanical models have been suggested to describe the relation between composition and tensile modulus for immiscible polymer blends and filled polymers.^{11,12} As an example, the parallel or rule-of-mixture (ROM) model predicts a linear relationship for the modulus of the composite or blend material, assuming that the two phases deform identically with equal strain. In Figure 5, predictions of different models are compared, i.e., the ROM (upper full line), the inverse rule of mixture (IROM) (lower full line), and the Halpin-Tsai (HT) model for spherical fillers with a Young's modulus value of 2 GPa (dashed line).¹²

The reduced Young's modulus of the composite (E_c/E_m) follows the behavior expected in the case of hard

crosslinked filler particles B2, i.e., a reinforcement mechanism based on well-separated phase morphology and closely predicted by the IROM or the HT model. However, the marked increase of Young's modulus for hard particles B3 cannot be explained by a filling effect alone. It is argued that the formation of a composition gradient between the soft matrix and the hard inclusions is a key factor in accounting for the hardness of these coating blends. The data suggests also that the formation of a more important interphase at 80°C enhances significantly the Young's modulus compared to the films at 40°C.

The behavior of the Young's modulus as a function of hard polymer content is fully captured by a three-compartment (TC) phenomenological model by introducing an additional elastic spring for the interphase region. To mimic the behavior of the experimental data properly, a parallel combination of matrix and interphase, in series with the filler, is required. The resulting composite modulus reads as:

$$(1) \quad \frac{1}{E_c} = \frac{\phi_m + \phi_i}{E_{m,i}} + \frac{\phi_f}{E_f}$$

$$(2) \quad E_{m,i} = \frac{\phi_m E_m + \phi_i E_i}{\phi_m + \phi_i}$$

The Young modulus of the matrix and the filler are, respectively, $E_m \approx 0.05$ GPa, $E_f \approx 2$ GPa. An arithmetic mean value $E_i \approx 1$ GPa is assumed for the modulus of the interphase compartment. It is assumed that the volume fractions ϕ_f and ϕ_i are proportional to the mass fraction w_f of the dispersed hard polymer, i.e., $\phi_f = F_f w_f$ and $\phi_i = F_i w_f$. The proportionality factors F_f and F_i are considered as adjustable parameters.¹¹

Atomic Force Microscopy

The evidence of a composition gradient between the soft and the hard components was further investigated by atomic force microscopy. Despite the success of TM-AFM for micro-structural characterization,¹³ the height images generally display only topographic information, whereas phase images reflect tiny variations of the local

Figure 6—PFQNM adhesion image (scan size = 1 μm) of polymer blend thin films with hard-to-soft ratio of 40:60 dried at 40°C (left) and 80°C (right).

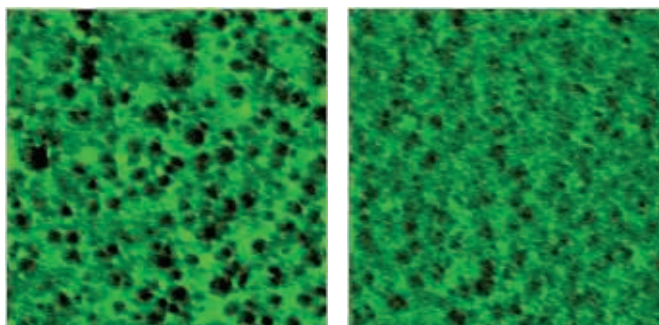


Table 8—Chemical and Mechanical Resistance of Cured Coatings^a

	Stain 1 Black Marker	Stain 2 Red Wine	Stain 3 Coffee	Scratch 1 15 in.	Scratch 2 10 ft.	Scratch 3 60 ft.
Blend (B3:B)	5	5	5	3	4	5
Benchmark	4	3	3	1.5	1.5	4
Competitor 1	2	3	4.5	2.5	3	4.5
Competitor 2	5	4	4	2	2.5	4
Ref. WB (1K)	0	3	3	N/A	N/A	N/A
Ref. SB (2K)	4	4	4	N/A	N/A	N/A

(a) Scale: 0–5; 5=best.

mechanical properties of the sample surface. The recent development of the peak force methodology (PFQNM) records the stiffness, adhesion, deformation, and dissipation properties of the polymer thin films in real time and simultaneously with the topography.¹⁴

AFM imaging with peak force quantitative nano-mechanical property mapping is based on the real-time analysis of the force-distance curves recorded at a frequency of about 2 kHz. Since the feedback loop is set on the peak force, the actual force is maintained constant during the imaging of the samples. From those force-distance curves, one can extract, for instance, the adhesion force at every point of the raster scan (corresponding to the lowest value of the force when the tip is retracted from the sample). *Figure 6* illustrates the data obtained for hard-to-soft ratio of 40:60 at a drying temperature of 40 and 80 °C. The hard spherical particles are much less adhering than the soft polymer matrix and therefore appear in black in the image. An intermediate zone around the particles is attributed to the presence of an inter-phase. The adhesion image for 80 °C is less contrasted compared to that of the sample dried at 40 °C, and the apparent diameter of the spherical hard particles is smaller. This indicates that the hard spheres are more embedded in the soft film. It is fully consistent with the model proposed above, which considers the presence of an interphase between the hard spheres and the soft polymer matrix when the drying temperature is 80 °C.

Performance of Cured Coatings in a Pigmented Formulation

The preferred product blend B3:B (40:60) was formulated as orange pigmented coatings for spray applications and compared with a similar formulation of internal and external commercial benchmarks. The choice of the orange color is dictated by the strong interaction of the pigments with the light that usually leads to poor curing.

The polymer dispersions were mixed with an industrial, ready-to-use, water-based orange pigment paste (15 pph, 70% in water). They were further formulated with liquid photoinitiators (Esacure™ HB, 1 pph, and Irgacure™ 819 DW, 0.5 pph). A rheology modifier (UCECOAT® 8460, 1 pph, 50% in water) was added until a target viscosity of ≈ 20 sec (Ford Cup 4) was obtained in order to provide a suitable rheological behavior for spray application. A

wetting agent (Byk™ 028, 1 pph) was used to provide a smooth defect-free surface after spray coating application.

The pigmented formulations were applied to MDF panels covered with white melamine paper and prepared by sanding with a thin aluminum oxide abrasive paper. A spray gun technique was used to give a wet thickness of 120–130 g/m². The coating was dried in a ventilated oven for 20 min at 40 °C and the hot dried coating was cured on a conveyor belt at a speed of 5 m/min, using a Ga-doped medium-pressure mercury lamp of 120 W/cm, followed by a medium-pressure mercury lamp of 120 W/cm. The cured coatings were tested for most significant performance areas, i.e., adhesion, stain resistance, and nail-scratch resistance. The wood adhesion (DIN 53151) was found to be good after an appropriate surface preparation using abrasive papers. The stain and the scratch resistances depict, respectively, the surface cure and the deep cure obtained in the difficult case of pigments in colors other than white.

The results of the stain resistance (EN12720) for the orange formulation after 24 hr are reported in *Table 8*. The product blend B3:B (40:60) shows a superior stain resistance compared with that of the benchmark, the competitors, the formulated water-based (1K), and the solvent-based (2K) industry standards. The results of the nail-scratch resistance for the orange formulation are reported directly after the curing (still hot), after 10 min, and after 60 min at ambient temperature. All the products increase their resistance within the observed time frame. The product blend B3:B (40:60) shows the best results immediately after the curing (when the panel is still hot) and reaches the maximum value after 60 min. This test indicates, for instance, the good stackability of the coated panels during their manufacture.

CONCLUSIONS

We have developed a novel proprietary emulsion technology to extend the application field of waterborne radiation-curable products. New hardcoat emulsions enable formulators to develop a high-solid, solvent-free UV hardcoat for spray application that better meets environmental requirements and delivers properties that are similar to a dedicated 100% UV resin.

The innovative blending possibilities associated with these multifunctional acrylate emulsions create a bridge to complex emulsion and dispersion micro-structures of

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hard and soft components that opens new horizons for high-performing applications. The controlled, photo-induced curing of droplets and particles in the water phase constitutes a real technological opportunity. Novel polyurethane dispersions permit the efficient curing of pigmented formulations with good adhesion combined with superior mechanical and chemical resistance.

ACKNOWLEDGMENTS

The authors are very grateful to J-N. Baurant, who has been in charge of the synthesis and emulsification work; to Th. Lardot and M. Berlier for sample preparation and mechanical analysis; and to A. Cornelis, P. Dauw, D. Martel, and J. Loris, who performed the formulation and testing. M. Tielemans wishes to give special thanks to S. Peeters for technical advice and to E. Ginsburger for his extensive review of the waterborne processes. Last, but not least, our deepest acknowledgments go to Prof. Dr. R. Lazzaroni and Dr. Ph. Leclère from the Laboratory for Chemistry of Novel Materials at University of Mons, Belgium, for their superlative expertise and support in atomic force microscopy. ^{CT}

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